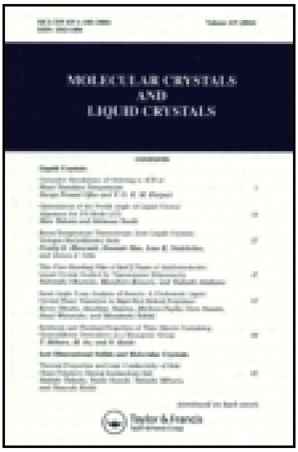

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Synthesis and Characterization of Liquid Crystalline Silsesquioxanes Containing Azobenzene Groups

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Liquid crystalline silsesquioxanes having calamitic mesogenic and azobenzene moieties were synthesized by the hydrosilylation reaction of an inorganic silsesquioxane cube and terminal alkenes using Karstedt's catalyst. Their chemical structures were confirmed by Fourier transform infrared (FTIR) and ^{1}*H- and* ^{29}*Si-NMR (nuclear magnetic resonance) spectra. These oligomers have good thermostabilities, with the degradation process starting above 265°C. Their mesomorphic and phase behavior were investigated using differential scanning calorimetry (DSC), polarizing optical microscopy (POM), X-ray diffraction (XRD), and thermogravimetric analysis (TGA) measurements. The results show that the silsesquioxanes exhibit a broad range of liquid crystalline phases at moderate temperature. The ultraviolet (UV)-induced cis–trans photoisomerization was also studied for the liquid crystalline silsesquioxanes in chloroform.*

Keywords Azobenzene groups; liquid crystals; silsesquioxanes

1. Introduction

Liquid crystalline polymers with mesogenic moieties attached to the polymer backbones via flexible aliphatic spacers of various lengths have been the subject of intensive research over last few years [1,2]. Particular interest in the synthesis and characterization of chromophore groups containing liquid crystalline polymers has increased recently because of their potential application in optical storage devices due to the reversibility of the *cis–trans* isomerization and the steric difference between the two isomeric states. Side-chain liquid crystalline polymers (SCLCPs) containing photochromic groups were first described by Ringsdorf et al. [3].

In the case of SCLCPs, mesomorphic properties depend on the nature of the polymer backbone, the length of the flexible spacer, and the rigidity of the mesogen. Within this group of SCLCPs, polysiloxanes have been the subject of much academic research and more limited industrial activity. Due to the exceptional rotational freedom found in the siloxane backbone, these materials have very low transition temperatures. In addition, liquid crystalline polysiloxanes have shown interesting electro-optical and thermo-optical properties [4, 5]. However, for many applications, the response of these high-molecular-mass materials to an electric field is slow. Hence, SCLCPs cannot be used as photonic

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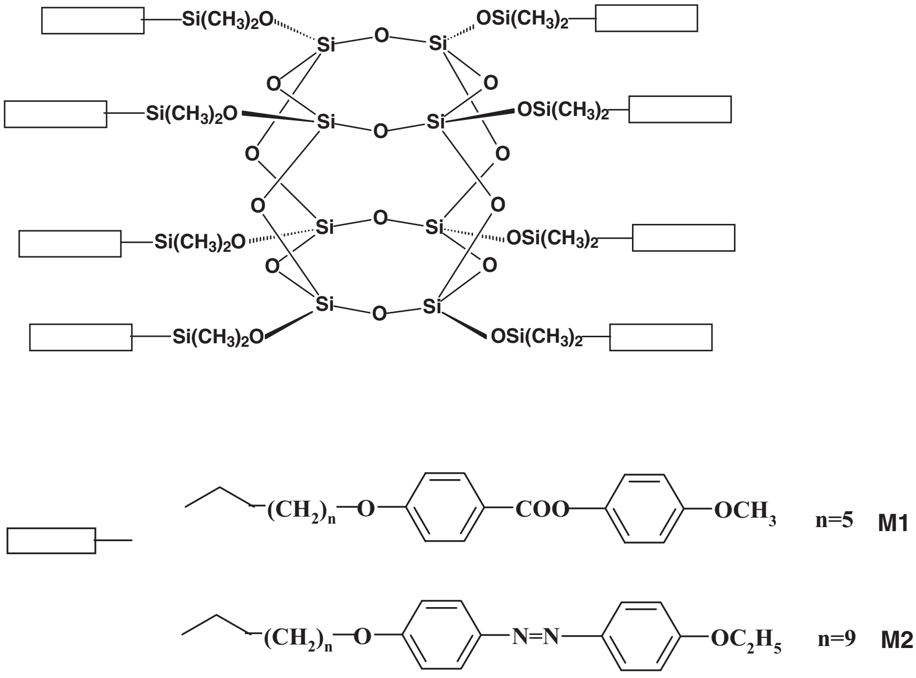
materials because a much faster response is necessary. In this context, many studies concentrate on hybrid low-molecular-mass liquid crystalline materials consisting of various backbones onto which liquid crystal (LC) moieties are attached. These compounds exhibit properties between low-molecular-mass LC crystals and polymeric liquid crystals due to their well-defined molecular mass and their low viscosity as compared with polymers. In particular, there has been significant interest concentrating on small ring systems with mesogenic units as substituents at silicon atoms [6–9]. Liquid crystalline cage structures based on double cyclosiloxane cores connected by oxygen bridges can be used in various applications [10–14], for example, as SiO_2 films (used for electrical materials, optical filters) or in the formation of inorganic–organic hybrid materials. In this paper, we described a series of novel LC azobenzene-functionalized silsesquioxanes (see Scheme 1) for electro-optical applications. The basic concept of this work was to use a side-chain silsesquioxane with one co-monomer being sensitive to light and the other being unable either to absorb light or to perform isomerization upon irradiation. The synthesis, characterization, and photochemical behavior of these chromophore-based liquid crystalline silsesquioxanes are discussed.



Scheme 1. General molecular structures for the silsesquioxanes containing azo-dye groups.

2. Experimental

2.1. Materials

All chemicals were purchased from Aldrich in the purest grade available and employed without further purification. All solvents were purified by standard methods; only toluene used in the hydrosilylation reaction was first refluxed over sodium and then distilled. The hydrosilylation catalyst–PTDD (platinum tetramethyldivinyl disiloxane complex in xylene (11 wt%))–was purchased from GE Silicon. Octakis(dimethylsiloxy)-T_8-silsesquioxane was purchased from Gelest, Inc.

2.2. Analytical

Fourier transform infrared (FTIR) spectroscopy was used to characterize the functional groups of the monomers and oligomers. IR spectra were recorded on a Perkin-Elmer Spectrum 2000 spectrophotometer with a resolution of 4 cm^{-1}. Liquid samples were cast on NaCl plates and solid samples were pressed into KBr pellets. A minimum of 16 scans were collected for each sample.

The photo-induced isomerization was carried out by irradiation with a mercury lamp B-100AP (100 W, Blak-Ray) in combination with a 365-nm filter. The UV-Visible (UV-Vis) spectra of all the oligomers were recorded in the 200- to 5000-nm region on a Perkin-Elmer Lambda 900 UV-Vis spectrophotometer in 10^{-2} M chloroform ($CHCl_3$) solution (1-cm quartz cuvette). The samples were then irradiated with non-polarized UV light for a total exposure time of 20 min. The distance between the UV lamp and the sample was fixed at 7.5 cm. The spectra of the irradiated samples at various intervals of times were recorded for the same spectral range. This procedure was repeated until reduction in absorption was achieved.

^{1}H- and ^{29}Si-NMR (nuclear magnetic resonance) analyses were performed in deuterated $CHCl_3$ and recorded on a Varian INOVA (400 MHz) spectrometer. Chemical shifts were assessed using residual $CHCl_3$ (^{1}H) and tetramethylsilane (TMS) (^{29}Si) as internal standards.

Thermogravimetric analyses (TGA) were carried out using a TA Instruments TGA Q50 thermogravimetric analyzer at a heating rate of 10°C min^{-1}. Samples of approximately 20–50 mg were placed in a platinum pan (in air) and immediately put into the furnace. Samples were heated in dry air to 800°C with ceramic yields based on decomposition to SiO_2.

Phase transition temperatures were determined with a Perkin-Elmer DSC-7 equipped with a liquid nitrogen cooling system at a heating rate of 10°C min^{-1} under a nitrogenous atmosphere. The reported thermal transitions were collected as scans during the second heating and cooling.

Polarizing optical microscopic (POM) studies of liquid crystalline transitions and optical textures was made using a bipolar microscope with a crossed polarizer and equipped with a Mettler FP82HT heating stage and a Mettler FP-90 central processor. The heating rate of 10°C min^{-1} was used. Samples were prepared as thin films placed between a glass slide and a glass cover slip.

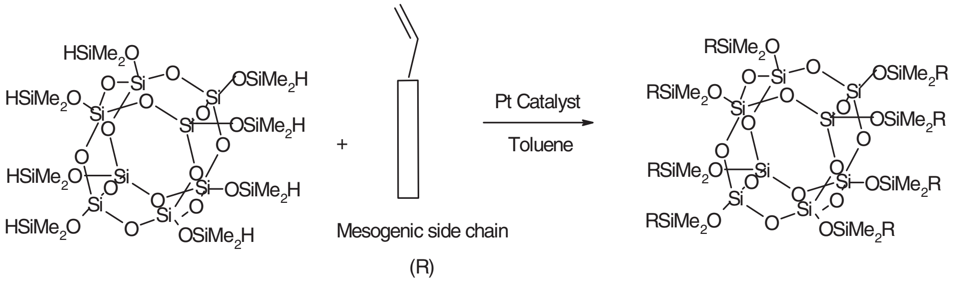
The X-ray diffraction (XRD) data for LC phases were obtained with a Bruker GADDS system, using CuKα radiation. The diffractometer was equipped with a Gobel mirror, monocarp collimator, and 2D Hi-Star detector.

2.3. LC Precursors

The monomer with methoxy end-group (M1) was synthesized by a previously described method [15]. The azo-dye monomer (M2) was synthesized from 4-ethoxyaniline via coupling with phenol and subsequent alkylation of 4-(4’-ethoxyphenylazo)-phenol with undec-10-enyl bromide. Both types of monomers play a significant role in the thermal properties of oligomers (Scheme 1). The structures of all the mesogens were confirmed by means of FTIR and ^{1}H-NMR. The transition temperatures for the monomers used were determined by differential scanning calorimetry (DSC) and confirmed by POM.

2.4. Synthesis of Silsesquioxanes Having an Azobenzene and a Mesogenic Moiety

Attachment of the mesogen and the monomer with an azobenzene group to the silsesquioxane, shown in Scheme 2, was performed by standard hydrosilylation with a platinum catalyst. The liquid crystalline silsesquioxane oligomers were prepared by a platinum-catalyzed reaction of the mesogenic alkenes with octakis(dimetylsiloxy)silsesquioxane (POSSX) using Karstedt's catalyst at 50°C in toluene.



Scheme 2. Synthetic route used to prepare the LC silsesquioxanes.

The synthesis of oligomer SSQ1 is given as an example. Anhydrous toluene (15 ml) was added to octakis(dimethylsiloxy)silsesquioxane (0.1 g, 0.098 mmol) under a dry nitrogenous atmosphere. The mixture was stirred for 5 min to allow for all (HSi-Me$_2$OSiO$_{15}$)$_8$ to dissolve. Monomer M2 (0.32 g, 0.83 mmol), followed by Pt–divinyltetramethdisiloxane (5 μl) catalyst, was then added dropwise into the flask. The mixture was allowed to stir at 50°C for 24 h. The reaction kinetics was followed by FTIR spectroscopy. Small amounts of excess reactant and solvent were removed effectively by vacuum evaporation using a high-vacuum pump. The resultant product was further recrystallized from CH$_2$Cl$_2$/methanol to obtain a viscous liquid in yield of 95%. NMR analyses of the final product indicated that eight azobenzene groups were attached to each cube on average. The above procedure was repeated for the synthesis of compounds SSQ2, SSQ3, and SSQ4.

For SSQ1: ^{1}H-NMR (400 MHz, CDCl3) (δ, ppm): 7.91 (m, 4H, Ar—**H**), 7.26 (m, 2H, Ar—**H**) 7.01 (m 2H, Ar—**H**), 4.15 (t, 2H, Ar—**OCH$_2$**), 3.96 (t, 2H, O**CH$_2$**CH$_3$), 2.51 (m, 2H, O—**CH$_2$**), 1.80 (dd, 2H, —**CH$_2$**), 1.57 (s, 3H, —**CH$_3$**), 1.46 (m, 12H, —(**C**H$_2$)$_6$), 0.49–0.52 (t, 2H, Si—**CH$_2$**), 0.10 (s, 6H, **CH$_3$**Si); ^{29}Si-NMR (79 MHz, CDCl$_3$), (δ, ppm): 13.1 (Si(CH$_3$)$_2$), −108.7 (SiO$_4$). FTIR (cm^{-1}):1254 (Si(CH$_3$)$_2$), 1094 (Si—O—Si).

3. Results and Discussion

3.1 Synthesis

In continuation of earlier studies on the synthesis of photoactive siloxane oligomers, we made an attempt to synthesis LC silsesquioxanes with azobenzene group of potential use in electro-optical displays or oligomeric dyes [16]. The introduction of the azobenzene group in the side chain offers the possibility to modify the degree of order by irradiation.

Table 1. LC behavior of silsesquioxanes

Cubes	Phase transition temperature (°C)	M1/M2 calculated	M1/M2 experimental[a]
SSQ1	Cr 93 N 112 I	0/100	
SSQ2	Cr 72 N 102 I	12.5/87.5	11.7/88.3
SSQ3	Cr 51 N 84 I	50/50	46.1/54.9
SSQ4	Cr 44 N 79 I	87.5/12.5	87.8/12.2

Note. Cr, crystal phase; N, nematic phase; I, isotropic phase.
[a]Final molar ratio calculated by ^{1}H-NMR.

The structures of M1 and M2 were characterized by FTIR and ^{1}H-NMR spectra, which were in agreement with the prediction. The LC transition temperatures for the monomers used were determined by DSC and confirmed by POM. Nonpolar mesogen M1 exhibits LC behavior (Cr 55 Sm A 64 I)–where Cr is crystal phase, Sm A is smectic A phase, and I is isotropic phase–and details of preparation and the results of POM and DSC measurements have been published previously [15]. In the DSC thermogram, the azo monomer (M2) displayed a single peak at about 62°C and no liquid crystalline phase transition was observed.

FTIR spectra of all LC silsesquioxanes indicated complete disappearance of Si—H stretching bands at 2145 cm^{-1} and of C=C stretching bands at 1643 cm^{-1}, and appearance of characteristic absorption bands of mesogens and the broad peaks of Si—O—Si stretching for the oligomers, indicating successful incorporation of monomers into the silsesquioxanes.

Structures of LC silsesquioxanes were also confirmed by ^{1}H-NMR and ^{29}Si-NMR. ^{1}H-NMR analysis indicated only β-hydrosilylation products and the absence of the Si—H peak at 4.72 ppm, which signified a fully substituted silsesquioxane for all oligomers. ^{29}Si-NMR spectra of the products gave two peaks assignable to each silicon atom in the compound. The final molar ratio composition of the co-oligomers (SSQ2–SSQ4) incorporating mesogens M1 and M2 was assessed by ^{1}H-NMR spectrometry by comparing the integrated signals in the aliphatic regions (methoxy resonance) of mesogen M1, located at 3.87 ppm, and in the aromatic regions of mesogens MI and M2. The results show a good agreement between the initial ratio and the oligomer composition, indicating that the reactivity of the monomer containing the azobenzene unit is similar to that of mesogen M1. These results are summarized in Table 1.

3.2. *Thermal Stability of Oligomers*

TGA of oligomers was carried out to study thermal stability and to determine the SiO_2 content after pyrolysis in air. Results of TGA analyses are shown in Table 2, with representative TGA thermograms (temperature profiles) shown in Fig. 1. The thermal decomposition temperatures at 5% weight loss (T_d), for oligomers SSQ1–SSQ4 are above 270°C and show that the synthesized LC silsesquioxanes have high thermal stability. Oligomer SSQ1 undergoes one-stage decomposition, while oligomers SSQ2–SSQ4 exhibit two mass changes. The initial decomposition of oligomers showing a weight loss in the 45%–55% range occurs during the first decomposition step. The inflection temperature of the oligomers between two mass changes decreased by increasing the amount of azo-dye groups in the silsesquioxane cube. It is attributed to the presence of the N=N group in the mesogenic core, which

Table 2. Thermogravimetric analysis data of synthesized LC silsesquioxanes

Cube	T_d (°C)[a]	T_{Inf} (°C)[b]	Calculated SiO_2 (%)	Expermental SiO_2 (%)
SSQ1	268	–	30.4	30.3
SSQ2	276	356	30.5	30.1
SSQ3	282	365	25.6	24.9
SSQ4	310	389	33.3	33.1

[a] Temperature of the samples at 5% loss weight.

[b] Inflection temperature of the samples between the two mass changes.

was expected to introduce some intra- or intermolecular π–π interaction and consequently brought down thermal stability. The TGA results were also used to calculate a substitution model for all synthesized oligomers via assessing the ceramic yield from SiO_2. Ceramic yields are close to the theoretical calculations of the average substitution of eight organic groups per cube. These results are summarized in Table 2.

3.3. *Liquid Crystalline Properties*

The phase transitions of all oligomers were determined by a combination of different techniques, including POM, DSC, and XRD. The studies by DSC and POM enable us to

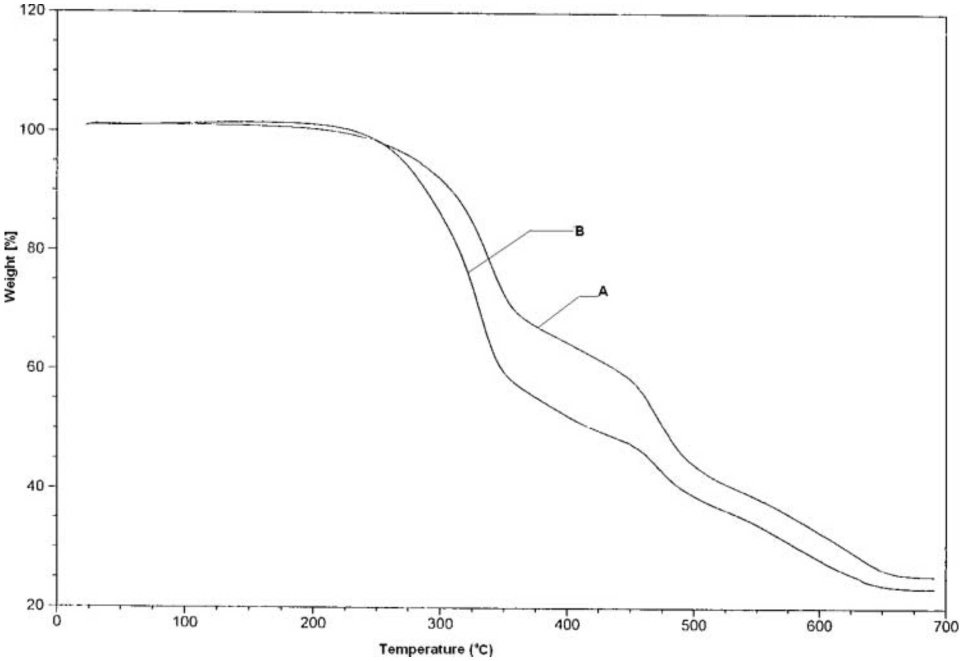


Figure 1. Weight loss (TGA): temperature profiles for silsesquioxanes at a rate of 10°C min^{-1} (A, SSQ2; B, SSQ3).

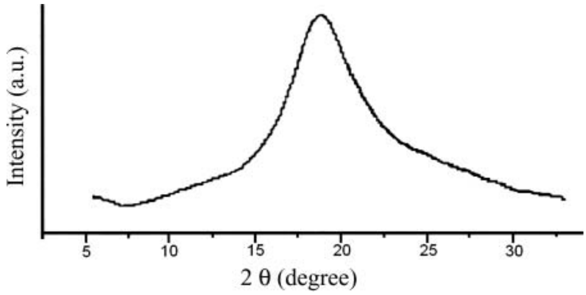


Figure 2. X-ray diffraction (XRD) of LC silsesquioxane SSQ1.

determine the transition temperatures. The corresponding transitions determined by DSC for these synthesized oligomers are included in Table 1.

For the oligomer containing 12.5% of the azobenzene moiety, a schlieren texture [17] could also be seen by POM; this observation combined with the results of DSC led us to the assumption that this oligomer exhibits a nematic phase. For the other oligomers containing more than 12.5% of the azobenzene group, no typical textures could be seen under the microscope and XRD was used to identify the mesophases. The DSC results demonstrate that both mesogenic moieties and the terminal groups have a high influence on the melting temperature and molecular arrangement. It was confirmed that liquid crystalline phases could be obtained through suitable rigid mesogenic cores, spacer length, and polarity at the center and terminals of the core. As can be seen in Table 1, by comparing the transition temperatures of the LC silsesquioxanes, the nematic phase interval for the co-oligomer compositions ($\Delta T = 30^\circ$ for SSQ2 and $\Delta T = 35^\circ$ for SSQ4) is higher than the mesophase interval for silsesquioxanes with only azobenzene groups ($\Delta T = 19^\circ$ for SSQ1). These experimental results indicate that increasing the amount of azobenzene groups incorporated into the silsesquioxane cage does not change the nature of the mesophase formed, but decreases the thermal stability of the mesophase. However, the 4-methoxyphenyl benzoate moieties (M1) in the oligomer systems may influence the liquid crystalline behavior of the silsesquioxanes. Liquid crystalline compounds are most commonly composed of flexible and rigid moieties, and phase separation into specific microstructures frequently occurs due to geometric and chemical differences between the two moieties. From SSQ2 to SSQ4, with an increase in mesogenic groups (M1) in the silsesquiosane cage, the isotropic transition becomes easier because probably these groups can dilute the interactions between azobenzene groups, thus depressing the clearing temperature (T_i). On the other hand, it is known that the silsesquioxane cage disturbs the mobility of the system [6], which can be an additional reason for the disorder in the mesogenic groups, causing depression of the melting point.

The nature of the mesophases exhibited by all oligomers described in this paper was assessed by XRD at variable temperatures above their melting point. Oligomer SSQ1 (see in Fig. 2), as well as the other azosilsesquioxanes, showed a diffuse, broad reflection at wide angles (associated with lateral packing, $d = 3.96$–5.00 Å), indicating the formation of the nematic phase [18–20].

3.4. Optical Properties

The optical properties of the silsesquioxanes with azo moieties were studied in solution ($CHCl_3$) by UV-Vis spectroscopy. The UV-Vis absorption spectra of the oligomers in

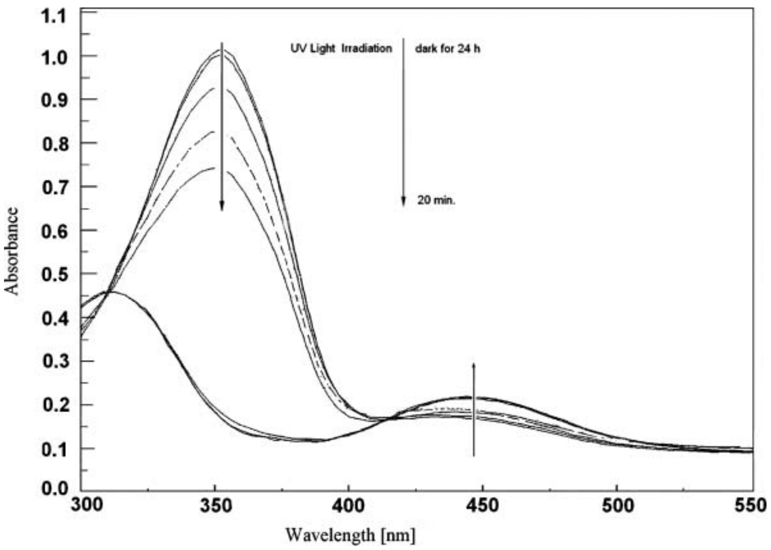


Figure 3. UV-Vis spectra of silsesquioxane SSQ2 solution under UV irradiation (365 nm).

solution were recorded in the 250- to 600-nm range. On exposure to UV light, the monomer with an azo-dye group and the oligomers can be transformed from the more stable *trans* form to the less stable *cis* form by photoisomerization. *Cis–trans* back-isomerization can take place either by a thermal or by a photochemical process. Figure 3 shows the change in the UV-Vis spectra of oligomer SSQ2 in $CHCl_3$ as a typical example of the photochemical behavior upon irradiation at $\lambda = 365$ nm. The UV-Vis spectra of all silsesquioxane oligomers show maximum absorption centered at 355 nm and a low intensity band at around 440 nm. The absorption spectrum of oligomers shows an additional strong UV absorption band at 255 nm. The λ_{max} at ~355 nm is assigned to the π–π^* electron transitions of *trans*-azobenzene, while the small shoulder at 440 nm is due to the n–π^*electron transition of the *cis*-isomer [21]. The absorption bands located between 250 nm and 300 nm corresponds to the ϕ–ϕ^* transition of the mesogenic phenyl benzoate units ($\lambda_{max} = 255$ nm). The ratio of the peak intensity of the (π–π^*) electron transitions of the azobenzene group to the intensity of the ϕ–ϕ^* electron transition of the aromatic rings gradually increases from SSQ4 to SSQ1, due to the increasing content of the azobenzene group in the silsesquioxane cage. The oligomer solution was exposed to nonpolarized UV light at 365 nm for various time intervals (Fig. 3). The UV irradiation leads to significant changes in the absorption spectra of oligomers. In this case, one might observe that the intensity of the absorption band at 355 nm decreases gradually, while the longer-wavelength maximum at 450 nm increases progressively with irradiation time. The absorption peak of π–π^* transition in the oligomer series almost disappeared after irradiation with UV light for 20 min. At the same time, the absorbance at about 255 nm undergoes no remarkable changes due to the absence of photochromic bonds in the mesogenic phenyl benzoate units (M1). The presence of isosbestic points at 308 and 413 nm indicates that photoisomerization is the only chemical transformation without other side reactions, such as photodegradation. We can observe that back-isomerization is much slower compared to with forward isomerization (*trans* to *cis*). When the solution is kept in dark at room temperature, the *cis* form slowly relaxed to the *trans* form, and the spectra gradually recovered to the original curve after 36–48 h at room temperature. The results indicate that the geometric *cis* form might return to the *trans* form gradually even without any exposure to UV light.

4. Conclusions

A series of side-chain LC silsesquioxanes bearing an azobenzene group were synthesized using octakis(dimethylsiloxy)silsesquioxane and two different promesogenic moieties. The TGA results displayed that thermal decomposition temperatures at 5% weight loss were greater than 270°C for all silsesquioxanes, which shows that the synthesized LC silsesquioxanes have good thermal stability. All the silsesquioxanes with azobenzene moieties showed the nematic phase. Their thermal behaviors strongly depend on the content of the different side-chain groups of the silsesquioxane cage. The temperature range of the nematic phase is widened by the addition of a 4-methoxyphenyl benzoate moiety to the siloxane cage. Under 365-nm UV irradiation, all the synthesized LC silsesquoxanes can undergo typical *trans–cis* (around 355 nm) and *cis–trans* ($\sim$ 450 nm) photoisomerizations of azobenzene, thus showing good photochromism.

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