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Synthesis and Properties of Liquid-Crystalline Cyclic Siloxanes Containing Azo Dye Groups

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The effects of incorporating an azo dye moiety as a nonlinear optically active chromophore with benzoyloxyphenyl-substituted mesogens to a cyclic siloxane backbone are reported. The liquid-crystalline (LC) cyclic oligosiloxanes were characterized by ^1H NMR, FT-IR, and UV-Vis spectra. The mesogenic properties of the oligomers were studied by differential thermal analysis, polarizing microscopy, and X-ray diffraction. The results show that all the cyclic oligosiloxanes exhibit the smectic phase except for the cyclic oligosiloxane with azo dye–only substituents, for which the LC state was not evident. The LC cyclic oligosiloxanes, when irradiated at 365 nm in chloroform solution, undergo a trans/cis isomerization of the azo dye moiety.

Keywords: azo dye; cyclic siloxanes; liquid crystals

1. INTRODUCTION

During the past decade, scientific research in the polysiloxane area has focused on the synthesis of new oligosiloxanes with special properties (i.e., liquid-crystalline behavior). Special attention was attributed to the oligosiloxanes containing dichroic dye moieties because of their potential application, particularly in reversible, optical, high-density data recording and data storage [1,2]. Cyclic siloxane oligomers are materials of significant technological interest for their potential applications in the fields of nonlinear optics. The siloxane backbone provides a high degree of flexibility to the oligomer and results in a liquid-crystalline (LC) state at a relatively low temperature.

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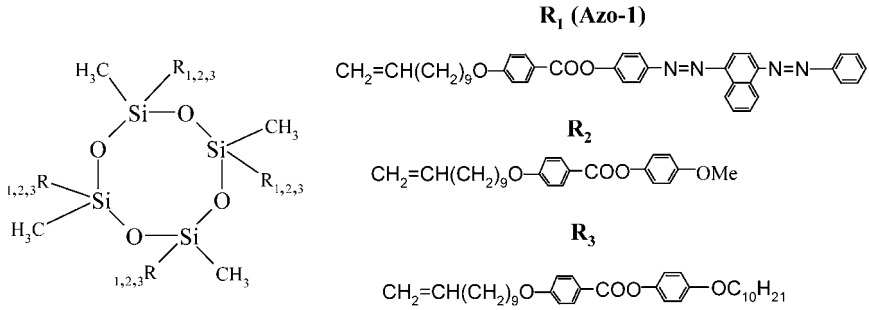


SCHEME 1 General formula of LC cyclic oligosiloxanes COSi1–COSi6.

Side-chain LC cyclic oligosiloxanes containing photochromic side groups were first described by Ortler *et al*. [3]. In the past few years, a number of new LC siloxanes with photochromic azobenzene-, spiropyrane-, and other azo-moieties in side chains were synthesized and used for reversible optical storage [4–6].

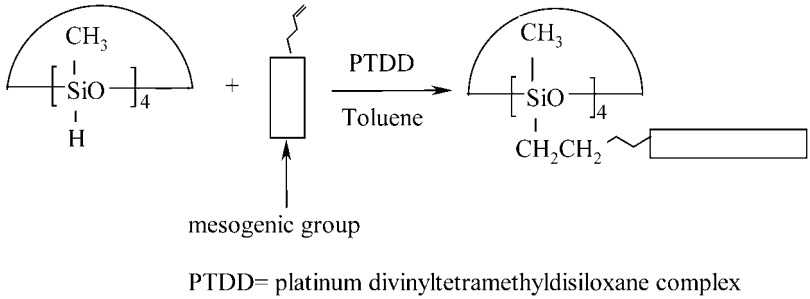
In this article, a series of novel photochromic side-chain LC cyclic tetramethyltetrasiloxanes containing an azo group (as shown in Scheme 1) were synthesized and characterized. The influences of a lateral attachment of the photochromic azo-moieties on the packing behavior of rod-like mesogens around the cyclic siloxane ring and changes in the thermal properties with varying compositions of the mesogens are discussed. Photochemical behavior of cyclic siloxanes in solution was also investigated.

2. EXPERIMENTAL

Materials and reagents were of commercial-grade quality and used without further purification unless otherwise noted. Toluene used in the hydrosilylation reaction was first refluxed over sodium and then distilled. All other solvents were purified by standard methods. The hydrosilylation catalyst [platinum tetramethyldivinyl disiloxane complex in xylene (11% wt)] was obtained from GE Silicon.

2.1. Synthesis

The alkene mesogenic side chain precursors: 4′-methoxyphenyl 4-(undec-10-enyloxy)benzoate, 4′-decyloxyphenyl 4-(undec-10-enyloxy)-benzoate mesogenic groups, and 4-(undec-10-enyloxy)benzoic acid were prepared by a conventional method described in earlier papers [7,8]. Esterification of the 4-(undec-10-enyloxy)benzoic acid with



SCHEME 2 Synthetic route of LC cyclic oligosiloxanes.

4[4-(phenylazo)-1-naphthylazo]phenol] (Disperse Orange 13 from Aldrich) was performed with *N,N′*-dicyclohexylcarbodiimide using a previously reported method [9]. The structures of all the mesogens were confirmed by means of FT-IR and ^{1}H NMR. Attachment to the cyclic tetramethyltetrasiloxanes, shown in Scheme 2, was performed using standard hydrosilylation chemistry with a platinum catalyst. Full experimental details of the hydrosilylation reaction, used to prepare the cyclic siloxane oligomers, are given in Ref. [9]. Hydrosilylation reactions were carried out in toluene at 50–60°C under argon. The FT-IR spectra of cyclic oligosiloxanes revealed the complete disappearance of the Si-H stretching band at 2163 cm^{-1}. ^{1}H NMR also confirmed the structure of the cyclic oligosiloxanes. The absence of remaining Si-H functions and of mesogens was confirmed by the absence of the corresponding signals in the ^{1}H NMR spectra (Si-H: 4.7 ppm, CH_2=CH-: 4.8–5.0 ppm and 5.7–6.0 ppm). Upon completion, the reaction solution was filtered into methanol to precipitate the product. This was done repeatedly until thin-layer chromatography (TLC) showed that no residual alkene remained in the product.

2.2. Characterization Techniques

^{1}H NMR was collected on a Varian Inova (500 MHz) spectrometer, using deuterated chloroform as a solvent and tetramethylsilane as the internal standard. FT-IR spectra of the synthesized mesogens and oligomers in the solid state by the KBr method or, if liquid, by casting films on NaCl discs, were obtained with Perkin-Elmer Spectrum 1000 spectrometer. Elemental analysis performed using a Euro Vector 3018 instruments for analysis of carbon, hydrogen, and nitrogen contents.

Differential scanning calorimetry (DSC) thermograms were obtained using a Perkin Elmer DSC-7, with a TAC 7/PC interface

and a controlled cooling accessory. The transition temperatures were taken from DSC traces of samples annealed by cooling from the isotropic melt corresponding to the maxima and the onset points of the enthalpy peaks for oligomers and low-molecular-weight samples, respectively, at a heating rate of 10°C/min.

Texture analysis was carried out by polarized optical microscopy (POM) on a Biolar polarization microscope equipped with a Mettler FP82HT heating stage and a Mettler FP-90 processor. Samples for POM analysis were prepared by dissolving about 1-5 mg of oligomer solution in volumes of 0.3 ml of $CHCl_3$ followed by casting two to three droplets of solution on a microscope slide cover. The films were not homogeneous in thickness; oligomer films with thicknesses between 1 and 5 μm exhibited the most recognizable textures.

Solutions of the azo monomer and oligomers in chloroform were irradiated with a UV lamp (30 W) at 365 nm (20°C), and corresponding UV measurements were performed with a Philips PU 8740 UV-Vis spectrometer.

X-ray diffraction measurements have been performed using a Philips X'Pert diffractometer fitted with a Guinier symmetrical focusing transmission photographic camera. In the case of the diffractometer, copper radiation filtered by a nickel absorption filter was applied, where as the Guinier camera worked with cobalt radiation. Diffractometer smectic-phase measurements were carried out using the reflecting method from flat samples aligned by glass substrate. The chosen temperature was maintained within ±0.1°C.

3. RESULTS AND DISCUSSION

3.1. Addition of Azo Dye Moiety to Cyclic Siloxane

The spectroscopic analysis confirmed the predicted molecular structures of the mesogenic units R_1–R_3 and LC cyclic oligosiloxanes COSi1–COSi6. Theoretical comonomers ratios and the final oligomer compositions determined by ^1H NMR for cyclic oligosiloxanes COSi1–COSi4 are shown in Table 1. The aromatic protons from phenyl benzoate and naphthalene moieties at 7.46–8.09 ppm and the methoxy (O-CH_3) resonance at 3.8 ppm from mesogen R_2 were used to calculate compositions using integral areas. The results show a good agreement between the initial monomer ratio and oligomer compositions, indicating reactivity of the azo-monomer is similar to that of the mesogen R_2. In case of oligomers COSi5–COSi6, the structure of the oligomers was confirmed by elemental analysis, because ^1H NMR analysis in this case is not sensitive enough. Because only the

TABLE 1 Compositions of Hydrosilylation Products as Determined by Elemental Analysis and ^{1}H NMR of the Cyclic Oligosiloxanes

	Elemental analysis (%)			AZO-1/R_2 ratio[a]		AZO-1/R_3 ratio[b]	
Oligomer	C	H	N	Theory	Determined	Theory	Determined
COSi1				1.0	1.0		
COSi2				0.75	0.78		
COSi3				0.50	0.54		
COSi4				0.25	0.23		
COSi5	79.97	9.26	2.50			0.25	0.23
COSi6	79.33	8.31	4.70			0.50	0.55

[a]Composition of hydrosilation products as determined by ^{1}H NMR of the cyclic oligosiloxanes.
[b]Composition of hydrosilation products as determined by elemental analysis.

azo-monomer contains a nitrogen element, the cyclic oligosiloxanes could be determined by the elemental analysis of the nitrogen. The data of the elemental analysis for the cyclic oligosiloxanes COSiO5–COSiO6 and the calculated molar fraction of the azo unit in cyclic oligosiloxanes are listed in Table 1.

3.2. Mesomorphic Properties

The mesomorphic properties of all cyclic oligomers COSi1–COSi6 and their precursor Azo-1 were investigated by POM and DSC. For the azo monomer, a defined melting point was observed by POM and no LC behavior could be detected, where as nonpolar mesogens R_2 and R_3 exhibited LC behavior. Thus, the smectic A_1 phase in the ranges of 51–132°C and 70–89°C was observed for R_2 and for R_3 precursors, respectively. Details of preparation and the results of POM measurements have been published previously [7,8]. Freshly cast and unheated films of the cyclic oligosiloxanes with azo dye moiety without any treatment are dark between crossed polarizers but exhibit birefringence domains when heated above the melting transition temperature. Oligomers from COSi2 to COSi4 exhibit a nonclassical texture, probably due to the reduced mobility of the side chain as the result of the steric hindrance. COSi6 and COSi7 oligomers exhibit very small fan textures after annealing for 24 h.

The values of phase-transition temperatures as well as their enthalpies are summarized in Table 2.

All the thermograms show two endothermic peaks, one of Tm at lower temperature and the other ascribed to the mesophase–isotropic

TABLE 2 Transition Temperatures (°C) of Cyclic Oligosiloxanes

Oligomer	Transition temperatures (°C)	$\Delta H_{S\text{-}I}$ (J/g)
COSi1	Cr 113 I	
COSi2	Cr 42 SmA 73 I	2.4
COSi3	Cr 38 SmA 80 I	2.9
COSi4	Cr 37 SmA 86 I	1.5
COSi5	Cr 39 SmA 103 I	2.7
COSi6	Cr 41 SmA 101 I	2.4

Note. Cr, crystalline phase; SmA, smectic phase A; I, isotropic phase.

phase transition (Ti) (Fig. 1). With increasing azo-mesogen content in siloxane ring, the LC phase range is decreased, because the crystallization temperature is slightly increased and at the same time the clearing temperature is decreased. This indicates that the order necessary for the formation of a mesophase is disturbed by the azo-mesogen. Additionally, the mesogenic properties of these cyclic oligosiloxanes depend on the length of the end terminal group in 4-alkoxyphenyl benzoate mesogen. When comparing oligomers COSi4 and COSi5 with the same azo group content but different terminal groups in nonpolar mesogens, both mesophase transition and clearing temperatures of COSi5 with a decyloxy terminal group are higher than those of COSi4 with a methoxy terminal group. This suggests that the presence of mesogenic moieties of different lengths ($d = 3.85$ nm for azo-dye and $d = 2.85$ nm for methoxy mesogen (calculated by means of HyperChem) makes the mesophase formation difficult.

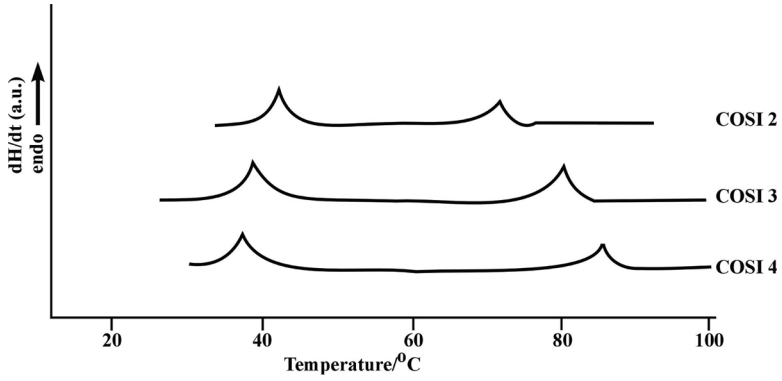


FIGURE 1 DSC curves of the cyclic oligosiloxanes COSi2, COSi3, and COSi4.

The presence of a mesogenic moiety of comparable length d ($\sim$4.0 nm in the case of decyloxy substituent) facilitates the molecular ordering favoring the LC properties.

The identification of the type of mesophase was also characterized by temperature-controlled X-ray diffraction of the powder samples. In general, the X-ray diagrams in low-angle range exhibit one or two sharp reflections that can be indexed as the 001 reflections of the layered smectic structure of parameter d (thickness of the smectic layers), and a diffuse band at wide angles, associated with the lateral packing, indicating the formation of a smectic phase. Furthermore, the first reflection intensity becomes weaker with the increase of the azo-group content in the siloxane ring as compared with the wide-angle reflection intensity, which is unchanged.

3.3. Photochemical Properties

The photochemical properties of all compounds were studied at 20°C for their solutions using the UV/Vis Philips PU8750 spectrometer in the 200 to 600-nm spectral range. The solution was prepared using $CHCl_3$ (0.2 g/l) and kept in the dark overnight for further experiments. The measurements were performed using a 0.2 cm path length quartz cuvette, 365 nm with UV lamp (nonpolarized source). The lamp power was 30 mW, and intensity at sample level was 2.4 mW/cm^2. Oligomers COSi2–COSi4, as well as their Azo-1 low-molecular-weight precursor

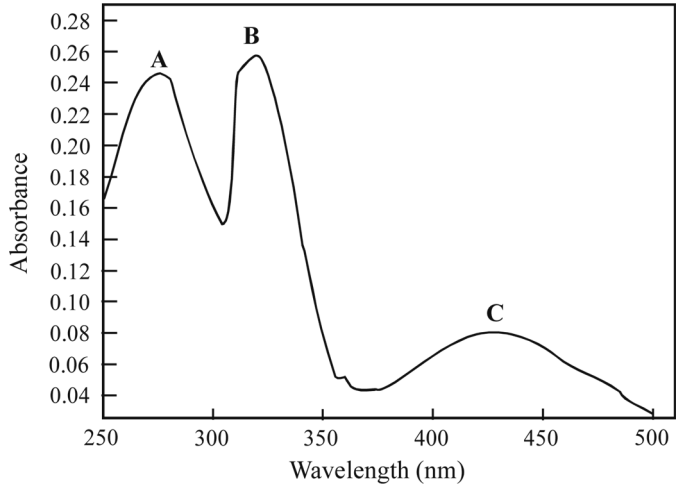


FIGURE 2 Characteristic UV-Vis spectra for COSi2 in chloroform.

TABLE 3 UV/Vis and IR Spectral Data of the Cyclic Oligosiloxanes

Oligomer	UV (nm)[a] Ar[b]	UV (nm)[a] –N=N[c]	$\pi \rightarrow \pi^*$ ε_{320} ($l\,mol^{-1}\,cm^{-1}$)	n-π^* ε_{425} ($l\,mol^{-1}\,cm^{-1}$)	IR (KBr) ν (cm^{-1})
COSi2	276	320	15 700	5 300	2936(m), 2855(w), 1729(s), 1606(s), 1519(s), 1490(w), 1263(s), 1057(s), 1003(m), 843(m), 805(m), 756(m), 686(m)
COSi3	276	321	11 400	4 200	2936(m), 2853(w), 1727(s), 1606 (s), 1519(s), 1490(w), 1263(s), 1057(s), 1003(m), 843 (m), 805(m), 753(m), 688(m)
COSi4	276	321	10 200	4 500	2934(m), 2855(w), 1728(s), 1607(s), 1519(s), 1490(w), 1263(s), 1057(s), 1009(m), 843(m), 803(m), 756(m), 686(m)
COSi5	276	323	17 700	5 400	2925(m), 2855(w), 2820(m), 1734(s), 1605(s), 1510(s), 1463(w), 1264(s), 1155(s), 1063(m), 843(m), 808(m), 761(m)
COSi6	276	323	13 300	6 000	2923(m), 2855(w), 2825(m), 1733(s), 1605(s), 1510(s), 1463(w), 1264(s), 1155(s), 1064(m), 842(m), 807(m), 761(m)

[a]In chloroform.
[b]UV absorption due to aromatic rings.
[c]UV absorption due to the π-π^* transition of N=N bond in the azo group.

show, in chloroform solution, a strong UV absorption band centred at about 320 nm (band B at Fig. 2) and a broad band around 425 nm (band C). These two bands are attributed to the π–π^* and n–π^* electronic transitions of the *trans*-azobenzene chromophore, respectively [7].

The band A at 276 nm is related to the absorption of aromatic mesogenic cores. Thus, the isomerization process of the azo moieties can be traced easily by a change in relative intensity of the B and C bands. The band B is related to monotonic decrease of the molar extinction coefficient (ε) of the maximum from 15,700 to 10,200 with increasing content of azo dye units in the siloxane rings in series COSi2–COSi4 (Table 3).

A slight bathochromic shift is also observed with decreasing content of azo dye moiety in siloxane rings. This shift could be at least partially responsible for the particular behavior of the n–π^* electronic transition band. The observed bathochromic and hypochromic shifts have been reported for optical polymers, and they have been related to interactions between neighboring chromophores [10,11]. All oligomers in solution undergo a *trans-cis* photoisomerization of the azo dye moiety at 365 nm in the π–π^* absorption region. The intensity of the $\pi \rightarrow \pi^*$ absorption band decreases, whereas that of the n$\rightarrow\pi^*$ increases with irradiation time. These phenomena are similar to those observed in other side chain polymers containing an azo group [12,13].

The dependence of time–relative absorbance (A/A_0 where A_0 and A are the absorbance of the sample at time 0 and t, respectively) indicates that the photoinduced isomerization rates in chloroform of the oligomers COSi3 and COSi5 are lower than those of the azo monomer (Azo-1) (Fig. 3) [14,15]. This result indicates that the cyclic oligomer

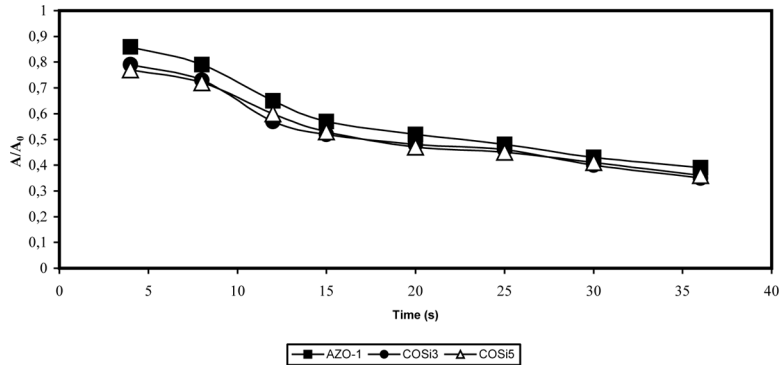


FIGURE 3 Decrease of the relative absorbance (A/A_0) in dependence of time upon irradiating with 365-nm light for AZO-1 (■), COSi3 (●), and COSi5 (▲) in chloroform at 20°C.

structure can affect the photoisomerization rate. It could be connected with the fact that the length-to-width ratio for the cyclo(oligosiloxanes) with azo groups (azo-mesogen contain naphthalene and three phenyl rings) is higher than the classical azo-polymers that contain only azobenzene groups. Additionally, the influence of the neighboring nonpolar groups could affect this relation between time and relative absorbance as well. Further study is needed for a complete understanding of the molecular packing mode. These results will be published elsewhere.

4. CONCLUSIONS

In this article, a series of novel cyclic tetramethyltetrasiloxanes with azo dye moiety was prepared and investigated. The cyclic siloxanes containing up to 75% azo-dye are LC, whereas at higher content the cyclic oligosiloxane is crystalline. Furthermore, an increase of azo dye moiety of the cyclic oligosiloxanes leads to narrowing the temperature range of the LC phase. The results also show that the solutions of the azo monomer and cyclic siloxanes in chloroform can undergo photoisomerization upon irradiation with 365-nm UV.

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