



Liquid crystalline silicon-containing oligomers

Ewa Biłacka-Florjańczyk^a, Joanna T. Sołtysiak^{b,*}

^aWarsaw University of Life Sciences-SGGW, Institute of Chemistry, Nowoursynowska 166, 02-797 Warsaw, Poland

^bIndustrial Chemistry Research Institute, Analytical Chemistry, Rydygiera 8, 01-793 Warsaw, Poland

ARTICLE INFO

Article history:

Received 3 December 2009

Received in revised form

12 April 2010

Accepted 22 April 2010

Available online 8 June 2010

Keywords:

Cyclo(oligosiloxanes)

Silsesquioxanes

Liquid crystalline oligomer

Structure-property relationships

ABSTRACT

Liquid crystalline siloxane oligomers with the same type of mesogenic groups (methoxyphenylbenzoate) but with different structures of siloxane cores (cyclooctasiloxane ring or octakisilsesquioxane cage) were synthesized. The set of oligomers with the same type of mesogenic groups but with different structure of siloxane cores gave a unique opportunity to study LC properties and structure relationships. The chemical structures of all compounds were confirmed using FTIR and ¹H NMR and ²⁹Si NMR spectroscopy. The thermal behaviour and the mesogenic properties of the siloxane oligomers were investigated using differential scanning calorimetry, polarized optical microscopy, and wide-angle X-ray diffraction. The mesogenic properties of side-chain liquid crystalline siloxane oligomers were discussed.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The key to the development of liquid crystalline properties in side-chain siloxanes is the flexibility of the siloxane backbone that allows the mutual orientation of the chain and the rigid mesogenic cores. At that time, the whole range of architectural synthetic possibilities was still being explored from calamitic side-chain siloxanes to flexible rod-like mesogens sometimes diluted by dimethylsiloxy groups along the siloxane backbone. In the case of the side-chain liquid crystalline oligomers, mesomorphic properties depend on the nature of oligomer backbone, length of flexible spacer and rigidity of mesogenic unit. Through the fixation of the mesogenic cores to a backbone, the phase transition temperatures are increased due to the material's higher viscosity. In this regard, side-chain oligomers, especially those containing siloxane backbone were synthesized, because the low glass transition temperatures and the low viscosities give rise to moderate phase transitions. Several reports about liquid crystalline cyclo(oligosiloxanes) having different mesogenic units have appeared since then, with special attention on their optical properties and potential applications as optical data storage [1–4]. In some studies, the comparison on the mesomorphic properties between cyclic oligosiloxanes and linear polysiloxanes were carried out [5–9]. In this case, the correlation between the length of the spacer and stability of the mesophases is similar to that, which is observed for of linear side-

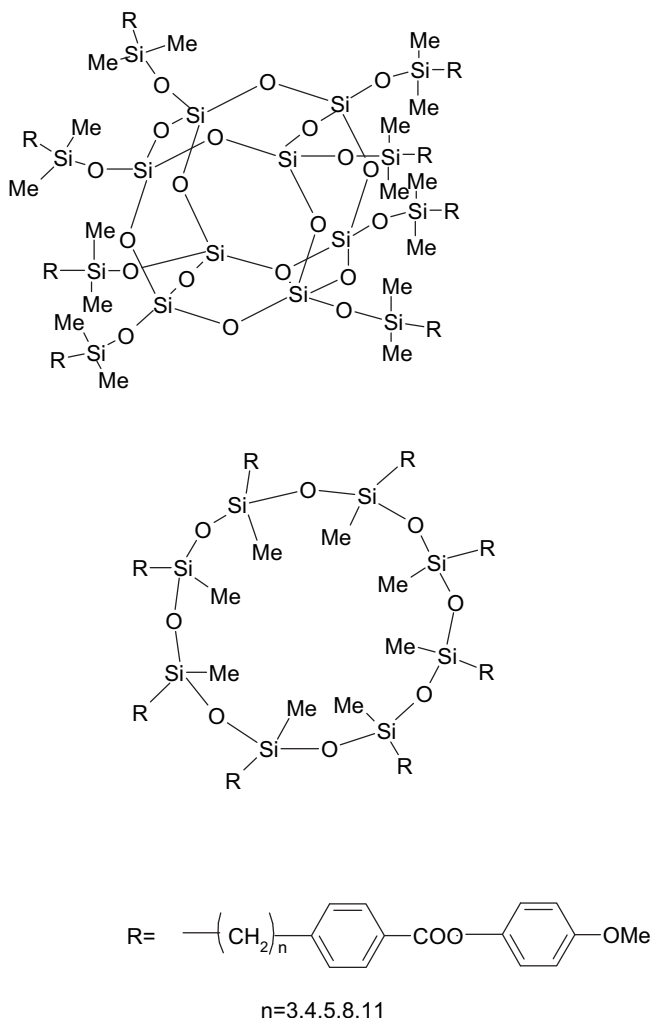
chain LC polysiloxanes. During the last few years, new types of LC organosilicon oligomers were synthesized, having two or more cyclic backbones connected via oxygen bridges [10–13]. Functionalized polyhedrals are considered as important building blocks with sizes of 1–3 nm and can be thought of as the smallest particles of silica possible. Silsesquioxanes are thus unique nanobuilding blocks that can be used to create a wide variety of hybrid materials, where precise control of nanostructures and properties is required. Various, experimental studies on LC silsesquioxanes reveal that covalently attaching of mesogenic substituents to the silsesquioxanes cores enables the nanocubes to form LC phases, which the promesogenic alkenes themselves do not exhibit [14,15]. Saez et al. [16] reported that octa-functionalized, liquid crystalline silsesquioxane molecules self-assemble into chiral nematic, columnar and rectangular columnar phases upon cooling whereas the alkene precursors exhibit only the chiral nematic phase. A very detailed study of modifications of cubic silsesquioxanes with various mesogens and subsequent coupling via Pt or Pd catalyst opens an alternative route to new LC materials reported by Laine et al. [17,18]. Richardson et al. [19] reported a hexadecamer, first-generation, octasilsesquioxane liquid crystalline dendrimers.

On the ground of above scientific research, we have been interested in the use of two different octa-functionalized siloxane oligomers as the matrices of potential fast responsive materials. Moreover, data on the influence of structure of different cyclic siloxane core on the properties in LC state are still lacking in literature.

Thus, in this article we present synthesis, characterization and phase behaviour of the liquid crystalline organic–inorganic

* Corresponding author. Tel.: +48 225682467; fax: +48 225682048.

E-mail address: joanna.soltysiak@ichp.pl (J.T. Soltysiak).



Scheme 1. Schematic representation of the series of liquid crystalline oligomers.

oligomers based to the two different siloxane cores: cyclo[octa(methylhydroxiloxane)]-D₈H and octakis(dimethylsiloxy)silsesquioxane- POSS. Their general structures are shown in Scheme 1. Oligomers of this type may be readily prepared in a one-step hydrosilylation, which can be considered as a general method for the synthesis between Si–H bond and alkene part of promesogenic monomers.

2. Experimental

2.1. Characterization

IR spectra were recorded on a Perkin–Elmer SPECTRUM 2000 spectrophotometer with 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.

¹H and ²⁹Si NMR solution spectra were obtained with Varian INOWA (400 MHz) spectrometer. Chemical shifts were assigned using residual CHCl₃ (¹H) and TMS (²⁹Si) as an internal standard.

Thermogravimetric analyses were carried out using a TA Instruments TGA Q50 thermogravimetric analyzer at a heating rate of 10 °C/min. Samples of approximately 20–50 mg were placed in a platinum pan in air and put immediately into the furnace. Samples were heated in dry air to 800 °C with ceramic yields based on decomposition to SiO₂.

Phase transition temperatures were determined with a Perkin–Elmer DSC-7 equipped with a liquid nitrogen cooling system, at a heating rate 10 °C/min under nitrogen atmosphere. The reported thermal transitions were collected during the second heating and cooling scans.

Polarized optical microscopic (POM) studies were conducted using a Biolar microscope equipped with a Mettler FP82HT heating stage and Mettler FP-90 central processor. The heating rate of 10 °C/min was used. Samples were prepared as thin films between glass slide and a glass cover slip.

The XRD data for LC phase were obtained with Bruker GADDS system, using CuK α radiation. The diffractometer was equipped with Gobel mirror, monocrap collimator, and 2-d HiStar detector.

2.2. Materials

All monomers used were purchased from Aldrich in the purest grade available and employed without further purification. Only 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—PTDD – (platinum tetramethyldivinyl disiloxane complex in xylene (11%wt)) was purchased from GE Silicon.

Octakis(dimethylsiloxy)-T₈-silsesquioxane was purchased from Gelest Inc.

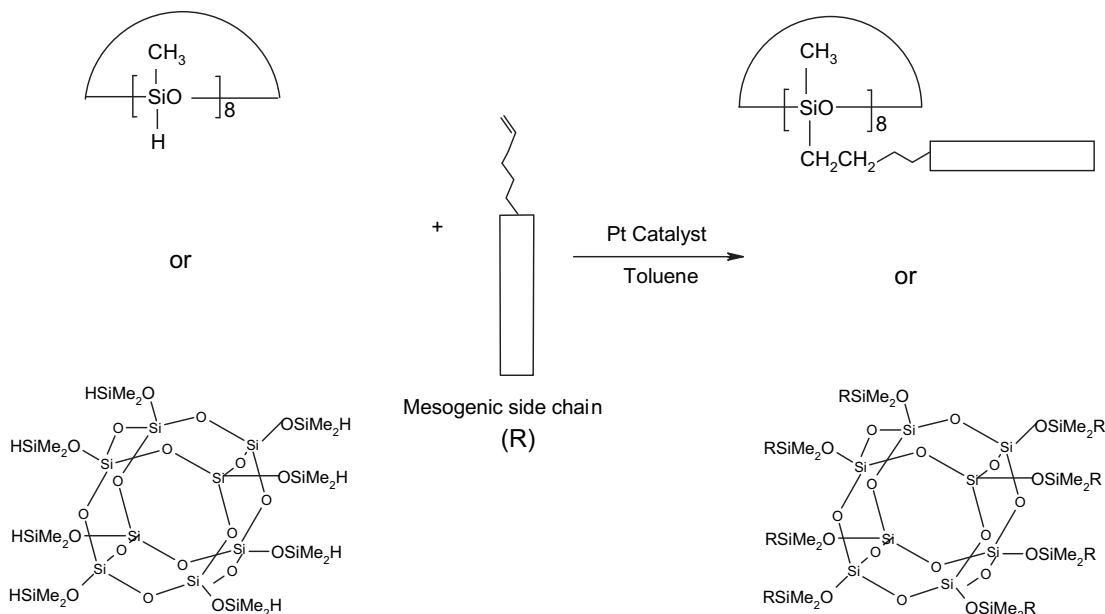
The individual cyclo[octa(methylhydroxiloxane)] (D₈H) was made by hydrolysis of methylchlorosilane, followed by pyrolysis and careful fractional distillation of the mixture of cyclic products [20,21]. Cyclo(octaoligosiloxane) was obtained in yields 23% and was used as the cyclosiloxane core for subsequent syntheses.

The alkene mesogenic side-chain precursor - 4'-methoxyphenyl-4-(ω -alkenyloxy)benzoate, was synthesized according to a previous report [20]. The structure of the mesogen was confirmed by means of FTIR and ¹H NMR. The transition temperatures determined by differential scanning calorimetry and confirmed by polarizing optical microscopy.

2.3. Synthesis

Attachment of mesogens to the cyclic siloxanes and silsesquioxanes, shown in Scheme 2, was performed using standard hydrosilylation chemistry with platinum catalyst. The liquid crystalline siloxane oligomers were prepared by platinum catalyzed reaction of the mesogenic alkenes with octamethyloctacyclosiloxane (OCSX) and octakis(dimethylsiloxy)silsesquioxane (POSSX) using Karstedt's catalyst at 50 °C in toluene. Full experimental details of the hydrosilylation reaction, used to prepare the cyclic siloxane oligomers, are given in reference [20].

Hydrosilylation reactions were carried out in toluene at 50–60 °C under argon. The reaction was followed by monitoring the disappearance of the Si–H stretching band at 2160 cm⁻¹ using FTIR spectroscopy. Upon completion of the reaction, the products were separated by precipitation into an excess of methanol and dried in vacuum oven at room temperature. This was done repeatedly until TLC showed no residual alkene remained in the product. The IR spectra of siloxane oligomers showed the complete disappearance of the Si–H stretching band at 2160 cm⁻¹ and olefinic C=C stretching band at 1640 cm⁻¹, Si–C stretching bands appeared at 1259 and 780 cm⁻¹. Characteristic Si–O–Si stretching bands appeared at 1166 cm⁻¹, 1155, and 1025 cm⁻¹. Additionally, NMR analysis indicated exclusive β -hydrosilylation with silsesquioxanes for all reactants. ¹H NMR traces: to the corresponding mesogenic group with the loss of the vinyl protons (CH₂=CH: δ = 5.85 and δ = 5.00), the appearance of triplet (CH₂–Si proton) at



Scheme 2. Synthesis of LC silicon oligomers with different backbones.

0.60 ppm. Complete absence of Si–H peak at ~ 4.2 ppm, signified a fully substituted POSS and OCS was also observed for all compounds. For silsesquioxanes, ^{29}Si NMR analysis revealed two different silicon peaks at 13.0 ppm and -108.7 ppm that represent both $\text{OSi}(\text{CH}_3)_2$ and SiO_4 respectively.

3. Results and discussion

3.1. Thermal analysis of oligosiloxanes

The thermal properties of the all oligomers were investigated by means of differential scanning calorimetry DSC and optical polarizing microscopy (POM). Additionally the TGA analysis of some compounds was conducted to study their thermal stability, and to determine SiO_2 content after pyrolysis in air. The results are summarized in Table 1 with representative TGA profiles in Figs. 1 and 2.

For all silsesquioxanes the data suggest high thermal stability in consideration of greater than 300°C of 5% weight loss temperature (T_d). Furthermore, for this silsesquioxanes series, four oligomers were found to have ceramic yield values within 0.5% theory, only the POSS-3 was within 2% of theoretical SiO_2 . Besides the Si–H stretching bands were not found in the IR spectra of hydrosilylation products, thus, we can conclude that all oligomers have an average substitution of eight organic groups per cube. The results obtained in air, indicate that the thermal decomposition began at temperatures about 200°C higher than isotropization temperatures so that the mesophase is not affected by decomposition phenomena and the obtained silsesquioxanes might be processed in the LC state.

The good thermal stability of silsesquioxanes may result from the more difficult decomposition of the siloxane cage than the side-chain mesogen in the oligomer systems. There is a possibility, that

in air the behaviour on heating may be different from the one observed in inert atmosphere, as oxygen plays an active role in the degradation process [22], but in our experiments POSS series, we didn't observed direct dependency of the weight loss temperature with increasing alkyl chain length, indicating that the effect of oxygen on their degradation patterns is little.

Thermogravimetric analysis of oligocyclosiloxanes has been well studied [23,24]. For example, Michalczyk and co-workers [25] have analysed the thermal behaviour of cyclic siloxanes and concluded that in cyclic siloxanes the core mobility was not drastically diminished, and consequently, the thermal degradation process has been strongly dependent on the side-chain component. Additionally, mechanism of decompositions of these materials was determined by bond energy factors. In the case of oligocyclosiloxanes under investigation [25], thermogravimetric analyses, showed the weight loss take place in a two step, leaving 2–4% amount of residue at 400°C . We have confirmed this observation by thermogravimetric analysis of OCS-3 (Fig. 2)

Thermogravimetric curve of OCS-3 showed a good thermal stability with initial temperature of weight loss at 295°C and leading to a final 11 wt % thermally stable residue at 796°C .

To summarize cyclic oligosiloxanes are thermally less stable than silsesquioxanes series. For example, decomposition of OCS-3 starts at temperatures lower 100°C than it was observed for POSS-3. Nevertheless the results obtained in air, indicate that the thermal decomposition in both cases began at temperatures about $150\text{--}200^\circ\text{C}$ higher than isotropization temperatures so that the mesophase is not affected by degradation phenomena and the obtained silsesquioxanes and cyclic siloxanes might be processed in the LC state.

3.2. Liquid crystalline properties of cyclo(oligosiloxanes) and silsesquioxanes

The liquid crystalline behaviour of the siloxane oligomers was investigated with DSC, POM and X-ray analysis. The mesophases were identified according to the classification system reported by Demus and Richter [26]. The DSC thermograms were highly consistent with the corresponding observations using POM. The phase transition temperatures of the two series of oligomeric siloxanes, obtained of the DSC thermograms (from second heating

Table 1
Thermogravimetric analysis (TGA) data of synthesized LC silsesquioxanes.

Silsesquioxanes	$T_d5\%$ ($^\circ\text{C}$)	Expt SiO_2 (%)	Cal SiO_2 (%)
POSS-1	323.7	29.97	30.37
POSS-2	313.3	29.01	29.33
POSS-3	365.3	27.70	28.33
POSS-4	369.2	25.40	25.80
POSS-5	358.8	22.41	22.95

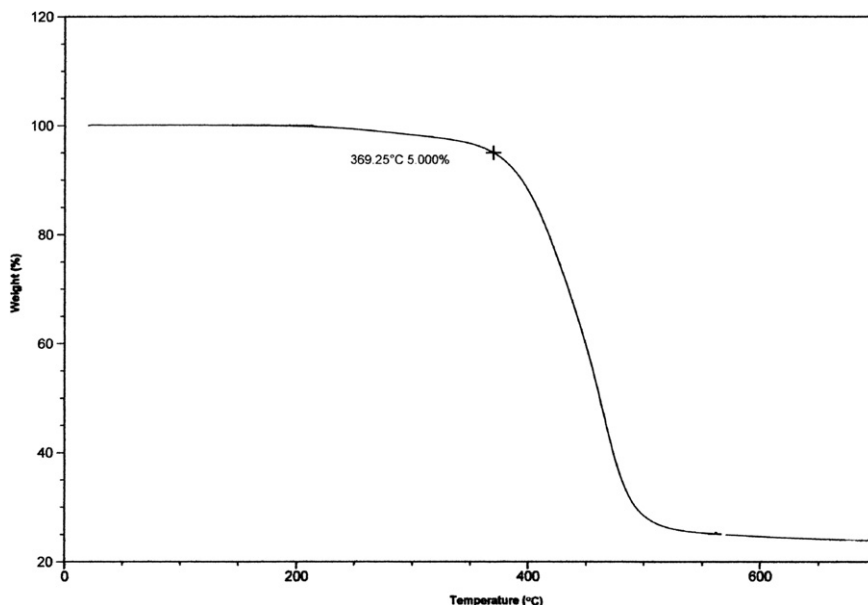


Fig. 1. TGA thermogram of the POSS-3.

scan) are summarized in Table 2. All phase transitions were reversible and did not change on repeated heating and cooling cycles.

Properties of these novel groups of side-chain LC organosilicon oligomers vary, as expected, with the length of a flexible spacer.

As it can be seen (Table 2) not all the oligomers exhibit LC properties. In the case of the shortest studied spacer (the propoxy), we did not observe existence of mesophase in cyclo(oligosiloxane) and silsesquioxane series as well. It is probably due to the fact, that short flexible spacers leave little freedom to individual mesogens at branching point.

For spacers longer than three carbon atoms a cyclic siloxane backbone provides the same useful feature as other oligomers in promoting LC properties for originally non-mesogenic, rigid low molecular mass compounds [27]. In the homologous series OCS-2- OCS-5, the nematic phase exists only for $n = 4$ and $n = 5$, while the other members of this series form also smectic phase. As the spacer length was increased

(OCS-2 to OCS-5) the range of the mesophase broadened as T_m decreased and T_i increased (Fig. 3). The increase in thermal stability of the LC phase was due to a decoupling function of the spacer on the motion of the oligomer core from those of the mesogenic groups. Therefore, a higher degree of ordering in a mesomorphic phase should be expected, leading to higher isotropization temperature. These results are similar to the observations for analogously substituted side-chain LC polysiloxanes, where a strong stabilization of the liquid crystalline state, particularly for the nematic phase, with increasing the length spacer has been observed [28]. Additionally, this behaviour was attributed to increased flexibility of the polymers, which would reduce the energy of disorientation of polymers in the LC phase.

In the series of the oligosiloxanes with the siloxane cage we observed the marked different phase behaviour in comparison with the cyclo(oligosiloxane) series. Silsesquioxanes with the propoxy

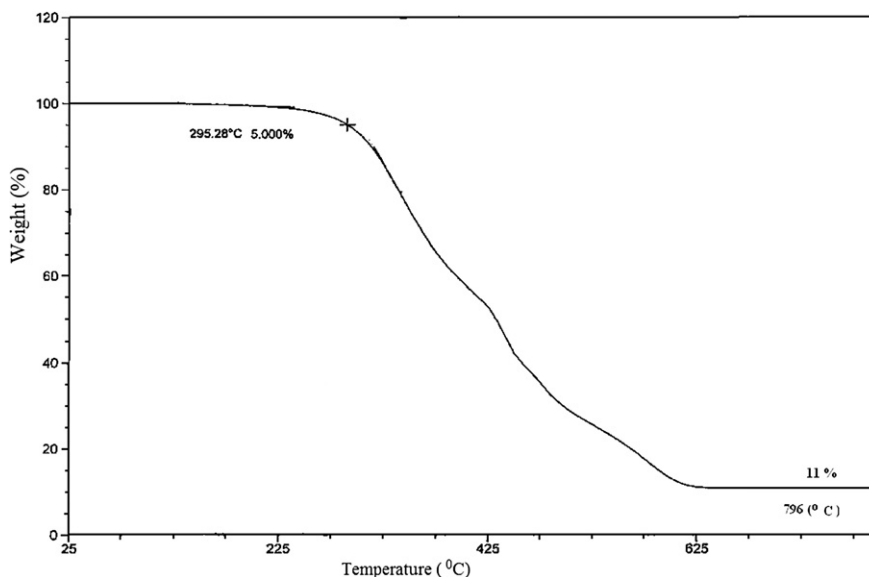


Fig. 2. TGA thermogram of the OCS-3.

Table 2
Transition temperatures of cyclo(oligosiloxanes) and silsesquioxanes series.

OCSX			POSSX		
X	n	Transition temperature [°C] ^a ΔH ₁ /J/g	X	n	Transition temperature [°C] ^a ΔH ₁ /J/g
OCS-1	3	Cr 42 I	POSS-1	3	Cr ₁ 49 Cr ₂ 79 [−2.58]I
OCS-2	4	Cr 55 N 74 [0.74]I	POSS-2	4	Cr ₁ 50 Cr ₂ 69 [−10.2]I
OCS-3	5	Cr 51N 103 [1.01]I	POSS-3	5	Cr ₁ 50 Cr ₂ 57 S ₁ 111 [4.89]I
OCS-4	8	Cr 45N 94 SmA 107 [2.54]I	POSS-4	8	Cr ₁ 38 S ₁ 58 SmA 123 [7.77]I
OCS-5	11	Cr 38 SmA 118 [3.72] I	POSS-5	11	Cr 59 SmA 133 [8.42]I

Cr₁ and Cr₂-crystalline phase, N-nematic phase S₁-smectic or soft-crystal phase, SmA- smectic a phase I-Isotropization Phase.

^a The transition temperature was determined during II heating cycle.

and butoxy spacer formed only crystalline phase (Cr₁ or Cr₂), which was confirmed by X-ray diffraction (Fig. 4).

For other LC silsesquioxanes, smectic phase was evidenced on heating from an initial crystalline or soft crystalline S₁ (or S_B) phase through the respective transition temperatures.

For example, POSS-4 shows three transitions during the heating in its DSC thermogram (Fig. 5). X-ray diffraction data analysis confirms that the first transition is from a crystalline phase to a soft crystalline phase (S₁), the second one from a S₁ phase to a less ordered SmA phase and the last one from a SmA phase to an isotropic phase.

The spacer between the siloxane cage and the mesogenic side group of LC silsesquioxanes played an important role in determining the mesogenic properties of the oligomer. The function of the spacer was to decouple the motion of oligomer cage, which tended to form a “bundle” conformation, from those of the mesogenic groups that were ordered in the liquid crystalline phase. The DSC results showed that on increasing the number of methylene units (from five to eleven) in the spacer, the temperature of melting point (T_m) changes rather irregularly and do not show uptrend or downtrend. However, the increase the isotropization temperature was observed and the thermal stability of the mesogenic phase and LC range both increased as the result.

Furthermore comparing with cyclo(oligosiloxanes) series, in POSS mesogens are grafted to octasilsesquioxane core via additional dimethylsiloxane group. Therefore, the total spacer length is considerably longer than in the former case and this effect is responsible for larger increase of T_i. In addition, the inherent incompatibility between polar inorganic siloxane cage and apolar methylene chain might contribute to stabilize the mesophase, because this effect should become pronounced in the case of long alkyl spacers. The incompatibility concerns not only the polar effects, but the differences in rigidity of the particular fragments of molecule as well. In comparison with octacyclosiloxane or tetra-cyclosiloxane [20] series bearing the same mesogen, the LC

silsesquioxanes show a more ordered smectic liquid crystalline phases between melting point and an isotropic transition, whereas the for example OCS-3 shows only nematic phase. It appears that the silsesquioxanes with a more rigid framework tends to form a more ordered structure.

The silsesquioxanes form a rigid cage substituted symmetrically in eight points above the surface whereas, the cyclic core of siloxanes can exist in different conformations, facilitating the ordering of molecules. Thereby in the former case, the longer flexible spacer is indispensable to overcome the difficulties connected with mesophase formation. Nevertheless, if it occurs the phase separation takes place and smectic phase arises. This tendency was supported by data of Mehl and Goodby [28] who synthesized LC siloxanes with tetrahedral core and cyanobiphenyl mesogenic group. These compounds generates partially bilayered smectic phase because, according to molecular modelling, the side chains are aligned forming rod-like structure despite of intuitively fully extended spherically shaped conformation. In our case the greater incompatibility, which arises with length of the spacer and methoxyphenylbenzoate mesogen favours the formation of more ordered structure, giving rise to higher isotropization temperature. In side-chain, polymers an odd-even effect is often seen as the spacer is varied [29]. In octacyclosiloxane series, the melting and isotropization temperatures are strongly influenced by the flexibility of cyclic core and molecular weight. It is assumed that cyclic core also generated similar effect on T_m and T_i like siloxane polymer backbone [30]. In silsesquioxane series, we have not observed this phenomenon; the absence of any strong odd–even effects suggests that these oligomers probably had the same orientation relationship between the siloxane cage and mesogens. Although early work has indicated that increasing flexibility of polymer backbone can lead to a lower T_i for certain mesogenic groups, the opposite effects are more typically observed [31, 32]. Our results for octa

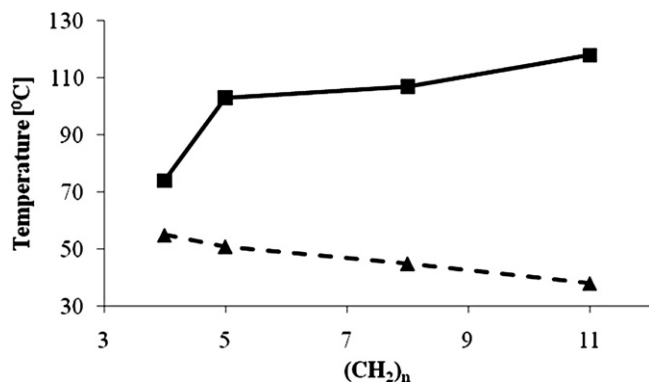


Fig. 3. Effect of the length mesogenic side-chains on the phase transition temperatures of the cyclic siloxanes.

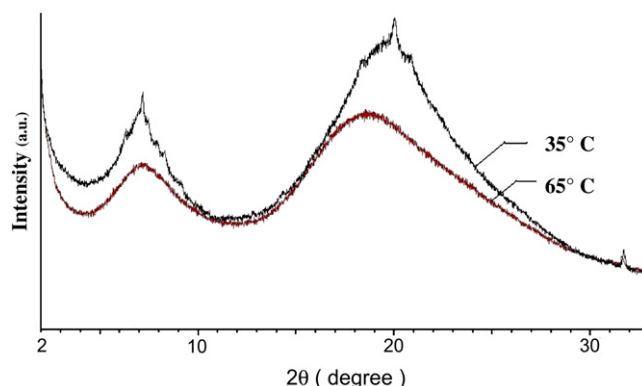


Fig. 4. X-ray diffraction diagram of the silsesquioxane POSS-1.

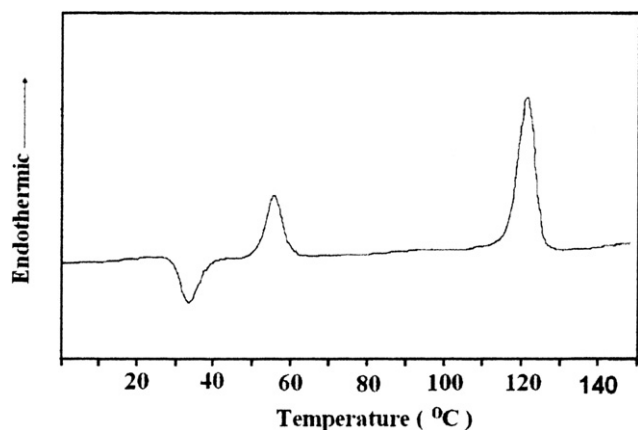


Fig. 5. DSC thermogram of POSS-4.

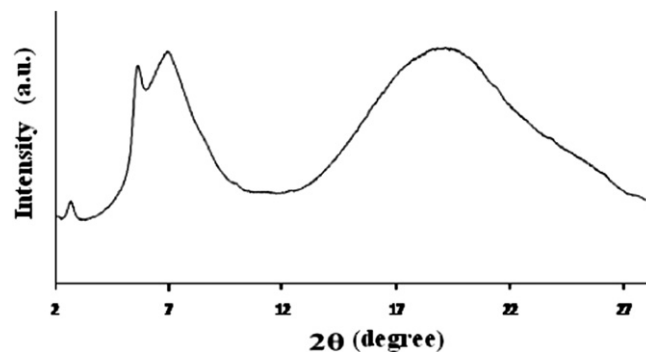


Fig. 7. X-ray diffraction diagram of the silsesquioxane POSS-5.

(cyclosiloxanes) with methoxyphenylbenzoate mesogen confirm this more general trend.

3.3. Texture analysis

Mesophase identification has been accomplished by POM observation and X-ray measurement. The optical textures of the octacyclosiloxanes and silsesquioxanes were investigated via POM with cold and hot stages. The cyclic siloxanes OCS-2 and OCS-3 show only schlieren texture while OCS-4 shows nematic and smectic phases (focal-conic texture). For longer spacer ($n = 11$) only smectic phase is observed. In the case of silsesquioxanes, most of them on cooling from isotropic state form unidentifiable texture where domains after long periods of annealing give a mosaic texture. The optical texture of POSS-3 is shown in Fig. 6.

X-ray studies can confirm the presence of the nematic and smectic A phases. The X-ray diffraction pattern of POSS-5 is showed in Fig. 7. The X-ray diffraction pattern of the smectic A phase showed one or two sharp reflections in the small-angle region and broad reflections in the wide-angle region. Diffuse, wide-angle halo at 4.4 Å typical for the lateral distance between mesogenic groups and a strong diffuse scattering at 12.8 Å, which was attributed to the periodicity of the arrangement of the silicones cores [33]. The sharp inner reflection ($d = 25.6$ Å and 44 Å) corresponding to the values for the first- and second-order smectic A peaks. Molecular modelling

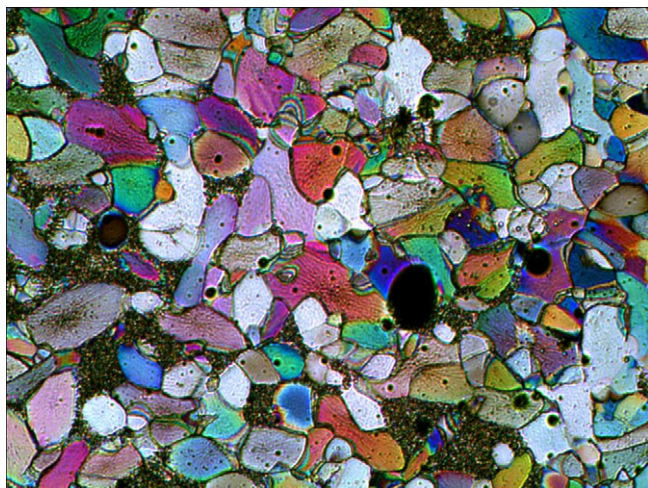


Fig. 6. POM micrograph of silsesquioxanes POSS-2 at 65 °C.

studies were performed to calculate lengths of the side-chain mesogen and the size of cube using the PM3 method. By a length of side-chain ($l = 29.4$ Å) we mean the length of the pendant group added to the length of Si-CH₃ group of the backbone on which the side chain is grafted. The Si-Si lateral distance in the octakis(dimethylsiloxy)-T₈-silsesquioxane cage is 3.1 Å. The values of d/l , observed for LC silsesquioxanes, indicate that the mesogenic groups are not fully extended and can be overlapped of the aromatic groups between neighboring layers. The sharp inner reflection ($d = 12.8$ Å) was also measured for the soft phase and the crystalline state (Fig. 3). The structures of the crystal or soft-crystal occurring in silsesquioxanes series will be the subject of a separate report.

4. Conclusions

Synthesis and characterization of two series of liquid crystalline siloxane oligomers containing methoxyphenylbenzoate mesogens were carried out by a hydrosilylation of cyclo[octa(methylhydrosiloxanes)] and octakis(dimethylsiloxy)silsesquioxanes with Si-H groups. The individual and the combined effects of the spacer and the type of siloxane core were investigated by using DSC, TGA, POM and X-ray methods. Almost all of the synthesized siloxane oligomers show liquid crystalline phase. The set of oligomers with the same type of mesogenic groups but with different structure siloxane cores gave a unique opportunity to study LC properties and structure relationships. The phase transition temperatures were strongly dependent on the siloxane core and length of the flexible spacer. With increasing the length of the spacer chain in cyclo (oligosiloxane) series the temperature of melting point changes a little, but clearing point increase slightly and led to the stabilization of the mesomorphic properties. In general, the effect of changing the siloxane frameworks from cyclic cores to cube cores gave comparable stabilities of mesophases.

Furthermore, silsesquioxanes exhibit a good thermal stability in air, and they are promising candidates for applications in various field. When heated in air, the completely organic moieties are oxidized and a silica-like phase is obtained, in amounts close to the POSS inorganic fraction.

Acknowledgment

The reported research was supported by Ministry of Science and Higher Education (grant No N205 03431/1568).

References

- [1] V.P. Shibaev, S.A. Ponomarenko, E.A. Rebrov, A. Yu Bobrovsky, N.I. Boiko, A. M. Muzafarov, *Liq. Cryst.* 21 (2001) 1–12.
- [2] T.J. Bunning, F.K. Kreuzer, *Trends Polym. Sci.* 3 (1995) 318–326.

- [3] R. Ortler, C. Braüchle, C. Miller, A. Riepl, G. Makromol. Chem. Rapid Commun. 10 (1989) 5–12.
- [4] F.-H. Kreuzer, D. Andrejewski, W. Haas, N. Häberle, G. Riepl, P. Spes, Mol. Cryst. Liq. Cryst. 199 (1991) 345–378.
- [5] R.D. Richards, W.D. Hawthorne, J.S. Hill, J. Chem. Soc. Chem. Commun. 2 (1990) 95–97.
- [6] T.J. Bunning, H.E. Klei, E.T. Samulski, W.W. Adams, R.L. Crane, Mol. Cryst. Liq. Cryst. 231 (1993) 163–174.
- [7] S.G. McNamee, T.J. Bunning, C.M. McHugh, C.K. Ober, W.W. Adams, Liq. Cryst. 17 (1994) 179–190.
- [8] H. Poths, R. Zentel, Macromol. Rapid Commun 15 (1994) 433–440.
- [9] P. Xie, Y. Wan, B. Zhou, J. Hou, D. Dai, Z. Li, R.B. Zhang, Makromol. Chem. Phys. 197 (1996) 745–752.
- [10] P. Xie, J.S. Guo, D. Dai, S.Z. Jin, D.S. Liu, R.B. Zhang, Polymers for Advanced Technologies 7 (1998) 98–103.
- [11] Md.Sh. Ahsan, S. Sasaki, Y. Kawakami, Reactive & Functional Polymers 67 (2007) 1200–1210.
- [12] P.G. Harrison, J. Organomet. Chem. 547 (1997) 141–183.
- [13] A. Kowalewska, W. Fortuniak, B. Handke, J. Organomet. Chem. 694 (2009) 1345–1351.
- [14] F.-K. Kreuzer, R. Maur, P. Spes, Makromol. Chem. Makromol. Symp 50 (1991) 215–228.
- [15] G.H. Mehl, J.W. Goodby, Angew. Chem. Int. Ed. Engl. 35 (1996) 2641–2643.
- [16] I.M. Saez, J.W. Goodby, J. Mater. Chem. 11 (2001) 2845–2851.
- [17] Ch Zhang, T.J. Bunning, R.M. Laine, Chem. Mater. 13 (2001) 3653–3662.
- [18] A. Sellinger, R.M. Laine, V. Chu, C. Viney, J. Polym. Sci., Part A: Polym. Chem. 32 (1994) 3069–3089.
- [19] I.M. Saez, J.W. Goodby, R.M. Richardson, Chem. Eur. J 7 (2001) 2758–2764.
- [20] E. Biatecka-Florjańczyk, J. Sołtysiak, W. Stańczyk, Polimery 40 (1995) 461–468.
- [21] J. Sołtysiak, Ph.D. dissertation, Warsaw University of Technology (1996).
- [22] C. Bolln, A. Tsuchida, H. Frey, R. Mülhaupt, Chem. Mater. 9 (1997) 1475–1479.
- [23] S.U.A. Redondo, E. Radovanovic, I.L. Torriani, I.V.P. Yoshida, Polymer 42 (2001) 1319–1327.
- [24] G. Camino, S.M. Lomakin, M. Lazzari, Polymer 42 (2001) 2395–2402.
- [25] M.J. Michalczyk, W.F. Farmeth, A.J. Vega, Chem. Mater. 5 (1993) 1687–1689.
- [26] D. Demus, L. Richter, Textures of Liquid Crystals. Verlag Chemie, Weinheim, 1984.
- [27] E. Biatecka-Florjańczyk, T. Ganicz, M. Pluta, W. Stańczyk, J. Organomet. Chem. 444 (1993) C9.
- [28] G.W. Mehl, J.W. Goodby, Chem. Ber. 129 (1996) 521–525.
- [29] M.S. White, in: S.J. Clarson, J.A. Semlyen (Eds.), Siloxane Polymers, RTR Prentice Hall, Englewood Cliffs, 1993 (Chapter 6, and references cited therein).
- [30] H. Finkemann, in: G.W. Gray (Ed.), Thermotropic Liquid Crystals, John Wiley & Sons, 1987 (Chapter 6, and references cited therein).
- [31] A.A. Craig, C.T. Imrie, Macromolecules 32 (1999) 6215–6220.
- [32] C.B. McArdle, Side Chain Liquid Crystalline Polymers. Blackie, London, 1989, (and references cited therein).
- [33] M.F. Achard, S. Lecommandoux, F. Hardouin, Liq. Cryst. 19 (1995) 581–592.