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Liquid crystalline silicon-containing oligomers

Ewa Białecka-Florjańczyk [a], Joanna T. Sołtysiak [b,*]

[a] Warsaw University of Life Sciences-SGGW, Institute of Chemistry, Nowoursynowska 166, 02-797 Warsaw, Poland
[b] Industrial Chemistry Research Institute, Analytical Chemistry, Rydygiera 8, 01-793 Warsaw, Poland

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ABSTRACT

Liquid crystalline siloxane oligomers with the same type of mesogenic groups (methoxyphenylbenzoate) but with different structures of siloxane cores (cyclooctasiloxane ring or octakissilsesquioxane 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 ^{1}H NMR and ^{29}Si 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.

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. Sołtysiak).

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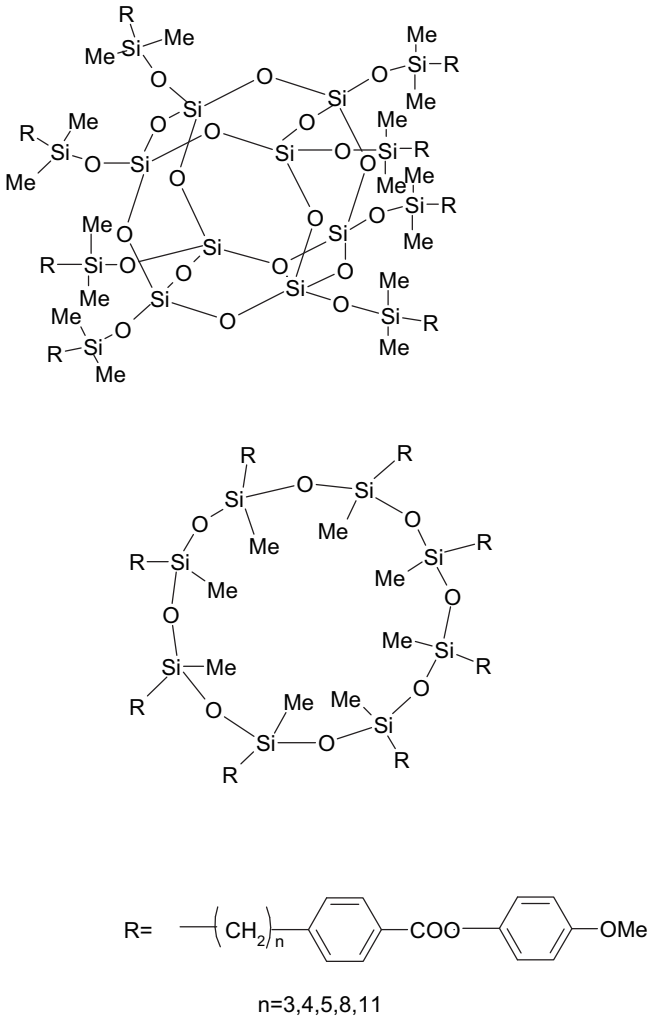

Scheme 1. Schematic representation of the series of liquid crystalline oligomers.

oligomers based to the two different siloxane cores: cyclo[octa (methylhydrosiloxane)]-D_8H 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 ^{29}Si NMR solution spectra were obtained with Varian INOWA (400 MHz) spectrometer. Chemical shifts were assigned using residual $CHCl_3$ (^1H) and TMS (^{29}Si) 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 SiO_2.

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 CuKα radiation. The diffractometer was equipped with Gobel mirror, monocarp 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)-T_8-silsesquioxane was purchased from Gelest Inc.

The individual cyclo[octa(methylhydrosiloxane)] (D_8H) was made by hydrolysis of methyldichlorosilane, 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(dimetylsiloxy)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 (CH_2=CH: $\delta = 5.85$ and $\delta = 5.00$), the appearance of triplet (CH_2–Si proton) at