

Novel oligocarbosilazanes bearing promesogenic end groups

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Abstract. A series of novel oligomers with promesogenic groups on both termini were prepared by a hydrosilylation reaction between well-defined telechelic oligocarbosilazanes end-fitted with vinylsilane (SiVi) groups and promesogenic compounds containing one reactive hydrosilane (SiH) group. We investigated the correlations between the structure of the resulting mesogen end-capped oligomers and their phase behavior as examined by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM).

Keywords: polymer synthesis, molecular engineering, telechelic oligomers, carbosilazane units, phase behavior

1. Introduction

The studies on oligomers with mesogenic chain-end groups are generally undertaken for two main reasons:

- to investigate the structure-property relationships, especially the dependence of liquid crystalline (LC) properties on the length of oligomeric linkages, and
- to obtain materials with relatively low molar mass which have reduced melt viscosity in a mesophase in comparison with traditional LC side-chain polymers, which is an important feature for many optoelectronic applications.

Current research in this area proved that many structures of intermediate molar mass (especially cyclic siloxanes) exhibit the fast electro-optical response characteristic for molar mass liquid crystals, and therefore they can find miscellaneous applications [1]. For many applications, such as LC displays, optical data storage materials, switches and shutters, linear, high molar mass materials

exhibit too long response time, when supramolecular orientation is driven by changes in external electric or magnetic fields [2].

LC dimeric compounds with various organosilicon linkages are already well known [3]. Nevertheless, very few papers are concerned with intermediate molar mass systems based on mesogen end-capped oligomers, especially with organosilicon linkages. According to Allen *et al.* [4], the LC materials derived from mesogen-terminated oligodimethylsiloxanes exhibit many interesting properties, among which the ability to generate biphasic materials with regularly distributed LC domains in a continuous amorphous phase.

The aim of this work was to prepare and characterize a series of telechelic organosilicon oligomers bearing the promesogenic groups on both chain-ends, and containing different linkages constituted of regularly distributed carbosil(ox)azane units.

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2. Experimental section

2.1. Materials

All syntheses were carried out under argon with exclusion of moisture. Solvents were distilled by standard methods and stored over a sodium mirror or molecular sieves. All substrates were used as received from suppliers.

The syntheses of SiH-containing mesogens were performed as reported elsewhere [5].

2.2. Synthesis of telechelic vinyl end-capped oligomers

The telechelic copolymers were synthesized by polyaddition *via* hydrosilylation using an excess of the divinyl-functionalized organosilicon monomers, according to a general procedure described previously [6]. Typically, an oligomer with an initial ratio $[\text{SiH}]_0/[\text{SiVi}]_0$ equal to 0.5 (oligomer 5, Table 1) was prepared as follows. In a flame-dried flask, 6.3 ml (25.30 mmol) of 1,4-divinyl-1,1,4,4-tetramethyldisilethylene, 2.2 ml (12.65 mmol) of 1,1,3,3-disilazane, and 8.5 ml of n-hexane were introduced *via* oven-dried syringes under argon. $27.5 \mu\text{l}$ ($3.16 \cdot 10^{-6}$ mol) of Karstedt's catalyst (PCO72 from ABCR, $1.15 \cdot 10^{-7}$ mol· μl^{-1}) were then added under stirring and argon at room temperature. The reaction medium was heated at 60°C for 24 h. The oligomer was recovered by several precipitations in methanol, and finally dried under vacuum to yield a colorless viscous oil-type material. Yield: 60%.

2.3. Synthesis of mesogen end-capped oligomers

The hydrosilylation reactions leading to the formation of oligocarbosilazanes bearing promesogenic end groups were performed following a procedure described previously with some minor changes [7]. In a typical experiment, 1 g (1.84 mmol) of mesogen B (see Figure 3), 1,1,3,3-tetramethyl-1-[5-(4'-undecyloxy-biphenyl-4-yloxy)-pentyl]-disiloxane) was dissolved in toluene (10 ml) in a flame-dried Schlenk tube equipped with an argon inlet. The telechelic oligomer 5 (see Table 1) (1 g, 1.66 mmol of Si-Vi end groups) and Karstedt's catalyst (PCO72 from ABCR, 10 μl of 3.5% solution in xylenes) were then added under argon, and the

reaction mixture was stirred at 60°C. The reaction was stopped after 24 h, and the solvent was removed under vacuum, yielding a yellowish solid. The oligomeric product was purified by multiple precipitations from dichloromethane/methanol, and finally dried under vacuum (75°C, 1 mmHg). Yield: 78%.

2.4. Physico-chemical techniques

^1H and ^{29}Si NMR spectra were recorded on a Bruker DRX spectrometer at resonance frequencies of 200 and 500 MHz respectively. FTIR spectra were obtained with a Perkin-Elmer 1760 spectrometer from 4000 to 450 cm^{-1} .

Differential scanning calorimetry (DSC) analyses were realized using a Perkin-Elmer DSC 4 calorimeter between -100 and 110°C , at heating and cooling rates of $10^\circ\text{C}\cdot\text{min}^{-1}$. Phase transitions were examined by polarizing optical microscopy (POM). POM studies were performed on thin ($50 \mu\text{m}$) specimens sandwiched between two glass slides. The samples were preconditioned and heated with a Linkam THMS hot stage (Linkam Scientific Instruments Ltd., Epsom, UK) at a rate of $5^\circ\cdot\text{min}^{-1}$. Relative intensity of light and digital images were recorded with a microscope (Polish Optical Works, Warsaw) and a CCD-4012A TV camera (Videotronic, Neumunster, Germany) using a PC computer for data acquisition and analysis.

3. Results and discussion

3.1. Preparation of starting oligomers with vinyl groups on both termini

Well-defined telechelic oligocarbosilazanes end-fitted with vinylsilane (SiVi) groups were first prepared by polyaddition *via* hydrosilylation using non-stoichiometric initial molar ratios of two reactive difunctional monomers, namely one deficient monomer with two hydrosilane (SiH) end groups and another one, used in excess, containing two Si-Vi terminal moieties (Figure 1).

By changing the nature of difunctional precursors (dicarbosilanes, disilazanes or disiloxanes), it was possible to obtain telechelic oligomers with different chemical structures in their main chains. This polymerization process provided a unique opportunity to generate alternating copolymers with car-

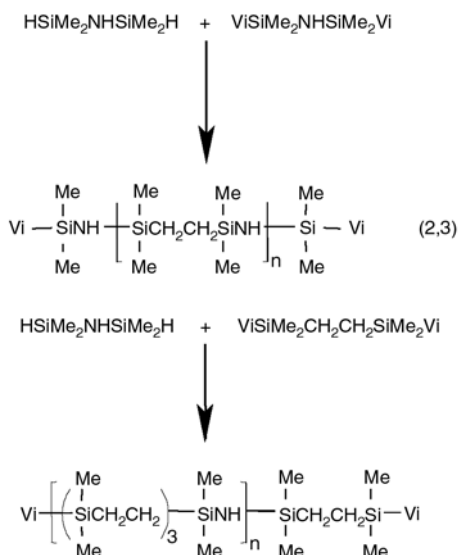


Figure 1. Synthesis of telechelic vinyl end-capped oligomers

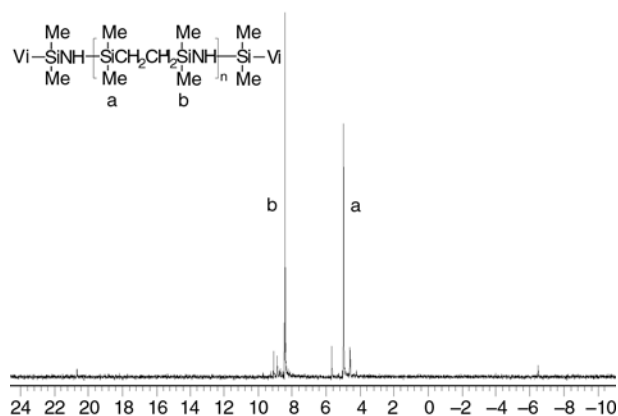


Figure 2. ^{29}Si NMR (CDCl_3) spectrum of telechelic vinyl end-capped oligomer 3 (see Table 1)

bosilane, silazane, and/or siloxane units arranged in a very regular way. The regularity of the copolymer structure was proved by ^{29}Si NMR (Figure 2 as an example).

Additionally, the variation of the initial molar ratio of precursors allowed for the synthesis of oligomers with varying molar masses [6]. The nature and proportions of difunctional monomers, as well as the

molar masses of the resulting divinyl-functionalized oligomers are given in Table 1.

3.2. Synthesis of mesogen end-capped oligomers

Two promesogenic compounds (A, B, Figure 3) containing one reactive SiH group were obtained by hydrosilylation of the corresponding alkene-terminated analogues with a large excess of commercially available tetramethyldisiloxane ($\text{HSiMe}_2\text{OSiMe}_2\text{H}$), as described previously [5].

The oligomers end-fitted with promesogenic groups were derived from the hydrosilylation reaction of divinyl-functionalized oligomers with SiH-containing mesogens. The reaction was monitored by FTIR, through the disappearance of the Si–H stretching band at 2130 cm^{-1} . The reaction conditions were typical for this type of process [7]. All the syntheses were carried out at 60°C in toluene under an inert atmosphere (Figure 3).

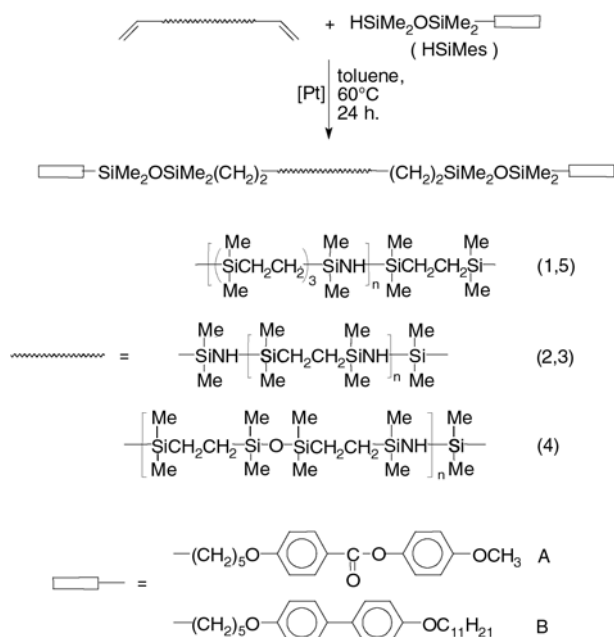


Figure 3. Synthesis of mesogen end-capped oligomers

Table 1. Structure and initial molar ratio (r) of precursor monomers and molar masses of divinyl-functionalized oligomers^a

| No. | SiH-ended monomer | SiVi-ended monomer | $r = [\text{SiH}]_0/[\text{SiVi}]_0$ | M_n^b (^1H NMR) |
|-----|---|---|--------------------------------------|-----------------------------|
| 1 | $\text{HSi}(\text{Me})_2\text{NHSi}(\text{Me})_2\text{H}$ | $\text{Vi}(\text{Me})_2\text{SiCH}_2\text{CH}_2\text{Si}(\text{Me})_2\text{Vi}$ | 0.75 | 2200 |
| 2 | $\text{HSi}(\text{Me})_2\text{NHSi}(\text{Me})_2\text{H}$ | $\text{Vi}(\text{Me})_2\text{SiNHSi}(\text{Me})_2\text{Vi}$ | 0.75 | 2200 |
| 3 | $\text{HSi}(\text{Me})_2\text{NHSi}(\text{Me})_2\text{H}$ | $\text{Vi}(\text{Me})_2\text{SiNHSi}(\text{Me})_2\text{Vi}$ | 0.80 | 1500 |
| 4 | $\text{HSi}(\text{Me})_2\text{OSi}(\text{Me})_2\text{H}$ | $\text{Vi}(\text{Me})_2\text{SiNHSi}(\text{Me})_2\text{Vi}$ | 0.85 | 1900 |
| 5 | $\text{HSi}(\text{Me})_2\text{NHSi}(\text{Me})_2\text{H}$ | $\text{Vi}(\text{Me})_2\text{SiCH}_2\text{CH}_2\text{Si}(\text{Me})_2\text{Vi}$ | 0.50 | 1200 |

^aExperimental conditions: solvent: n-hexane, $T = 60^\circ\text{C}$, Karstedt's catalyst: PCO72, $[\text{Pt}]_0/[\text{SiH}]_0 = 2.5 \cdot 10^{-4}$

^bMolar mass as determined by ^1H NMR using the ratio of intensities associated with resonance signals due to vinylic protons (5.6–6.4 ppm) from SiVi end groups and methylene protons (0.4 ppm) from carbosilane units of organosilicon skeleton

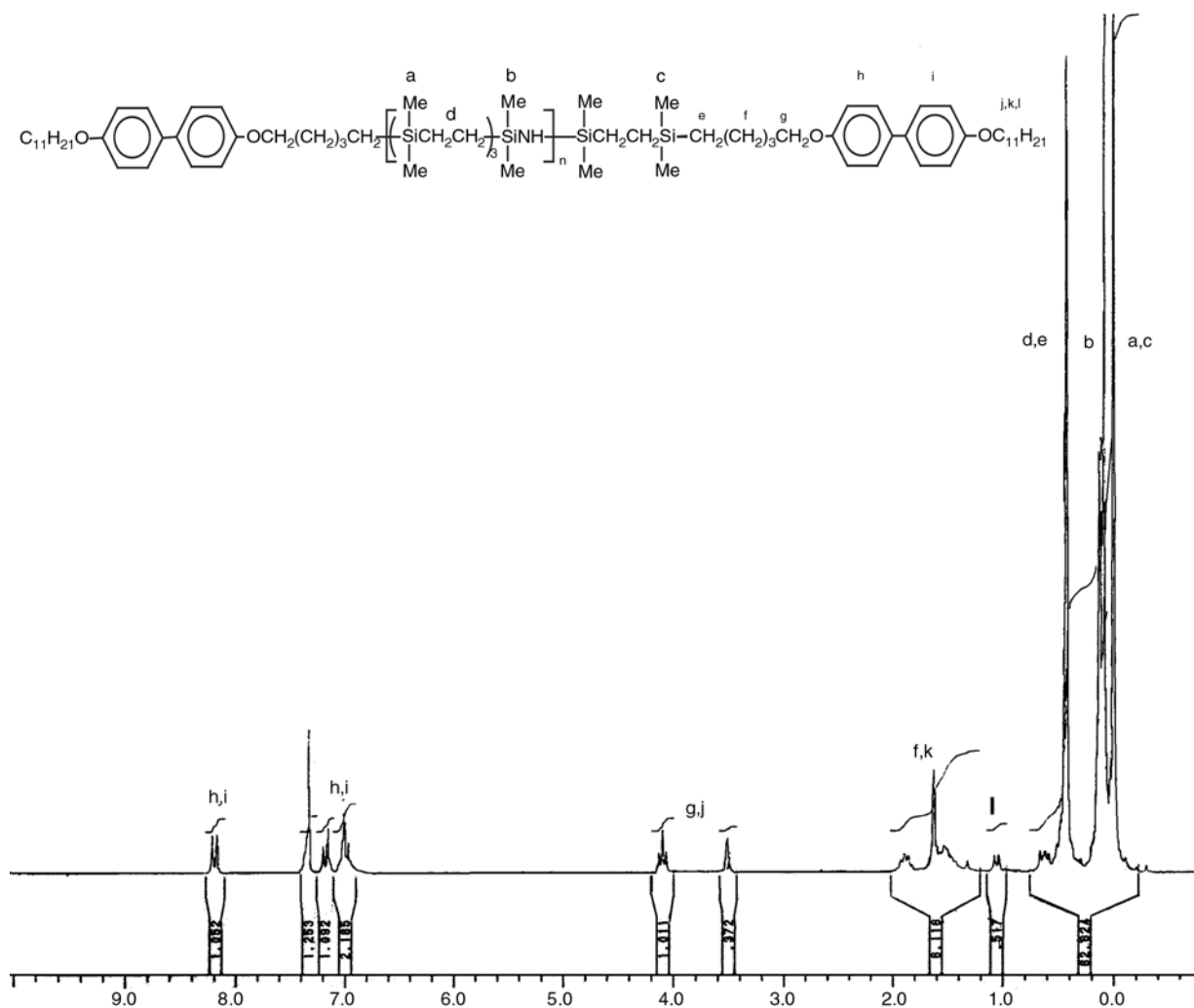


Figure 4. ^1H NMR (CDCl_3) spectrum of telechelic mesogen end-capped oligomer B5 (see Table 2)

In all instances, the reactions were completed within 24 h, and led to the formation of the desired products. The structures of the resulting mesogen-terminated oligomers were confirmed by ^1H (Figure 4 as an example) and ^{29}Si NMR.

3.3. Properties of mesogen end-capped oligomers

The mesomorphic properties of the telechelic oligocarasil(ox)azanes end-capped by a promesogenic group were evaluated through DSC and POM analyses. The results of the studies are summarized in Table 2.

Table 2. Properties of telechelic oligomers end-capped by promesogenic groups

| Starting oligomers | | | MesSiH | Resulting oligomers | | | |
|--------------------|------------------|---------------|------------------|---------------------|---------------|---|---|
| No. | M_n [g/mol] | T_g [°C] | No. ^a | No. | T_g [°C] | other phase transitions [°C] | microscopic observations |
| 1 | 2200 | -69 | A | A1 | -61 | none | isotropic liquid |
| | | | B | B1 | -58 | none | birefringent droplets disappearing at 77°C |
| 2 | 2200 | -82 | A | A2 | -65 | none | isotropic liquid |
| | | | B | B2 | -63 | none | birefringent droplets disappearing at 72°C |
| 3 | 1500 | -77 | A | A3 | nd | none | isotropic liquid |
| 4 | 1900 | -89 | B | B4 | -83 | K -37 M(?) 84 I (heating) none (cooling) | birefringent droplets disappearing at 85°C |
| 5 | 1200 | -81 | B | B5 | -63 | K -40 M(1) 35 M(2) 57 I (heating) I 57 M(2) 45 M(1) (cooling) | various LC-like textures seen in the whole volume of the sample |

nd: not detected, K: crystal, M(?), M(1), M(2): possible mesophases of unknown nature, I: isotropic

^aTemperature transitions of starting vinyl-terminated mesogens (in °C): A: K 56 N 74 I [8], B: K 89 SmA 141 I (according to POM and DSC analyses)

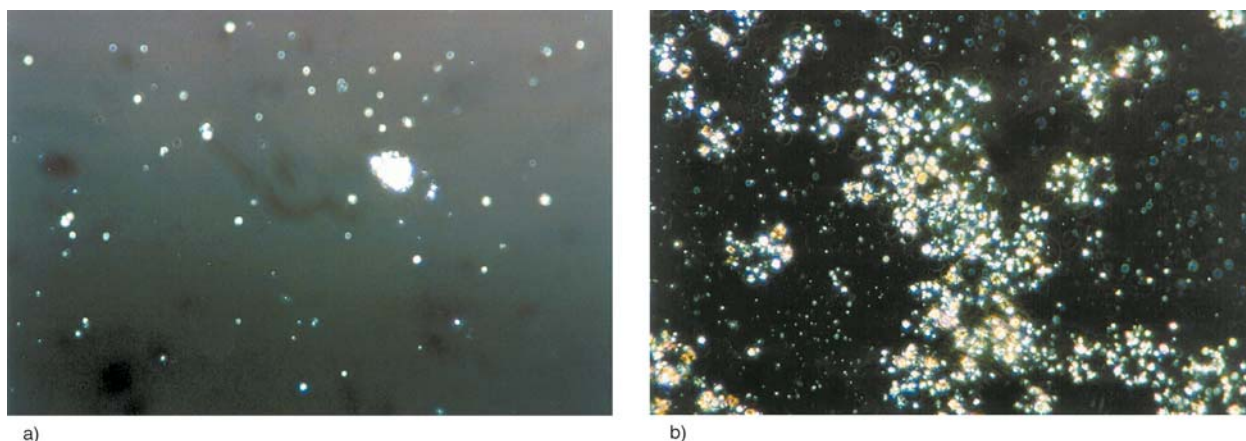


Figure 5. POM micrographs of mesogen end-capped oligomers: (a) B1 at 23°C; (b) B2 at 23°C

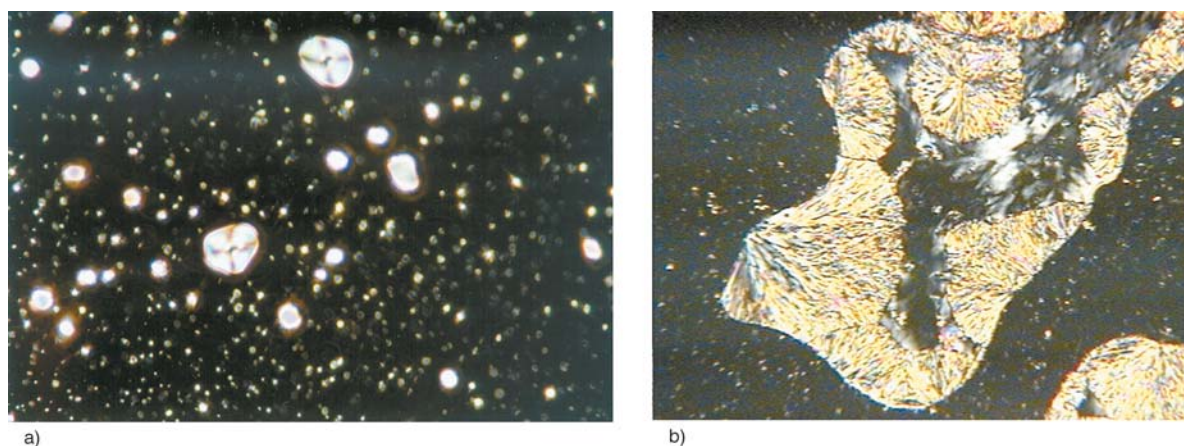


Figure 6. POM micrographs of mesogen end-capped oligomers: (a) B4 at 63°C; (b) B5 at 37°C

Birefringent droplets of LC-like textures were observed only for the products based on mesogen B. In contrast, judging from DSC and microscopic studies, oligomers containing mesogen A (compounds A1, A2 and A3, Table 2) did not exhibit any mesomorphic properties. Although both starting mesogens exhibit LC properties in a free form [8, 9], it was previously found that mesogen A, when attached as a side chain to polymers with relatively low molar ratio of functional units, produced materials with poor or even no LC properties [5, 7, 8]. Therefore, during the course of our research, we directed our attention to mesogen B which was reported to be more effective in systems with a low degree of functionalization [7, 9].

In the case of samples B1 and B2, small birefringent droplets ‘dissolved’ in an amorphous phase were observed by POM (Figure 5).

The birefringent droplets underwent isotropization at 72–77°C, which was well-visible in microscopic images. However, there were no signals correspon-

ding to these typical phase transitions in the DSC traces.

The oligomers B4 and B5 were characterized by shorter carbosil(ox)azane linkages than those of B1 and B2, and therefore possessed higher contents of promesogenic groups within their structure. Thus, they displayed much higher ‘density’ of the birefringent droplets, and exhibited weak transition peaks on DSC thermograms, corresponding to phase transitions observed by microscopy (Figure 6). In the case of sample B5, the droplets were of such a large size that the internal change of their textures at 37°C could be observed by POM, which was in accordance with the DSC analysis (Figure 7).

4. Conclusions

The phase behavior of telechelic oligocarbosil(ox)azanes end-capped by a promesogenic group seems to depend on two main parameters, namely the

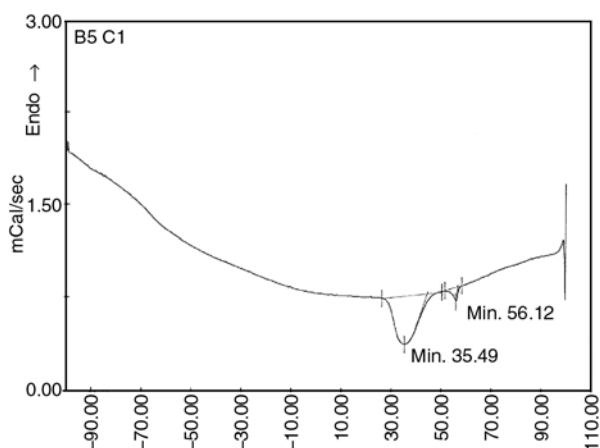


Figure 7. DSC thermogram (on cooling) of mesogen end-capped oligomer B5

structure of the promesogenic precursor and the molar mass of the starting oligomer.

It turns out that the most relevant parameter is the structure of promesogenic entities, although the molar mass of oligomeric linkages is also an important factor, strongly influencing the phase behavior of mesogen-terminated oligomers.

None of the materials containing mesogen A exhibited birefringence, regardless of the structure and length of the oligomeric linkages used. However, the oligomers based on mesogen B displayed birefringent droplets, whose size increased with decreasing the length of the carbosilazane linkages. These novel mesogen end-capped oligocarbosi(ox)azanes should be more thoroughly investigated by complementary techniques, such as X-ray diffraction, in order to characterize precisely their mesophases and to get a better insight into their potential liquid crystalline properties.

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