Supermolecules Containing a Tetrahedral Core: A New Class of Liquid-Crystalline Siloxanes

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It is shown that supermolecules with a tetrahedral symmetry and appropriate side-chains exhibit liquid-crystalline phase behaviour. The use of an optimised hydrosylation reaction allows for the synthesis of materials that have four mesogenic groups attached to a siloxane core, where the conformation and the configuration are unambiguous. The materials show low glass transition temperatures and, depending on the spacer length, complex liquid-crystalline morphologies.

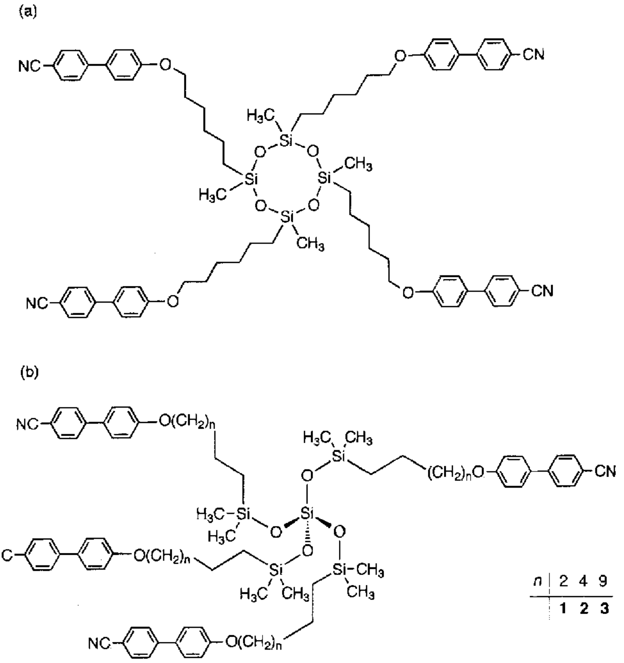
Liquid crystalline oligomeric materials, which form a distinct class of supermolecules, have been of interest recently because they are good candidates as systems that combine the properties of low molar mass liquid crystals, for example low viscosity and fast switching times, with the mechanical stability and absence of crystallinity observed in some polymeric systems.

The possibility of synthesising oligomeric materials with defined topological, configurational and conformational features has, until recently, centered mainly on the development of substituted cyclic systems[1,2] [see Scheme 1(a)]. However, there are very few reports in the literature concerning the use of well-defined molecular systems and cores that allow for the control of the concentration of different conformers in oligomers and even fewer where the resulting supermolecular structure has a cubic symmetry[3]. By reacting tetrakis(dimethylsiloxy)silane with a variety of alkenyloxy-cyanobiphenyls, it was possible to generate a set of tetrahedrally substituted mesogenic supermolecules of uniform structure and conformity, as depicted in Scheme 1(b).

The use of a tetrahedral core in the generation of thermotropic liquid crystals is an unusual choice; intuitively the fully extended spherically shaped conformation, as shown in Figure 1(a), would at first sight seem to be the most stable form. Classically such a molecular shape should disfavour mesophase formation. However exploratory molecular modelling studies reveal that, even in the gas phase at absolute zero, the conformation where the side-chains are aligned is the more energetically favoured conformation, as shown in Figure 1(b).

The monomers were synthesised according to previously published methods[4]. The hydrosilation reaction of tetrakis(dimethylsiloxy)silane with mesogenic monomers bearing olefinic end groups, in the presence of a catalytic amount of Karstedt's catalyst, was carried out in toluene at room temperature. The reaction was aerated as previously described in the literature[5]. The addition of a small amount of triphenylphosphane, in order to convert the catalyst to a less reactive platinum triphenylphosphane complex, was used to facilitate a controlled termination of the reaction. The products were isolated by precipitation upon addition of methanol. The platinum triphenylphosphane complex remained in solution allowing for the easy isolation of products, which are not discoloured or contaminated by platinum residues. The hydrosilation reaction, which was optimised in order to avoid β addition of the olefinic double bonds, is described in the Experimental under the preparation of material **1**.

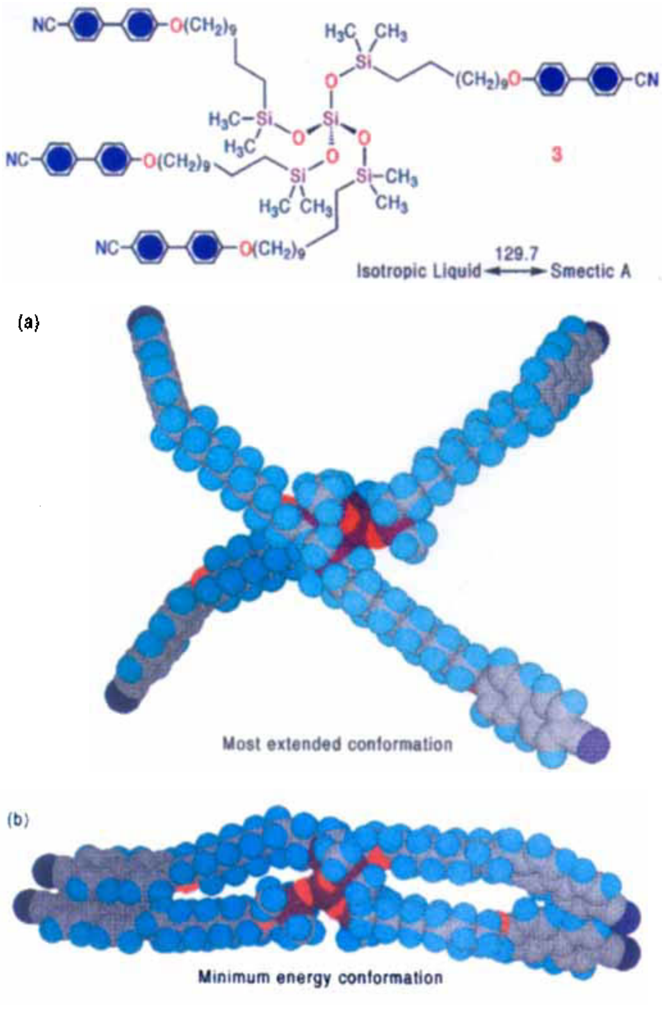
Scheme 1. (a) Structure of a mesogenic cyclic oligomeric siloxane. – (b) Molecular structures of the tetrahedrally substituted siloxane materials



n	2	4	9
	1	**2**	**3**

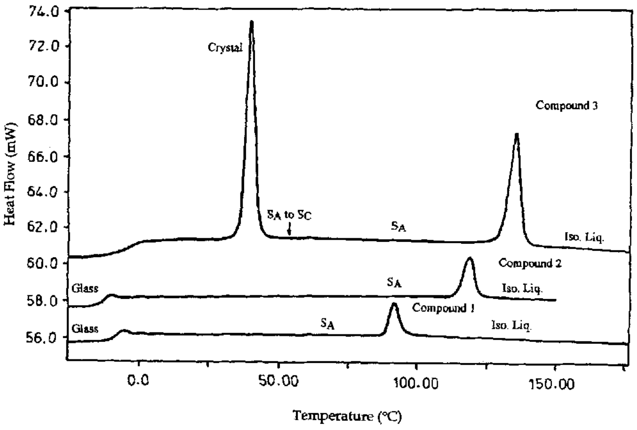
Calorimetric measurements reveal that the final products **1** to **3** exhibit liquid crystal phases. Thermograms of the

Figure 1. (a) Structure of compound **3** in its fully stretched conformation. – (b) Energetically minimised structure of compound **3** showing aligned side chains



second heating cycles for these materials are shown together in Figure 2, and the values for transition temperatures and associated enthalpies are listed in Table 1.

Figure 2. DSC traces of the materials (second heating cycles, scan rate 10 °C min^{-1})



When the number of methylene units is increased from four to eleven carbon atoms, the isotropization temperature increases accordingly from 88.7 to 129.7 °C. Additionally an increase in the size of the enthalpy peak transition occurs, which suggests an increase in the ordering of the molecules in the liquid-crystalline phase with increasing spacer length. All of the materials exhibited glass transitions in the region of −5 to −15 °C. The values of the related specific heats (0.31 to 0.36 J g^{-1} K^{-1}) in this region were found to be similar. Materials **1** and **2** exhibited only one liquid-crystalline phase whereas material **3** shows upon heating a transition to an additional phase at 38.7 °C. The isotropization temperatures of the materials were found to be comparable with those of cyclic siloxanes bearing four side-chains of a similar structure[6]. However, the solidification temperatures of the tetrahedrally substituted systems were found to be much lower. For example, the cyclic analogue of compound **2** exhibits a glass transition or recrystallisation well above room temperature (~50–60 °C), whereas the tetrahedrally substituted material produces a non-crystalline material that has a low solidification temperature (−14.7 °C).

Table 1. Transition temperatures and enthalpy data for compounds **1** to **3** (results obtained by DSC measurements)

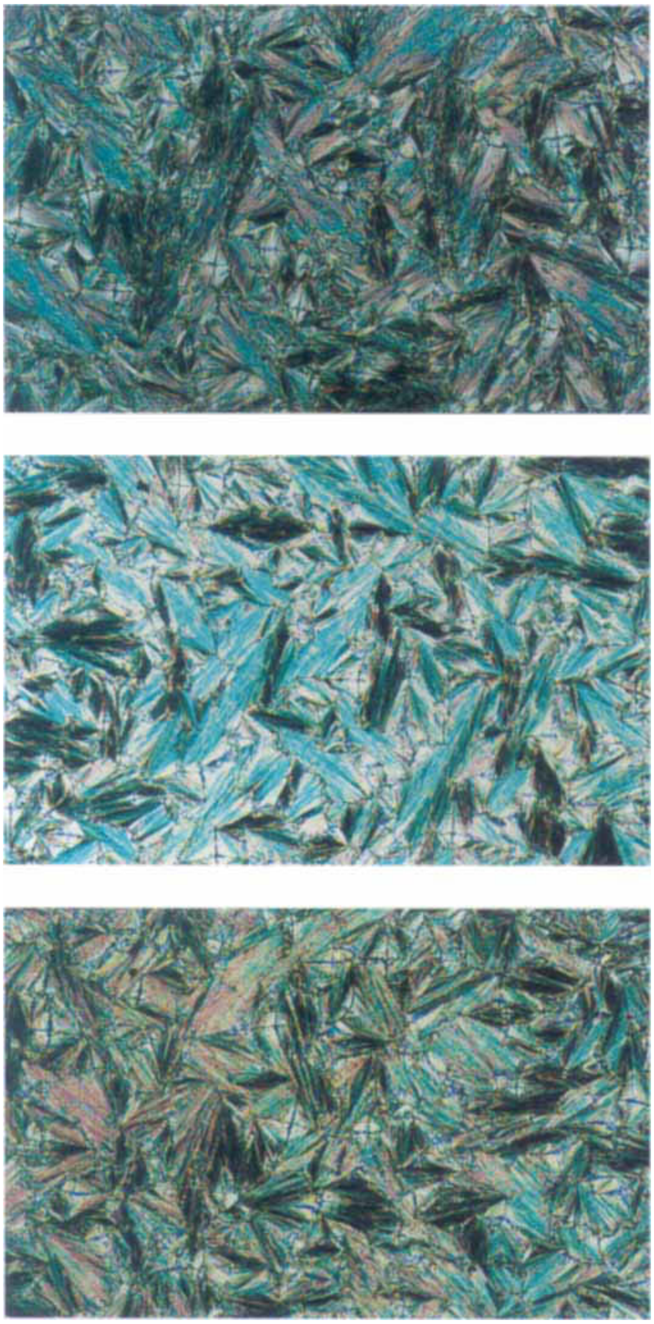
Compd	Spacer	Tg (°C)	ΔCp ($Jg^{-1}K^{-1}$)	S_X (°C)	ΔH ($J g^{-1}$)	S_A-Iso Liq (°C)	ΔH ($J g^{-1}$)
1	4	-9.6	0.34	-	-	88.7	4.85
2	6	-14.7	0.36	-	-	118.7	7.83
3	11	-6.3	0.31	38.7	18.29	129.7	12.34
Cycl.[a]	6	57	-	-	-	118	5.6

[a] Data taken from ref.[6] (cycl. ≙ cyclic).

Optical polarised light microscopy was used to identify the phases of materials **1** and **2** and the high temperature phase of **3** as smectic A. A typical photomicrograph of the texture of this phase is shown for compound **3** in Figure 3, top photo. For material **3**, upon cooling, a smectic C phase preceding the transition to a soft crystal phase appeared to be formed. This phase is characterised by a broken focal-conic texture as shown in the middle photo of Figure 3. No transition enthalpy was observed; this suggests that the transition to the smectic C phase is a second order type. The bottom photo of Figure 3 is a photomicrograph of the soft crystal phase of compound **3**.

The X-ray diffraction patterns for materials **1** and **2**, in their smectic A phases, showed a wide angle reflection centred at 4.4 Å, which is typical value for the lateral distance between the mesogenic units. At smaller angles, a diffuse reflection at 8.2 Å and a sharp reflection at 24.0 Å was found for compound **1**. Similarly, for compound **2** a diffuse reflection was found at 8.2 Å and a sharp reflection at 28.2 Å. Although no macroscopic ordering of the samples could be achieved, the results obtained for the small angle reflections correspond well to a smectic-like layering which has interdigitation of the mesogenic cores. The trichotomous nature of the molecules allows for different packing characteristics to exist for the molecules in the smectic A phase.

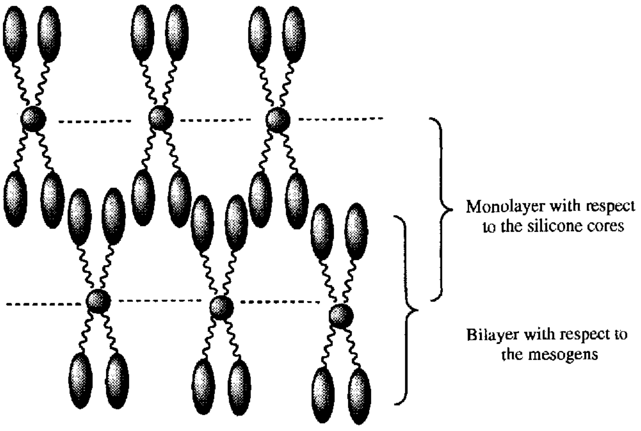
Figure 3. Top: Defect texture of the smectic A phase of compound **3** at 125 °C. – Middle: Defect texture of the smectic C phase of compound **3** at 42 °C. – Bottom: Defect texture of the soft crystal phase of compound **3**



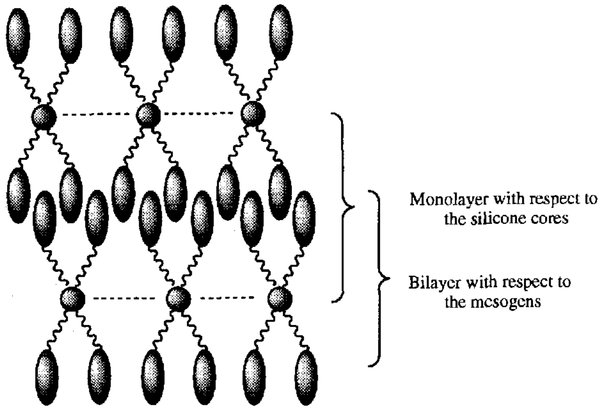
Thus, we must consider the separate interactions of the mesogenic cores, the alkyl spacers and the silicon cores. Internal phase separation could lead to the smectic A phase being described as an S_{Ad} phase, with respect to the mesogens, and a monolayer S_{A1} phase with respect to the cores. Consequently, two possible models can be proposed for the interdigitated structure of the smectic A phase, which are shown in Schemes 2 and 3. Scheme 2 shows a more likely arrangement; Scheme 3 shows a more ordered arrangement. It has not yet been determined which phase structure or if a mixture of both applies.

The diffuse reflection found at 8.2 Å is attributed to a periodicity in the distance of the methylated siloxane cores of the molecules. Similar reflections have also been observed for some cyclic siloxane systems, as shown in the densitometer traces reported in reference 2. Heating the materials above their isotropization temperatures leads to the expected loss of the small angle reflections and to a broadening of the wide angle reflections, thereby giving a diffuse maximum centered around 4 Å.

Scheme 2. Schematic representation of the smectic A_d phase (**1** and **2**)



Scheme 3. Model showing pairing of the mesogenic units (**1** and **2**)



Material **3** was found to exhibit a more complicated phase behaviour in comparison to compounds **1** and **2**. At high temperatures X-ray diffraction studies showed a wide angle halo at 4.4 Å, a diffuse reflection at 8.2 Å. A point like meridian refection at 41.1 Å, which was found to be at right angles to the main axis of the sample tube, was also observed. These reflections can be attributed to the formation of a smectic A_d phase, as suggested for the materials **1** and **2**. Upon cooling from the smectic A_d to isotropic liquid transition, an increase of the layer spacing was observed, as shown in Table 2. As the rotational freedom of the molecules decreases with failing temperature, better microscopic orientational ordering of the samples is thought to

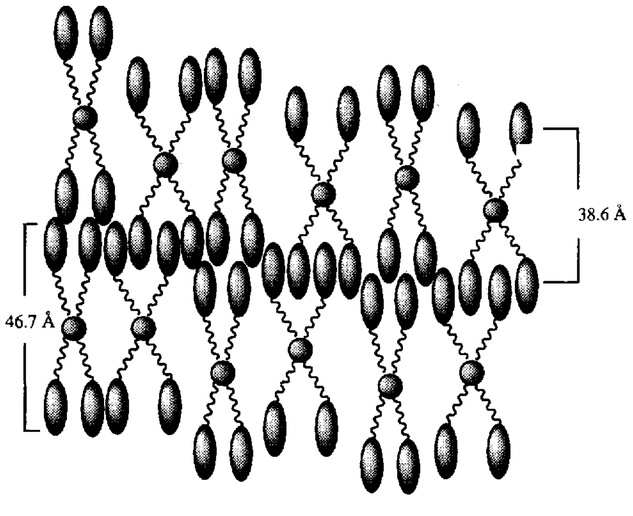
Table 2. Spacings obtained by X-ray diffraction

Compound	T (C°)	d-spacings (Å)			
1	25	24.0	-	8.2	4.4
2	25	28.2	-	8.2	4.4
3	70	46.7	38.7	8.2	4.4
3	100	41.1	-	8.2	4.4
3	125	39.5	-	8.2	4.4

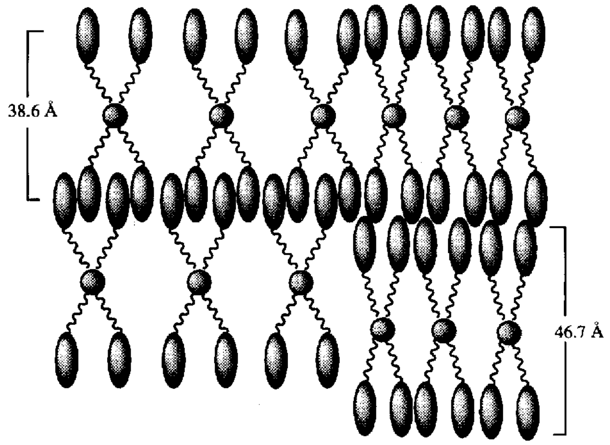
occur, which in turn leads to a small increase of the lattice dimensions.

Cooling the sample further to 70 °C leads to the occurrence of distinct reflections at 46.7 and 38.7 Å, which were of roughly similar intensity. Annealing the material at a higher temperature, and then over a period of 24 h at 70 °C, prior to X-ray diffraction studies, assured that nucleation of the low temperature crystal phase did not occur. This confirms that the reflections are not artefacts of the solid phase. For these results to be in agreement with the evidence obtained by microscopy (which clearly shows the occurrence of focal-conic domains with hyperbolic and elliptical lines of optical discontinuity typical of the smectic A phase) the existence of two sub-lattices is required. The reflection at 38.7 Å can be attributed to a smectic A_d phase where the mesogens overlap completely; the lattice with a distance of 46.7 Å fits a smectic A_2 phase structure where only the cyano groups overlap. As extensively interdigitated smectic A phases usually occur at lower temperatures with respect to the smectic A_2 phase, this odd behaviour requires further exploration and explanation. The occurrence of this form of behaviour can be explained by the presence of a biphasic or incommensurate S_A phase, or even a $S_{\tilde{A}}$ antiphase[7]. The formation of such arrangements can be explained as follows. As the order of the system increase upon cooling, the intermolecular packing of the three segments of the molecules causes increasing internal phase separation. At a certain temperature a denser packing can be achieved by the formation of two sublattices. This means that the energy penalty, which some mesogenic systems suffer by allowing only overlap of the cyano groups and not the whole mesogenic core, is compensated if some of the alkyl chain regions are filled with methylated silicon cores. Possible mesophase structures are shown in Schemes 4 and 5. Scheme 4 shows a biphasic arrangement, whereas Scheme 5 shows a more ordered structure fitting an incommensurate ordering.

Scheme 4. Schematic representation of the structure of the smectic A_d phase (**3**)



Scheme 5. Schematic representation of the structure of the proposed incommensurate smectic A_d phase (**3**)



Thus, materials **1**, **2** and compound **3** at high temperatures form an smectic A_d phase with respect to the mesogenic cores, whereas the siloxane molecular centres are organised in monolayers. At lower temperatures material **3** forms a smectic A_d biphasic or incommensurate phase with respect to the mesogens. In this context the arrangement of the cores should be described as a bilayer. The lack of calorimetric evidence for a first order phase transition suggests that this process is either second order or continuous. In addition, compound **3** appears to show a transition to the smectic C phase just before recrystallisation. At present the complicated phase behaviour of this material is the subject of further detailed investigations.

It has been shown that mesogenic materials with a tetrahedrally substituted siloxane core exhibit smectic A phases. With increasing alkyl spacer length, the isotropization temperatures and the transition enthalpies increase. Complex phase behaviour was observed for the material that has a long methylene spacer unit. The materials with the short spacers are distinguished from analogous cyclic siloxanes with similar sidechains in that they exhibit no crystal phases and have low glass transition temperatures.

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Experimental

Modelling studies were performed on a Silicon Graphics workstation (Indigo XS24, 4000) using the Molecular Simulations Cerius^2 v 1.6 software package employing a universal force field. Within Cerius^2 the conjugate gradient algorithm was used to locate the confirmation with the lowest potential energy. The minimisation calculations were performed until the root mean square (RMS) force reached 2×10^{-6} Kcal mol^{-1} Å^{-1}. The software package operates under the assumption that the molecules consist of hard particles, held together by elastic forces, in vacuum, at absolute zero, in an ideal motionless state.

The Infrared spectra were recorded on a Perkin-Elmer 783 spectrometer. NMR spectra were obtained using a Jeol JNM-GX 270 MHz spectrometer. Thermal microscopic studies were performed using a Zeiss Universal polarising microscope in conjunction with a Mettler FP52 microfurnace and a FP5 control unit. Calorimetric experiments, relative to an indium standard[8] (T_{tr} 156.63°C, ΔH 28.45 J g^{-1}, observed: 156.56°C, ΔH 28.61 J g^{-1}), were carried out using a Perkin-Elmer DSC 7 calorimeter. Phase transition temperatures were given as the endothermic onset in the second heating scans (scan rate: 10 K min^{-1}). Glass transition temperatures were read at the greatest rate of change in the heat capacity. The temperature, above 50°C, was controlled to ±0.5°C by placing the samples in a microfurnace equipped with a Eurotherm EPC 900 temperature control unit.

Synthesis of Tetrakis{[(4'-cyanobiphenyl-4-yl)oxybutyl]dimethylsiloxy}silane (**1**): A solution of tetrakis-(dimethylsiloxy)silane (0.083 g, 0.25 mmol), 3.0–3.5% solution of Karstedt's catalyst in xylene (3 µl) and toluene (15 ml) was prepared. A gentle stream of air was blown through the solution for 20 seconds. A solution of 4-(1-butenyloxy)-4'-cyanobiphenyl (0.275 g, 1.1 mmol) in dry toluene was added dropwise at room temperature over a period of 1 h. During this time the solution, which was originally colourless, developed a faint yellowish colour. The reaction was monitored by IR spectroscopy. A few minutes after completion of the addition of the monomer, no Si–H absorption could be detected by IR spectroscopy. A small amount (ca. 5 mg) of triphenylphosphane was added and the solution was concentrated under reduced pressure. The oligomeric material was purified by precipitation into methanol. The product was separated by filtration. The process of consecutively dissolving and precipitating the product with methanol was repeated until the remaining starting monomer could not be detected by chromatographic methods. After drying in vacuo the product was collected as a white tacky substance in a yield of 0.21 g (63%). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3020 (Ar–H), 2940 (C–H), 2220 (C≡N), 1600 (Ar), 860 (C–H). – ^{1}H NMR (CDCl$_3$/TMS): δ = 7.65 (m, 4H, Ar–*H*), 7.52 (m, 2H, Ar–*H*), 6.95 (m, 2H, Ar–*H*), 3.96 (t, 2H, ArOC*H*$_2$), 1.78 (m, 2H, OCH$_2$C*H*$_2$), 1.55 (m, 2H, C*H*$_2$CH$_2$Si), 0.64 (t, 2H, C*H*$_2$-Si), 0.12 [s, 6H, (C*H*$_3$)$_2$-Si]. The absence of a peak in the vicinity of δ = 2.1 in the ^{1}H NMR spectra indicates that no β addition of the olefins had taken place, and that the oligomeric materials were therefore single compounds.

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