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Synthesis of novel tri-podal mesogenic alkenes and side-chain polysiloxanes

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Abstract

Low molecular weight tri-podal biphenyl- and benzoate-type mesogens $[C_6H_5C_6H_4O(CH_2)_5SiMe_2CH_2CH_2SiMe_2]_3CH$ (**4**), $[C_{11}H_{23}O(C_6H_4)_2O(CH_2)_5SiMe_2]_3CH$ (**5**) and $[MeOC_6H_4OC(O)C_6H_4O(CH_2)_5SiMe_2]_3CH$ (**6**) ($C_6H_4 = 1,4$-phenylene) were obtained, from branched silyl substituted methane precursors $[CH_2{=}CH(Me)_2Si]_3CH$ (**1**) and $(HMe_2Si)_3CH$ (**2**). The biphenyl-containing ones (**4**) and (**5**) were converted into terminal alkenes, which were subsequently hydrosilylated with poly(methylsiloxanes). The polymer derived from (**5**) exhibited mesomorphic properties. Such systems have the potential to significantly increase the density of liquid crystal rod-like structures in side chains of linear polymers (or dendritic liquid crystal polymers).

Keywords: Liquid crystalline polymers; Polysiloxanes; Functionalisation of polymers; Nonlinear polymers; Structure–property relationships

1. Introduction

Liquid crystal polymers, in which rigid, mesogenic side-chains are attached to polymer backbones via flexible spacers, are a significant class of novel materials with richly diverse architectures. Their properties can be adjusted by introducing changes into the structures of the polymer chain, the flexible spacer or most especially the mesogen. Other factors, such as molecular weight and polydispersion play an important role. These polymer systems are now being considered for application in nonlinear optics, pyroelectric detectors and display devices [1,2]. Compared with low molecular weight liquid crystals such polymers show enhanced mechanical properties and offer possibility of the use of them as free standing films in optical applications. However, higher molecular weight and higher viscosity of polymer, lengthen the response time of such materials to external magnetic or electric fields and this feature restricts many potential applications [3]. Hybrid materials (oligomers or dendrimers of various generations) have thus been studied. The latter, often polymers of high molecular weight, approach spherical geometry at higher generations and give materials of relatively low viscosity [4,5]. An especially interesting combination of properties, viz low viscosity and wide temperature range for mesophase formation, is shown by polymers with paired, dimesogenic systems [6], attached to silsesquioxane core [7].

In our search for low melt viscosity liquid crystals, that form glasses above ambient temperature, as is typical for oligomeric systems based on cyclic, cubic or star shape molecules [3,8], we have described a series of tetrakis-substituted methanes and silanes [9]. The starting materials $[C(SiMe_2H)_4$ and $Si(SiMe_2H)_4]$ for the synthesis of star systems seemed to show promise

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[1] Authors wish to present this paper in memory of the late Prof. Colin Eaborn FRS.

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for the synthesis of polymers, bearing mesogens in side-chains.

We report here on synthetic methods leading to novel liquid crystals from "trisyl" type [tris(trimethylsilyl)]methane compounds [10,11], $HC(SiMe_2Vi)_3$ (**1**) and $HC(SiMe_2H)_3$ (**2**). Some of these can be modified to give liquid crystal oligomers and polymers.

2. Experimental

2.1. Materials and methods

All organometallic syntheses were carried out under argon with exclusion of moisture by use of Schlenk techniques. Solvents were dried by standard methods and stored over sodium mirrors or molecular sieves.

$HCBr_3$ (Aldrich), chlorodimethylvinylsilane (ABCR), $MgSO_4$ (Aldrich), chlorodimethylsilane (ABCR), Karstedt's catalyst ($Pt_2[(ViSiMe)_2O]_3$, 3.5% sol. in xylenes, ABCR), $LiAlH_4$ (Aldrich), MeLi (1.6 M sol. in Et_2O, Aldrich), allyl bromide (Aldrich) and poly(methylsiloxane) ($M_n = 2150$, $IP = 1.23$, ABCR) were used as supplied.

The ^1H, ^{13}C and ^{29}Si NMR spectra were recorded in $CDCl_3$ or C_6D_6 solutions with Bruker AC 200 or DRX 500 spectrometers. The progress of hydrosilylation was followed by the disappearance of the Si–H absorption (at 2160 cm^{-1} for poly(methylsiloxane), 2105 cm^{-1} for $HSiMe_2Cl$ and $C_6H_5C_6H_4O(CH_2)_5SiMe_2H$, 2120 cm^{-1} for $HC(SiMe_2H)_3$) by use of an ATI Mattson spectrometer. Mass spectra were obtained using ThermoQuest Finnigan GC/MS. Thermal behaviour was studied by differential scanning calorimetry (DSC) using a DuPont DSC-910 instrument. Phase transitions were verified by optical microscopy and X-ray diffraction studies.

2.2. Syntheses

2.2.1. Rod-like alkenes

4-(4-Pentenyloxy)biphenyl $[CH_2{=}CH(CH_2)_3OC_6H_4C_6H_5]$, 4′-methoxyphenyl-4-(4-pentenyloxy)benzoate $[CH_2{=}CH(CH_2)_3OC_6H_4C(O)OC_6H_4OCH_3]$ and 4′-undecanyloxy4-(4-pentenyloxy)biphenyl $[CH_2{=}CH(CH_2)_3OC_6H_4C_6H_4OC_{11}H_{23}]$ were made by the literature methods [12,13].

2.2.2. Silyl-substituted methanes

A solution of $HCBr_3$ (2.4 ml, 0.028 mol) in 10 ml of dry THF was added dropwise during 1 h to a stirred mixture of chlorodimethylvinylsilane (11.4 ml, 0.084 mol), magnesium turnings (2.2 g, 0.09 mol) and dry THF (50 ml). The mixture was heated under reflux for 2 h, then cooled to room temperature. Ice (40 g) was added slowly. The mixture was filtered and the organic phase separated, washed twice with 15 ml of cold water, then dried over $MgSO_4$ and filtered. Solvent was distilled off and the product, $[HC(SiMe_2Vi)_3]$ (**1**), was obtained under reduced pressure (97 °C/1 mm Hg). Yield: 2.1 g (40.7%); ^1H NMR ($CDCl_3$) δ: −0.55 (1H, s, CH), 0.18 (18H, s, $SiCH_3$), 5.75 (2H, m, $^1J = 14.7$, $^2J = 1.45$ Hz, $CH_2{=}$), 6.28 (1H, m, $^1J = 14.7$; $^2J = 1.45$ Hz, $=CH$); ^{13}C NMR ($CDCl_3$) δ: 1.2 (SiMe), 1.5 (CH), 130.3 ($CH_2{=}$), 142.4 ($=CH$); ^{29}Si NMR: ($CDCl_3$, INEPT) δ: 7.24; Anal. Calc. for $C_{13}H_{28}Si_3$: C, 58.13; H, 10.51. Found: C, 58.01; H, 10.42%. GC/MS. *m/z*: 268 [10%, M^+], 253 [100%, $M^+ - CH_3$], 241 [95%, $M^+ - CH{=}CH_2$], 226 [35%, $M^+ - CH_3 - CH{=}CH_2$], 214 [15%, $M^+ - 2(CH{=}CH_2)$], 199 [12%, $M^+ - CH_3 - 2(CH{=}CH_2)$], 97 [2%, $(CH_3)(CH_2{=}CH)SiC^+$], 85 [10%, $(CH_3)_2(CH_2{=}CH)Si^+$], 73 [9%, Me_3Si^+].

Tris(dimethylsilyl)methane $[HC(SiMe_2H)_3]$ (**2**) was synthesised according to [14].

2.2.3. Hydrosilylation of 4-(4-pentenyloxy)biphenyl with chlorodimethylsilane

A mixture of 4-(4-pentenyloxy)biphenyl (4 g, 16.78 mmol), toluene (20 ml), chlorodimethylsilane (1.59 g, 16.8 mmol) and Karstedt's catalyst (20 µl of 3.5% soln. in xylenes, 2.1×10^{-4} mol Pt/mol Si–H) was stirred under argon at 60 °C for 24 h. The solvent was evaporated to leave white, solid $ClSiMe_2(CH_2)_5OC_6H_4C_6H_5$ (yield – 5.6 g, 100%).

^1H NMR (C_6D_6) δ: 0.22 (6H, s, $SiCH_3$), 0.65 (2H, t, $J = 1.0$ Hz, Si–CH_2), 1.35–1.62 (6H, m, C–$(CH_2)_3$–C), 3.67 (2H, t, $J = 1.90$ Hz, OCH_2), 6.90, 7.25 (9H, m, aromatic protons); Anal. Calc. for $C_{19}H_{25}ClOSi$: C, 68.54; H, 7.57. Found: C, 68.34; H, 7.67%.

*2.2.4. Synthesis of 4-biphenyloxypentyldimethylsilane (**3**)*

The product from the preceding experiment 4-biphenyloxypentyldimethylchlorosilane (16.78 mmol) was dissolved in dry diethyl ether (20 ml), then $LiAlH_4$ (0.65 g, 17.13 mmol) was added and the mixture was heated under reflux for 6 h.

The solvent was removed under vacuum and the black, solid residue dissolved in hot toluene (30 ml). The solution was filtered and the solvent removed under vacuum to give white crystals of $HSiMe_2(CH_2)_5OC_6H_4C_6H_5$ (**3**). Yield: 3.45 g (70%); ^1H NMR (C_6D_6) δ: 0.05 (6H, d, $J = 3.71$ Hz, $SiCH_3$), 0.55-(2H, m, $^1J = 1.0$; $^2J = 3.10$ Hz, Si–CH_2), 1.25–1.75 (6H, m, C–$(CH_2)_3$–C), 3.65 (2H, t, $J = 1.90$ Hz, O–CH_2), 4.15 (1H, m, $J = 3.71$ Hz, Si–H), 6.95, 7.15 (9H, m, aromatic protons); Anal. Calc. for $C_{19}H_{26}OSi$: C, 76.47; H, 8.79. Found: C, 76.21; H, 8.85%.

*2.2.5. Hydrosilylation of tris(dimethylvinylsilyl)methane (**1**) with 4-biphenyloxypentyldimethylsilane (**3**)*

A mixture of tris(dimethylvinylsilyl)methane (**1**) (0.76 g, 2.83 mmol) and Karstedt's catalyst (20 µl of 3.5% solution in xylenes, 5.1×10^{-4} mol Pt/mol Si–H) was added to 4-biphenyloxypentyldimethysilane (**3**) (2.1 g, 7.0

mmol) in toluene (10 ml). The mixture was stirred at 60 °C for 72 h and the solvent evaporated to leave a brown solid that was extracted with CH_2Cl_2. The extract was filtered and the solvent evaporated to leave white solid, which was recrystallised from hot methanol (30 ml) to give $HC[Si(Me)_2(CH_2)_2Si(Me)_2(CH_2)_5OC_6H_4C_6H_5]_3$ (**4**) (2.01 g, 74%); ^1H NMR ($CDCl_3$) δ: −0.59 (1H, s, CH), −0.12 (18H, s, HC–Si$\mathit{Me_2}$), 0.18 (18H, s, H_2C–Si$\mathit{Me_2}$–CH_2), 0.35 (12H, m, $^1J=1.40$; $^2J=7.70$ Hz, Si–CH_2–CH_2–Si), 0.56 (6H, m, $^1J=7.70$, $^2J=1.0$ Hz, Si–$\mathit{CH_2}$$(CH_2)_4$), 1.28–1.45 (18H, m, C–$(\mathit{CH_2})_3$–C), 4.05 (6H, t, $J=1.90$ Hz, O–CH_2), 6.90, 7.25 (27H, m, aromatic protons); ^{13}C NMR ($CDCl_3$) δ: −5.2 (CH), −3.9 (HC–Si$\mathit{Me_2}$), 0.6 (CH_2–Si$\mathit{Me_2}$–CH_2), 7.7 ($\mathit{CH_2}$–Si–CH), 11.1 (–$(CH_2)_5$–Si–$\mathit{CH_2}$), 14.8 ($(CH_2)_4$–$\mathit{CH_2}$–Si), 23.8, 29.1, 30.1 (–C–$\mathit{CH_2}$–C), 68.1 (O–CH_2), 114.8, 126.6, 126.7, 128.1, 128.7 (aromatic carbon atoms); ^{29}Si NMR ($CDCl_3$, INEPT) δ: 2.77 (Si–$(CH_2)_5$), 4.00 (Si–CH); Anal. Calc. for $C_{70}H_{106}O_3Si_6$: C, 72.25; H, 9.19. Found: C, 72.39; H, 9.08%.

2.2.6. Hydrosilylation of mesogenic alkenes with tris(dimethylsilyl)methane

The general procedure is described below:

Karstedt's catalyst (10 μl of 3.5% solution in xylenes, 5.5×10^{-4} mol Pt/mol Si–H) was added to a mixture of the mesogenic alkene (3.2 mmol) and tris(dimethylsilyl)methane (**2**) (0.2 g, 1.04 mmol) in dry toluene. The mixture was stirred at room temperature for 12 h, then for 92 h at 60 °C. The product was separated by multiple precipitation from dichloromethane/methanol and solvent removed under vacuum.

Tri-podal methanes (**5**) and (**6**) with, respectively, 4′-undecanyloxybiphenyl-4-(4-pentenyloxy) and 4′-methoxyphenyl-4-(4-pentenyloxy)benzoate moieties were obtained, in 76% (0.83 g) and 74% (0.89 g) yield.

(**5**) ^1H NMR (C_6D_6) δ: −0.25 (1H, s, CH), 0.08 (18H, s, $SiCH_3$), 0.68 (6H, m, $^1J=1.0$; $^2J=7.25$ Hz Si–CH_2), 0.96 (9H, t, $J=1.0$ Hz, C–CH_3), 1.20–1.75 (12H + 48H, m, Si–C–$(CH_2)_2$–C + O–C–C–$(\mathit{CH_2})_8CH_3$), 1.78–1.81 (12H, m, –CH_2–C–O), 3.95, 4.02 (6H + 6H, t, OCH_2), 6.95, 7.1, 8.15, (24H, m, aromatic protons); ^{13}C NMR (C_6D_6) δ: −5.8 (HC), 2.0 ($SiCH_3$), 12.6 (C–CH_3), 18.7 (CH_2Si), 25.3–31.4 (–C–$\mathit{CH_2}$–C), 69.1, 71.4 ($\mathit{CH_2}$ CH_2O), 76.5, 77.1 (CH_2O), 115.5–134.5 (aromatic carbon atoms); ^{29}Si NMR: (C_6D_6 INEPT) δ: 6.2; Anal. Calc. for $C_{91}H_{142}O_6Si_3$: C, 77,17; H, 9.22. Found: C, 77.02; H, 9.05%.

(**6**) ^1H NMR (C_6D_6) δ: −0.25 (1H, s, CH), 0.07 (18H, s, $SiCH_3$), 0.65 (6H, m, $^1J=1.0$; $^2J=7.25$ Hz, Si–CH_2), 1.25–1.70 (12H, m, Si–C–$(CH_2)_2$–C), 1.85 (6H, m, –CH_2–C–O), 3.75 (9H, s, OCH_3), 4.05 (6H, m, $J=1.25$ Hz, CH_2–O), 6.95, 7.1, 8.15, (24H, m, aromatic protons); ^{13}C NMR (C_6D_6) δ: −5.6 (HC), 2.1 ($SiCH_3$), 18.6 (CH_2Si), 25.3, 35.2 (–C–$\mathit{CH_2}$–C), 55.8 (OCH_3), 69.1 ($\mathit{CH_2}CH_2O$), 76.5 (CH_2O), 115.5–134.5 (aromatic carbon atoms); ^{29}Si NMR: (C_6D_6 INEPT) δ: 6.3; Anal. Calc. for $C_{64}H_{81}O_{12}Si_3$: C 68.18; H, 7.34. Found: C, 67.98; H, 7.20%.

2.2.7. Functionalisation of silyl-substituted methanes (4) and (5) by reaction with methyl lithium and allyl bromide

Compound (**4**) or (**5**) (0.76 mmol) in dry THF (10 ml) was added dropwise to a solution of MeLi (2 mmol) in THF (10 ml) at room temperature. The reaction mixture was heated under reflux for 5 h to give a deep red solution of the lithium derivative.

The mixture was cooled to 0 °C and allyl bromide (0.12 ml, 0.8 mmol) was added dropwise. The mixture was stirred for 4 h at 0 °C and the solvent evaporated under vacuum at 0 °C to leave red, semi-solid product, that was partly extracted with toluene (20 ml). The extract was filtered and the solvent evaporated to leave a yellow solid that was recrystallised from hot ethanol (15 ml).

Allyl derivatives: $CH_2{=}CHCH_2C[SiMe_2(CH_2)_2Si\text{-}SiMe_2(CH_2)_5OC_6H_4C_6H_5]_3$ (**7**) and $CH_2{=}CHCH_2C[Si\text{-}[SiMe_2(CH_2)_5OC_6H_4C_6H_4O(CH_2)_{10}CH_3]_3$ (**8**) were obtained, respectively, in 88% (0.81 g) and 73% (0.63 g) yield.

(**7**) ^1H NMR ($CDCl_3$) δ: −0.17 (18H, s, Si$\mathit{Me_2}$–$(CH_2)_5$), −0.05 (18H, s, Si$\mathit{Me_2}$–CH), 0.23 (12H, m, $^1J=7.70$; $^2J=1.0$ Hz, Si–CH_2–CH_2–Si), 0.38 (6H, m, $J=1.0$ Hz, $(CH_2)_4$–$\mathit{CH_2}$–Si), 1.28–1.45 (18H, m, C–$(CH_2)_3$–C), 3.35 (2H, m, $^1J=1.40$; $^2J=1.0$ Hz, CH_2–C=C), 3.91 (6H, t, $J=1.25$ Hz, O–CH_2), 4.95 (2H, m, $^1J=1.40$; $^2J=1.80$ Hz, CH_2=C), 5.95 (1H, m, $^1J=1.40$; $^2J=1.80$ Hz, CH=), 6.90, 7.25 (27H, m, aromatic protons); ^{13}C NMR ($CDCl_3$) δ: −2.1 (Si$\mathit{Me_2}$–$(CH_2)_5$), 0.7 (Si$\mathit{Me_2}$–CH), 7.9 ($\mathit{CH_2}$–Si–CH), 11.2 ($(CH_2)_5$–Si–$\mathit{CH_2}$), 14.8 ($(CH_2)_4$–CH_2–Si), 23.8, 29.1, 30.1 (–C–$\mathit{CH_2}$–C), 47.3 ($\mathit{CH_2}$–C=C), 68.1 (O–CH_2), 114.8, 126.6, 126.7, 128.1, 128.7 (aromatic carbon atoms), 138.6 (CH_2=), 142.4 (CH=); ^{29}Si NMR ($CDCl_3$) δ: 2.1 (Si–$(CH_2)_5$), 7.8 (CH_2=CH–C–Si); Anal. Calc. for $C_{73}H_{110}O_3Si_6$: C, 72.84; H, 9.22. Found: C, 72.60; H, 9.07%.

(**8**) –^1H NMR ($CDCl_3$) δ: −0.16 (18H, s, Si$\mathit{Me_2}$–$(CH_2)_5$), −0.04 (18H, s, Si$\mathit{Me_2}$–CH), 0.22 (12H, m, $^1J=7.70$; $^2J=1.0$ Hz, Si–CH_2–CH_2–Si), 0.37 (6H, m, $J=1.0$ Hz, $(CH_2)_4$–$\mathit{CH_2}$–Si), 0.92 (9H, t, $J=1.0$, C–CH_3), 1.28–1.49 (18H + 48H, m, C–$(CH_2)_3$–C + O–C–C–$(\mathit{CH_2})_8CH_3$), 3.34 (2H, m, $^1J=1.40$; $^2J=1.0$ Hz, CH_2–C=C), 3.91, 3.93 (6H + 6H, t, $J=1.25$ Hz, O–CH_2), 4.94 (2H, m, $^1J=1.40$; $^2J=1.80$ Hz, CH_2=C), 5.92 (1H, m, $^1J=1.40$ $^2J=1.80$ Hz, CH=), 6.91, 7.26 (27H, m, aromatic protons); ^{13}C NMR ($CDCl_3$) δ: −2.2 (Si$\mathit{Me_2}$–$(CH_2)_5$), 0.8 (Si$\mathit{Me_2}$–CH), 7.7 ($\mathit{CH_2}$–Si–CH), 11.3 ($(CH_2)_5$-Si-$\mathit{CH_2}$), 14.8 ($(CH_2)_4$–CH_2–Si), 23.8–32.4 (–C–$\mathit{CH_2}$–C), 47.3 ($\mathit{CH_2}$–C=C) 68.1, 69.2 (O–CH_2), 115.6–132.8 (aromatic carbon atoms), 138.9 (CH_2=), 142.2 (CH=); ^{29}Si NMR ($CDCl_3$) δ: 1.9 (Si–$(CH_2)_5$), 7.2 (CH_2=CH–C–Si); Anal. Calc. for $C_{94}H_{146}O_6Si_3$: C, 77.84; H, 10.11. Found: C, 77.61; H, 9.98%.

*2.2.8. Synthesis of side-chain linear polysiloxanes (**9**) and (**10**)*

A precursor (**7**) or (**8**) (0.67 mmol) was dissolved in toluene (10 ml) and poly(methylsiloxane) ($M_n = 2150$) (0.36 g, 0.6 mmol of Si–H) and Karstedt's catalyst (10 μl of 3.5% solution in xylenes, 1.5×10^{-3} mol Pt/mol Si–H) were added. The mixture was stirred under argon at 60 °C for 96 h and the solvent evaporated to leave white, semi-solid product. This was purified by multiple precipitation from CH_2Cl_2/MeOH and the solvent removed under vacuum.

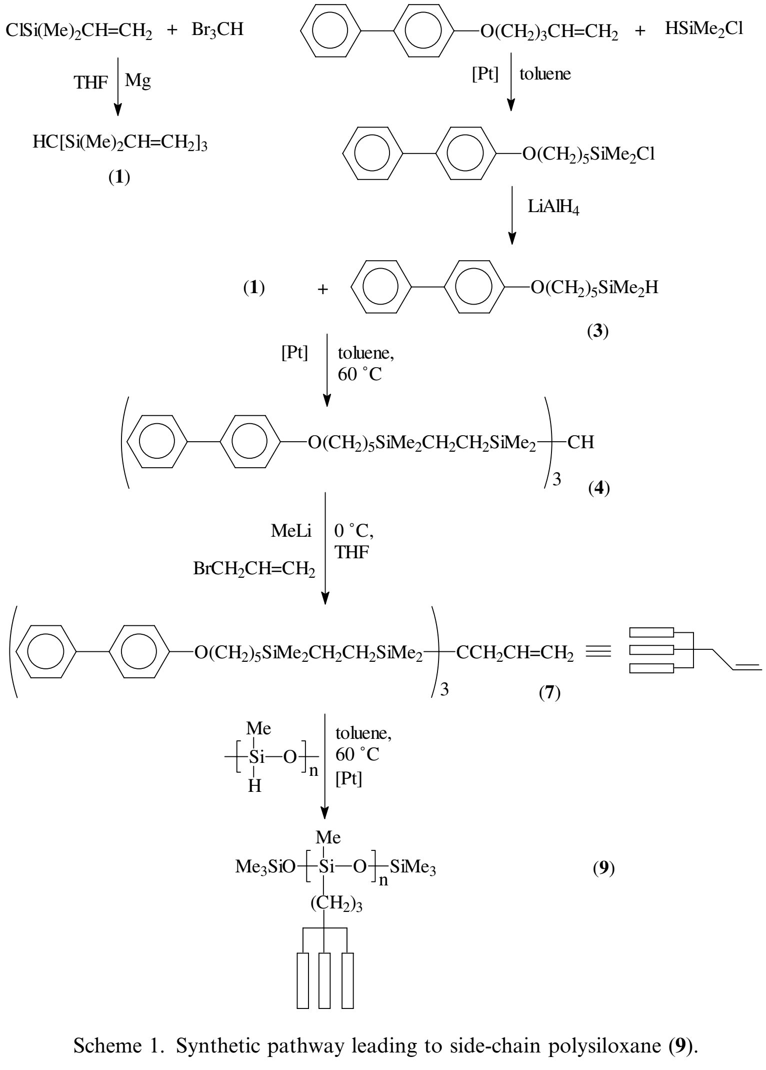
The polysiloxanes (**9**) and (**10**) were obtained, respectively, in 59% (0.45 g) and 61% (0.64 g) yield.

(**9**) ^1H NMR (C_6D_6) δ: 0.04 (s, $SiMe_3$ polymer end groups), 0.12 (3H, s, O–Si–Me from main chain), 0.24 (18H, s, Si–C–SiMe_2), 0.29 (18H, s, $CH_2Si(Me)_2CH_2$), 0.40 (12H, s, $SiCH_2CH_2Si$), 0.51–0.61 (8H, m, $SiCH_2(CH_2)_4$ + O–Si–CH_2), 0.73–0.78 (8H, m, O–$SiCH_2CH_2CH_2C$ + Si–CH_2CH_2–$(CH_2)_3$), 1.36–1.55 (8H, O–$SiCH_2CH_2CH_2C$ + Si–$(CH_2)_2$–CH_2–$(CH_2)_2$), 1.70 (6H, m, O–CH_2CH_2), 3.73 (6H, m, OCH_2), 6.71, 6.93, 7.24, 7.40–7.56 (27H, aromatic hydrogen atoms); ^{29}Si NMR (C_6D_6) δ: −21.5 (Si–O), 2.9 (Me_3Si end groups), 4.1 (Si–$(CH_2)_5$), 7.0 (C–Si–$(CH_2)_3$).

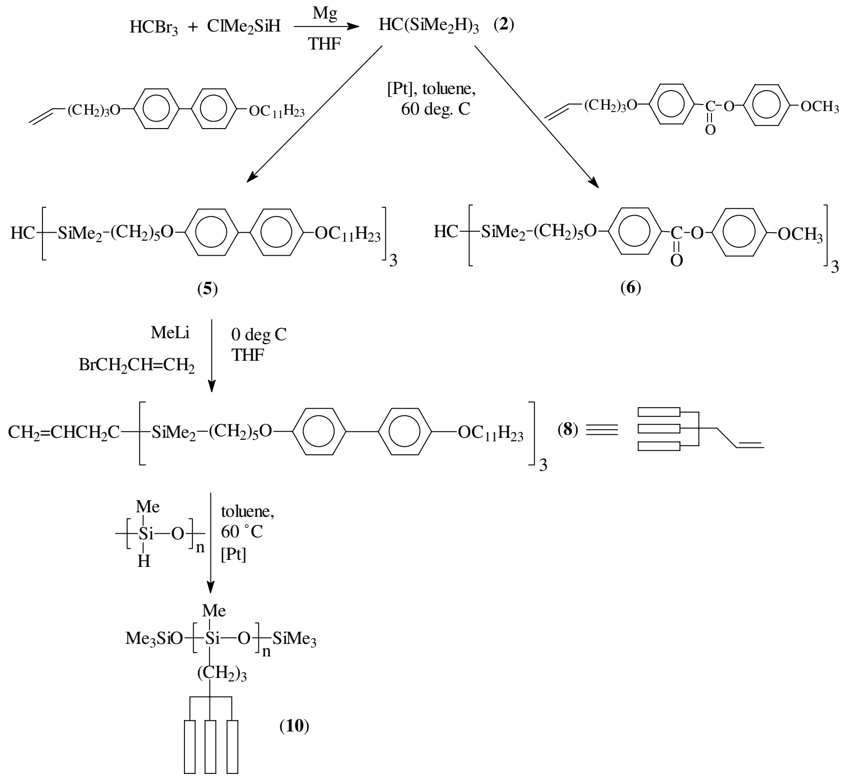
(**10**) ^1H NMR ($CDCl_3$) δ: 0.08 (18H, s, –C–SiMe_2–C–), 0.12 (3H, s, O–Si–Me from main chain), 0.45 (12H + 2H, s, $SiCH_2$), 0.81 (9H, m, CH_3), 1.21–1.29 (4H + 6H, m, Si–$CH_2(CH_2)_2C$ + $SiMe_2CH_2CH_2$), 1.32–1.35 (6H + 30H, m, $SiMe_2CH_2CH_2CH_2$ + $OCH_2CH_2(CH_2)_5$), 1.71–1.83 (6H + 6H, m, O–CH_2CH_2), 3.76, 3.89 (6H + 6H, m, OCH_2), 6.79–6.91, 7.0–7.12, 8.05–8.13 (27H, aromatic hydrogen atoms); ^{29}Si NMR ($CDCl_3$) δ: −21.7 (Si–O), 3.9 (Me_3Si end groups), 7.1 (Me_2Si).

3. Results and discussion

There appears to be a growing demand for multipodal mesogens as a way of increasing density of liquid crystal moieties attached to polymer backbones. Such taper-shaped side groups, based on 3,4,5



Scheme 1. Synthetic pathway leading to side-chain polysiloxane (**9**).



Scheme 2. Synthetic pathway leading to side-chain polysiloxane (**10**).

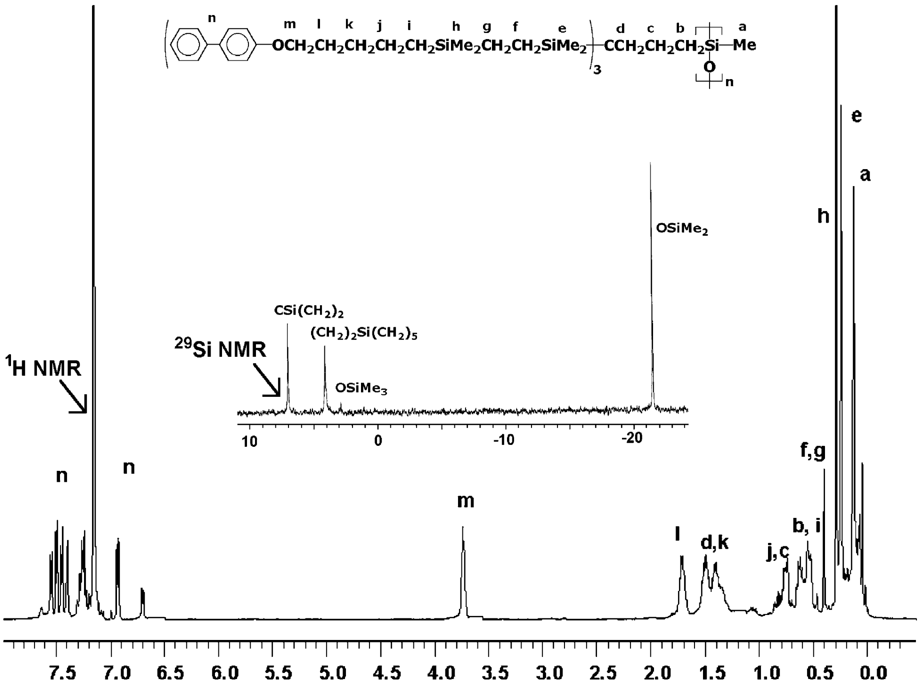


Fig. 1. MHz ^{1}H NMR and ^{29}Si NMR of side-chain polysiloxane (**9**).

substituted benzene rings, have recently been attached to polymethylmethacrylate backbone [15]. The syntheses involve, however, 11-steps and the short flexible spacers leave little freedom to individual mesogens at branching point.

Such problems are avoided in the syntheses of the branched multi-rod type side-chain polymers described here (Schemes 1 and 2). The tri-functional methanes – $[CH_2{=}CH(Me)_2Si]_3CH$ (**1**) and $(HMe_2Si)_3CH$ (**2**), can be easily made by Grignard type coupling reactions and the longer spacer between the mesogenic rods and the polymer backbone allows more flexibility for orientation of the mesogenic fragments. Longer spacers (8–10 atoms separating polymer chain from a mesogen) usually better decouple motions of the mesogens from the polymer backbone [16]. The simplest model mesogenic rod-like alkene, 4-(4-pentenyloxy)biphenyl, was modified by hydrosilylation with chlorodimethylsilane to give $Cl(Me)_2$ $Si(CH)_5OC_6H_4C_6H_5$, which was subsequently reduced with $LiAlH_4$ to 4-biphenyloxypentyldimethylsilane (**3**) with an overall yield of 70%. A simple hydrosilylation of (**1**) with a threefold excess of (**3**) gave the tri-podal substituted methane (**4**) (Scheme 1). The acid C–H moiety in methane (**4**) [11] was quantitatively lithiated (MeLi) and the lithium salt functionalised by reaction with allylbromide. The substituted branched alkene (**7**) was attached to commercially available poly(methylsiloxane) ($M_n = 2150$, IP = 1.23) by the addition of Si–H bonds in the polymer across allyl functions in the methane. The new polymer (**9**) has branched side-chain substituents at each silicon atom along the siloxane chain (see ^1H NMR and ^{29}Si NMR, Fig. 1). Neither (**7**) nor the side-chain polysiloxane (**9**) exhibits liquid crystalline properties. The simple biphenyl rod-like system is known to be a rather ineffective mesogen [17,18], but it was used here as a model to prove the effectiveness of the individual steps of the synthetic pathway.

We considered that the crowded branched structure of methane derivative (**7**) or (**8**) can be responsible for the poor alignment of the "rods" and hence weak mesomorphic properties. We therefore proceeded with syntheses of derivatives bearing rod-like moieties already shown to give mesomorphic properties in the expectation that these would be strengthened on transfer to polymer systems.

Synthetic routes to polymers containing the established mesogenic groups [19], 4′-methoxyphenyl-4-(4-pentenyloxy)benzoate and 4′-undecanyloxy-4-(4-pentenyloxy)biphenyl, were simplified (Scheme 2). The use of $(HMe_2Si)_3CH$ (**2**) as a precursor in the place of $[CH_2{=}CH(Me)_2Si]_3CH$ (**1**) made it possible to synthesize mesogenic alkenes by direct hydrosilylation, without reaction with HMe_2SiCl and subsequent reduction with $LiAlH_4$ (Scheme 1). Two low molecular weight branched mesomorphic derivatives (**5**) and (**6**) were made (Scheme 2), and the following phase transitions: K 98 °C N 124 °C I (**5**) and K 6 °C SmA 40 °C I (**6**) (where K, N, SmA and I denote crystal, nematic, smectic A and isotropic phases, respectively) were established by DSC (Fig. 2) and X-ray diffraction studies. A limitation, on the incorporation of mesogen (**6**) into polymer systems, arises from the sensitivity of its ester bond towards MeLi. A search for an alternative route is under way. Mesogen (**5**), on the other hand, can be readily attached to linear poly(methylsiloxane) via the mesomorphic alkene (**8**) (K 101 °C N 126 °C I) to give the liquid crystalline side-chain polymer (**10**) (K 85 °C SmA 98 °C I) (DSC, Fig. 3). The mesophase temperature range for this novel polymer is narrower than the one of the parent alkene (**8**). However, due to the flexibility of polysiloxane chain a mesophase

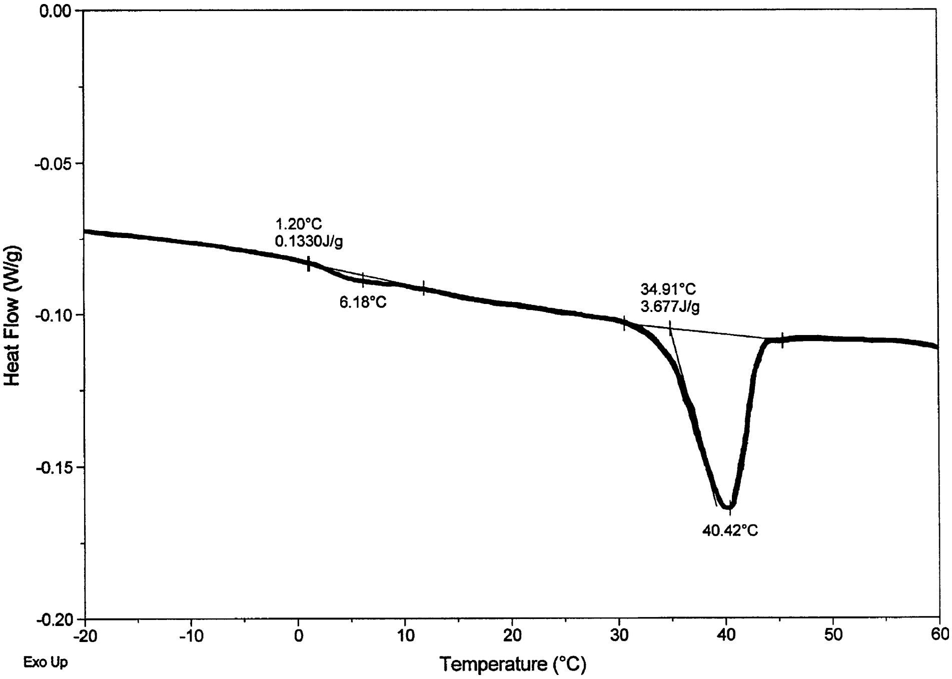


Fig. 2. DSC trace of low molecular branched mesomorphic methane (**6**), heating, 5 deg/min.

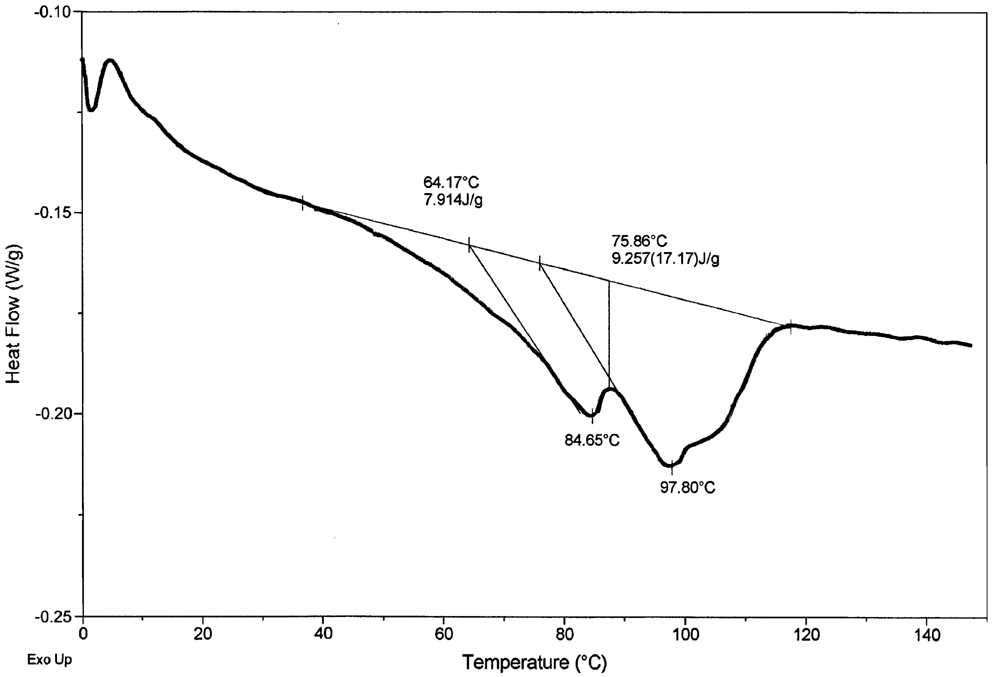


Fig. 3. DSC trace of side-chain polysiloxane (**10**), heating, 5 deg/min.

of higher order is generated (SmA) at a temperature lower by almost 20 °C.

4. Conclusions

Three novel model tri-podal methane derivatives (**4**–**6**) were made by hydrosilylation of $[CH_2{=}CH(Me)_2\text{-}Si]_3CH$ (**1**) with $H(Me)_2Si(CH_2)_5OC_6H_4C_6H_5$ or hydrosilylation of $CH_2{=}CH(CH_2)_3OC_6H_4C(O)O\text{-}O)OC_6H_4OCH_3$ or $CH_2{=}CH(CH)_3C_6H_4C_6H_4OC_{11}H_{23}$ with $(HMe_2\text{-}Si)_3CH$ (**2**). Compounds (**4**) and (**5**) were further converted into terminal tri-podal alkenes and the mesogenic groups were attached to linear poly (methylsiloxane).

The branched methanes (**5**) and (**6**), and terminal alkene (**8**) exhibited mesomorphic properties as well as the side-chain polysiloxane (**10**). Neither of the low molecular weight systems nor the polysiloxane, bearing the unsubstituted biphenyl type mesogen, gave liquid crystalline materials. We have shown that simple silyl substituted methanes (**1**) and (**2**) can be used for the synthesis of novel polysiloxanes with tri-podal side-chains containing rod-like substituents. At the moment, the only limitation appears to be that the mesogen must not contain functional groups prone to attack of MeLi.

The use of this general method should make it possible to synthesise polymer systems with high mesogenic density in four to six simple synthetic steps. Such novel and simple mesogenic groups should be easily attached to polymer systems (e.g., dendritic polysiloxanes [20,21] or polycarbosilanes [22]) in which the number of available sites is limited.

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References

[1] K.M. Blackwood, Science 273 (1996) 909.
[2] H. Hattori, T. Uryu, Liq. Cryst. 26 (1996) 1085.
[3] T.J. Bunning, F.-H. Kreuzer, Trends Polym. Sci. 3 (1995) 318.
[4] M.C. Coen, K. Lorenz, J. Kressler, H. Frey, R. Mulhaupt, Macromolecules 29 (1996) 8069.
[5] H. Lang, B. Luhmann, Adv. Mater. 13 (2001) 1523.
[6] S. Diele, S. Oelsner, F. Kuschel, B. Hisgen, H. Ringsdorf, Mol. Cryst. Liq. Cryst. 155 (1988) 399.
[7] G.H. Mehl, A.J. Thornton, J.W. Goodby, Mol. Cryst. Liq. Cryst. 332 (1999) 455.
[8] I.M. Saez, J.W. Goodby, Liq. Cryst. 26 (1999) 1101.
[9] A. Kowalewska, P.D. Lickiss, R. Lucas, W.A. Stańczyk, J. Organomet. Chem. 597 (2000) 111.
[10] C. Eaborn, J.D. Smith, J. Chem. Soc., Dalton Trans. (2001) 1541.
[11] C. Eaborn, J. Chem. Soc., Dalton Trans. (2001) 3397.

[12] M. Mausac, F. Hardouin, H. Richard, M.F. Archard, G. Sigaud, H. Gasparoux, Eur. Polym. J. 22 (1986) 137.

[13] M. Itoh, R.W. Lenz, J. Polym. Sci. Part A: Polym. Chem. 29 (1991) 1407.

[14] C. Eaborn, P.B. Hitchcock, P.D. Lickiss, J. Organomet. Chem. 252 (1983) 281.

[15] E. Zeng, K.I. Jacob, M.B. Polk, Polymer 43 (2002) 2169.

[16] C. Pugh, A.L. Kiste, in: D. Demus, J. Goodby, G.W. Gray, H-W. Spiess, V. Vill (Eds.), Handbook of Liquid Crystals, vol. 3, Wiley–VCH, Weinheim, 1998, p. 160.

[17] S.J. Sargeant, W.P. Weber, Macromolecules 26 (1993) 2400.

[18] T. Zhang, S.-Y. Park, B.L. Farmer, L.V. Interrante, J. Polym. Sci. A 41 (2003) 984.

[19] T. Ganicz, W.A. Stańczyk, N.K. Gladkova, I. Śledzińska, Macromolecules 33 (2000) 289.

[20] J.W. Goodby, in: D. Demus, J. Goodby, G.W. Gray, H.-W. Spiess, V. Vill (Eds.), Handbook of Liquid Crystals, vol. 2A, Wiley–VCH, Weinheim, 1998, pp. 412–413.

[21] J. Chojnowski, M. Cypryk, W. Fortuniak, M. Ścibiorek, K. Wijas, Macromolecules 36 (2003) 3890.

[22] T. Ganicz, W.A. Stańczyk, E. Białecka-Florjańczyk, I. Śledzińska, Polymer 40 (1999) 4733.