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Liquid crystal dimers with organosilicon spacers as models for side chain LC polymers

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Abstract

A series of six mesogenic dimers were prepared containing terminal 4’-methoxyphenyl-4-octenyloxybenzoate groups, of the general formula $[MeOC_6H_4O(O)CC_6H_4O(CH_2)_8SiMe_2]_2R$, where $R = –CH_2–$, $–(CH_2)_2–$, $–(CH_2)_3–$, $–SiMe_2–$, –O– and –NH–. Their liquid crystal properties were compared with those of the structurally relevant side chain polymers with the same mesogenic moiety: polycarbosilanes, polyethylene, and polysiloxane. It is shown that the low molecular dimers can be used as models for evaluating and predicting mesogenic characteristics of macromolecular systems with backbones structurally equivalent to spacers of the dimers. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Liquid crystal dimers; Organosilicon spacers; Liquid crystal organosilicon polymers

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1. Introduction

In recent years, methods of synthesis of polycarbosilanes — a new group of organosilicon side chain liquid crystal polymers — were developed [1–3] and properties of these polymers were reviewed [4]. This new group of materials appears to be of importance as polycarbosilanes generate mesophase in a temperature range covering the gap between side chain systems based on purely organic main chains and the inorganic ones. Moreover, their thermal and hydrolytic stability [5] exceeds that of structurally related organometallic polymers — side chain polysiloxanes, that are being widely studied as materials for electro-optical applications.

The structure of polycarbosilane main chain can be varied and so can be their liquid crystal properties, by changing of the length of the carbon atom sequence in a $–[(CH_2)_nSi]–$ backbone that affects its flexibility. Direct comparison of properties of these polymers, made by ring opening polymerization of strained silacyclobutanes, is a subject of some approximation, as usually for polymer systems, as a result of variation in molecular weight and polydispersity.

In course of studies on twin oligomers, it has been suggested that much of the properties of polymer systems are contained within these dimers having the same flexible spacers and the same mesogenic moieties [6]. The concept was developed and has been used for modeling of the main chain liquid crystal polymers [7,8]. However, it was also applied to side chain polysiloxanes and the dimers with siloxane spacers revealing strong analogy of thermal properties of the mesomorphic state with structural characteristics of the relevant liquid crystal phases [9].

The first purpose of this study is to examine liquid crystal properties of the carbosilane dimers as a function of a spacer R [from $–CH_2–$ to $–(CH_2)_3–$] in comparison with the relevant side chain polycarbosilanes (Fig. 1). Preliminary results concerning X-ray studies have been presented for two such cases [10].

We are convinced, however, that such an approach could be useful not only for comparing properties of side chain liquid crystal polymers within one type of a backbone and so we expanded the study of dimers to the models of polysiloxanes, polysilanes and polysilazanes, even though not all of these macromolecular liquid crystal systems were already synthesized.

Synthesis of the relevant liquid crystal dimers was carried out by catalytic hydrosilylation of mesogenic alkene with organosilicon spacers containing active Si–H bonds in terminal positions. The whole synthetic process is shown

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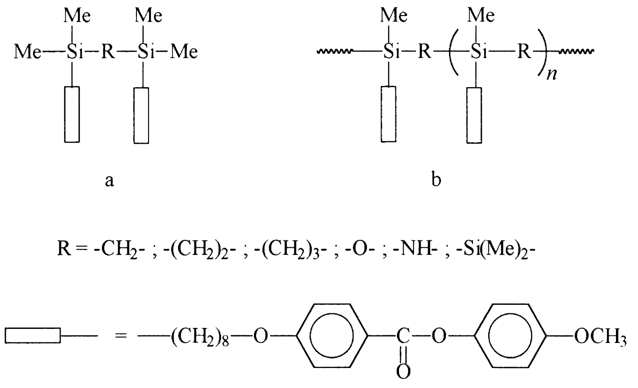

Fig. 1. LC dimers and LC side chain polymers.

in Fig. 2, including preparation of bis(dimethylsilyl)-methane and bis(dimethylsilyl)propane, the two organosilicon spacers that are not commercially available.

2. Experimental

All the organometallic syntheses, including hydrosilylation were carried out under dry nitrogen, to exclude oxygen and moisture from the reaction systems.

2.1. Instrumentation

Infrared (IR) spectra were obtained using Specord M 80 spectrometer for solutions in sodium dried toluene, stored over molecular sieve 4 Å. Nuclear magnetic resonance (NMR) spectra were recorded at 200 and 300 MHz using, respectively, Bruker AC and Bruker MSL spectrometers (with residual benzene as internal reference). GLC analyses were carried out with a Hewlett Packard 9890 chromatograph fitted with a flame-ionization detector; the packing was 10% OV-101 on Gas Chrom Q. Mass spectra were obtained by use of a Finnigan MAT95 spectrometer. Thermal properties of mesogenic dimers and polymers were studied by differential scanning calorimetry (DSC) (Du Pont DSC-910) calibrated with an indium standard. Molecular weight of polymers were measured by gel-permeation chromatography (GPC) on Waters columns 1000A and 500A using a Wyatt/Optilab 902 Interferometric Refractometer. The system was calibrated using monodisperse polystyrene standards. The values of transition temperatures are from the second heating run, at 10 K min^{-1}. Mesophase textures were investigated independently, by optical microscopy, using polarized light and a Linkam THNS 600 hot stage. X-ray diffraction measurements have been performed on free standing samples. The layer spacings in smectic phases were determined with a high-temperature Guinier camera with CoKα monochromatic radiation. Diffraction patterns of magnetically oriented samples were also obtained in a flat camera (CuKα radiation). Aligned samples were produced from the isotropic melt into the mesophase in a magnetic field of 1.5 T.

2.2. Synthesis of organosilicon spacers

Tetramethyldisiloxane ($HMe_2SiOSiMe_2H$) (Dow Corning), tetramethydisilazane ($HMe_2SiNHiMe_2H$) (Huls) and 1,2-bis(dimethylsilyl)ethane (Huls) were commercial products that were dried with $LiAlH_4$ prior to

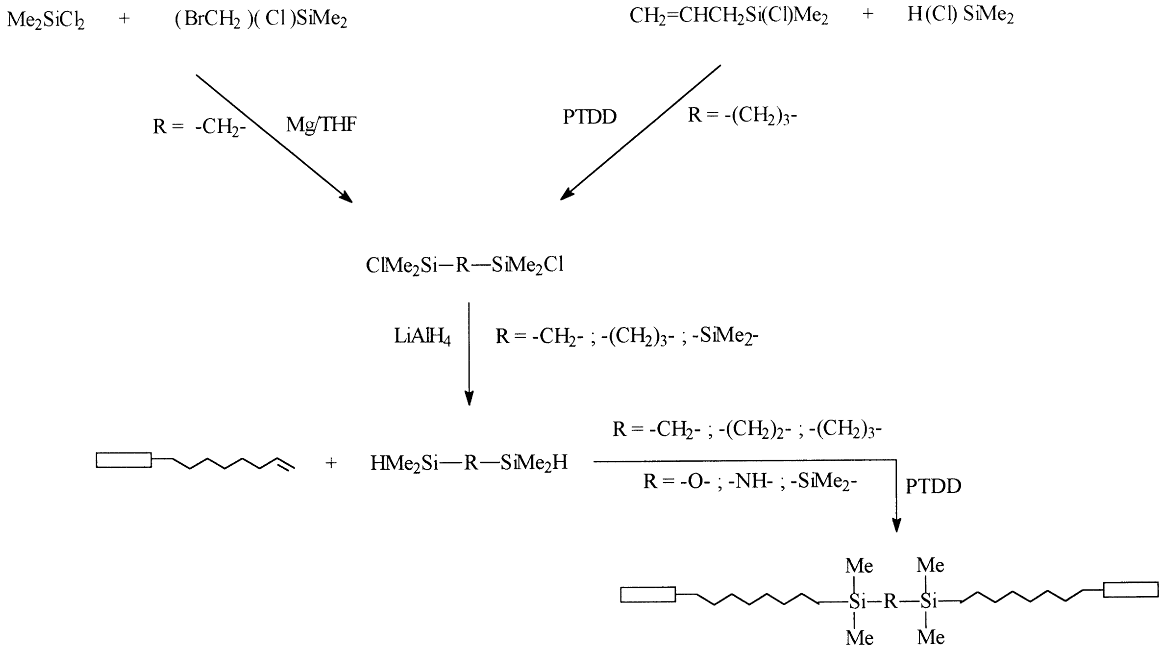

Fig. 2. Synthetic pathways for LC dimers.

hydrosilylation of a mesogenic alkene and distilled under reduced pressure. 1,3-Dihydro(hexamethyl)trisilane ($HMe_2SiSi(Me_2)SiMe_2H$) was made from commercial 1,3-dichloro(hexamethyl)trisilane (ABCR), according to the general method described below. Syntheses of bis(dimethylsilyl)methane ($HMe_2SiCH_2SiMe_2H$) and 1,3-bis(dimethylsilyl)propane ($HMe_2SiCH_2CH_2CH_2\ SiMe_2H$) were carried out as described below.

2.3. Synthesis of bis(dimethylsilyl)methane

This compund was synthesized according to the procedure described by Greber [11]. A modification, involving the use of diluted stoichiometric mixture of both organosilicon reactants, allowed for the increase in the yield of the intermediate product $ClMe_2SiCH_2SiMe_2Cl$ up to 60%. A solution of Me_2SiCl_2 (Dow Corning) (67 g. 0.52 mol) and $ClMe_2SiCH_2Br$ (Aldrich) (48.2 g, 0.26 mol) in THF (100 ml) were added dropwise, under nitrogen, to a dry, flamed three-neck flask, containing 6.32 g of Mg turnings for 3 h. Then the reaction mixture was diluted with THF (150 ml) and it was stirred vigorously at room temperature for further 3 h. Mg salts were filtered off and washed twice with THF (50 ml). The THF solution was concentrated by distillation under reduced pressure and the product distilled to give 31.4 g of bis(dimethylchlorosilyl)methane, b.p. 58°C–60°C/8 mmHg (lit. 174–176°C/760 mmHg [11]). The dichloro derivative (17 g, 0.085 mol) in Et_2O (50 ml) was added slowly at room temperature to a flask containing $LiAlH_4$ (2.3 g) in Et_2O (100 ml). After addition (l h) the reaction mixture was kept at reflux temperature, while progress of the reaction was followed by gas chromatography. When the reduction was completed (8 h), the mixture was poured into ice water (200 ml) (temperature 1–2°C) and the organic layer was separated, dried with $MgSO_4$ and distilled to give 8.5 g of $HMe_2SiCH_2SiMe_2H$, b.p. 102–103.5°C (yield 76%).

^1H NMR (in C_6D_6), δ: -0.32 (*t*, Si–CH_2Si), 0.08 (*d*, $SiMe_2$), 4.21 (*m*, Si–H).

2.4. Synthesis of 1,3-bis(dimethylsilyl)propane

Literature synthetic methods, involving telomerization of 1-methyl-1-silacyclobutane with chlorodimethylsilane [12] and coupling of chlorodimethylsilane with 1.3-dibromopropane [13] proved to be of little importance because of a very low yield of the desired product –, respectively, 5% and 12% of the bis(dimethylsilyl) propane (as checked by GC/MS). The three-step process, described first by Andrianov [14], was applied, but using more efficient initiation of the Grignard reaction and also a different hydrosilylation catalyst. A mixture of dimethyldichlorosilane (Dow Corning) (129 g, 1 mol) and allyl bromide (Aldrich) (71.5 g, 0.6 mol) was added dropwise, over 1.5 h to stirred Mg turnings (15 g, 1 mol) in Et_2O (500 ml). The reaction was initiated with 1,2-dibromoethane (Aldrich, 5 ml). After the addition was completed, the reaction mixture was stirred under reflux for 12 h. Mg salts were filtered off under nitrogen, Et_2O was removed by distillation under reduced pressure and the liquid residue was distilled to give 30 g (0.3 mol) of $CH_2{=}CHCH_2SiMe_2Cl$ (yield 50%), b.p. 108–110°C. Hydrosilylation of allyldimethylchlorosilane ($CH_2CHCH_2SiMe_2Cl$) (16.75 g, 0.125 mol) with dimethylchlorosilane (Me_2SiHCl) (Aldrich)(10.6 g, 0.112 mol) was carried out under standard conditions [15], in the presence of platinum tetramethyldivinyldisiloxane (PTDD) (Alfa Products, 170 μl of 3.5% solution in vinyl-terminated polydimethysiloxane (7.6×10^{-5} mol Pt mol^{-1} of the Si–H). The reaction mixture was stirred under dry nitrogen for 3 h, and distilled at reduced pressure, to give 11.8 g (yield 46%) of $ClMe_2SiCH_2CH_2CH_2SiMe_2Cl$, b.p. 110–112°C/35 mmHg. It was then reduced with $LiAlH_4$, according to the general procedure described above for preparation of $HMe_2SiCH_2SiMe_2H$, to give 6.7 g of 1,3-bis(dimethylsilyl) propane (yield 81%), b.p. 141–143°C.

^1H NMR (in C_6H_6) δ: 0.04 (*d*, $SiMe_3$), 0.63 (*m*, CH_2–Si), 1.47 (*m*, C–CH_2–C), 4.12 (*m*, Si–H).

2.5. Synthesis of liquid crystal dimers

The six dimers of general formula $[MeOC_6H_4O(O)C\text{-}C_6H_4O(CH_2)_8SiMe_2]R$, where R = $-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-SiMe_2-$, –O–, –NH–, were made via hydrosilylation of 4'-methoxyphenyl-4-octenyloxybenzoate [16] with Si–H terminated spacers ($HMe_2SiRSiMe_2H$), in the presence of PTDD. Since the synthetic procedures used to prepare the dimers were essentially the same, only one representative example is given below.

In a typical hydrosilylation reaction 4'-methoxyphenyl-4-octenyloxybenzoate (1.0 g, 2.82 mmol) was dissolved under dry nitrogen in dry (sodium mirror) toluene (10 ml) and then bis(dimethylsilyl)methane (156 mg, 1.18 mmol) was added into a Schlenk tube containing the solution. After addition of a catalyst — 3.5% PTDD solution in xylene (5 μl, 2.6×10^{-4} mol Pt mol^{-1} of the Si–H) — the reaction mixture was stirred for 45 h at room temperature. The product was separated by addition of methanol and centrifuged at 5°C. The crude dimer was purified by several dissolutions (methylene chloride) and precipitations (methanol) until it was free from the excess of mesogenic alkene (TLC on Kieselgel 60F 254 with chloroform as the eluent). The hydrosilylation yielded 0.26 g (29%) of the dimer with bis(dimethylsilyl)-methylene spacer. The same procedure was applied for the synthesis of dimers with other organosilicon spacers (^1H NMR spectra are shown in Fig. 3).

2.6. Synthesis of liquid crystal organosilicon polymers

All the side chain polymers had the same mesogenic 4'-methoxyphenyl-4-octyloxybenzoate pendant moieties [Mes = $(CH_2)_8OC_6H_4C(O)OC_6H_4OCH_3$]. Polymers, used in this study, were the ones based on the main-chain structure of poly(l-methyl-l-silaethylene) – $[CH_2Si(Me)(Mes)]$–; DP = 86, $M_w/M_n = 1.11$ and of

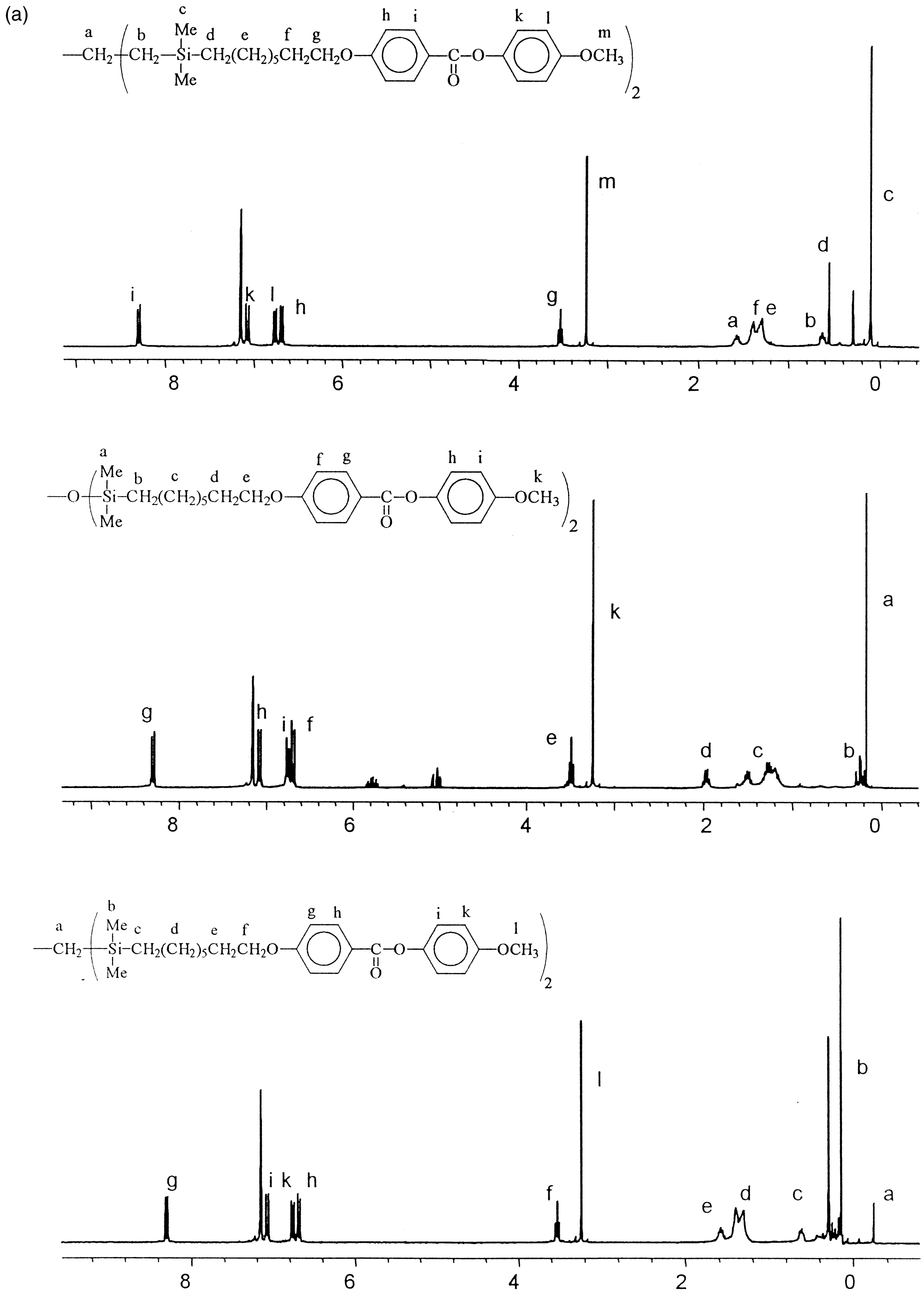

Fig. 3. ^{1}H solution NMR spectra of LC dimers.

poly(l-methyl-l-silabutane)– $[CH_2CH_2CH_2Si(Me)(Mes)]$–; DP = 457, $M_w/M_n = 2.04$. Polyethylene,– $[CH_2CH(SiMe_2Mes)]$–; DP = 75, $M_w/M_n = 1.7$, was synthesized according to published methods [17,18]. Polysiloxane, $-[Si(Me)Mes)O]_n-$; DP = 32, $M_w/M_n = 2.2$, was obtained via hydrosilylation of the standard mesogenic alkene with poly(methylhydrosiloxane) (Aldrich) using general procedure described by Boileau et al. [19].

3. Results and discussion

In three out of four presented cases, where comparison between a dimer and an equivalent polymer is possible (Table 1, entries 1–3a), the structure of each polymer main-chain is reflected by the structure of a corresponding dimer with the same sequence of atoms in a spacer and the same mesogens at terminal silicon atoms. The only

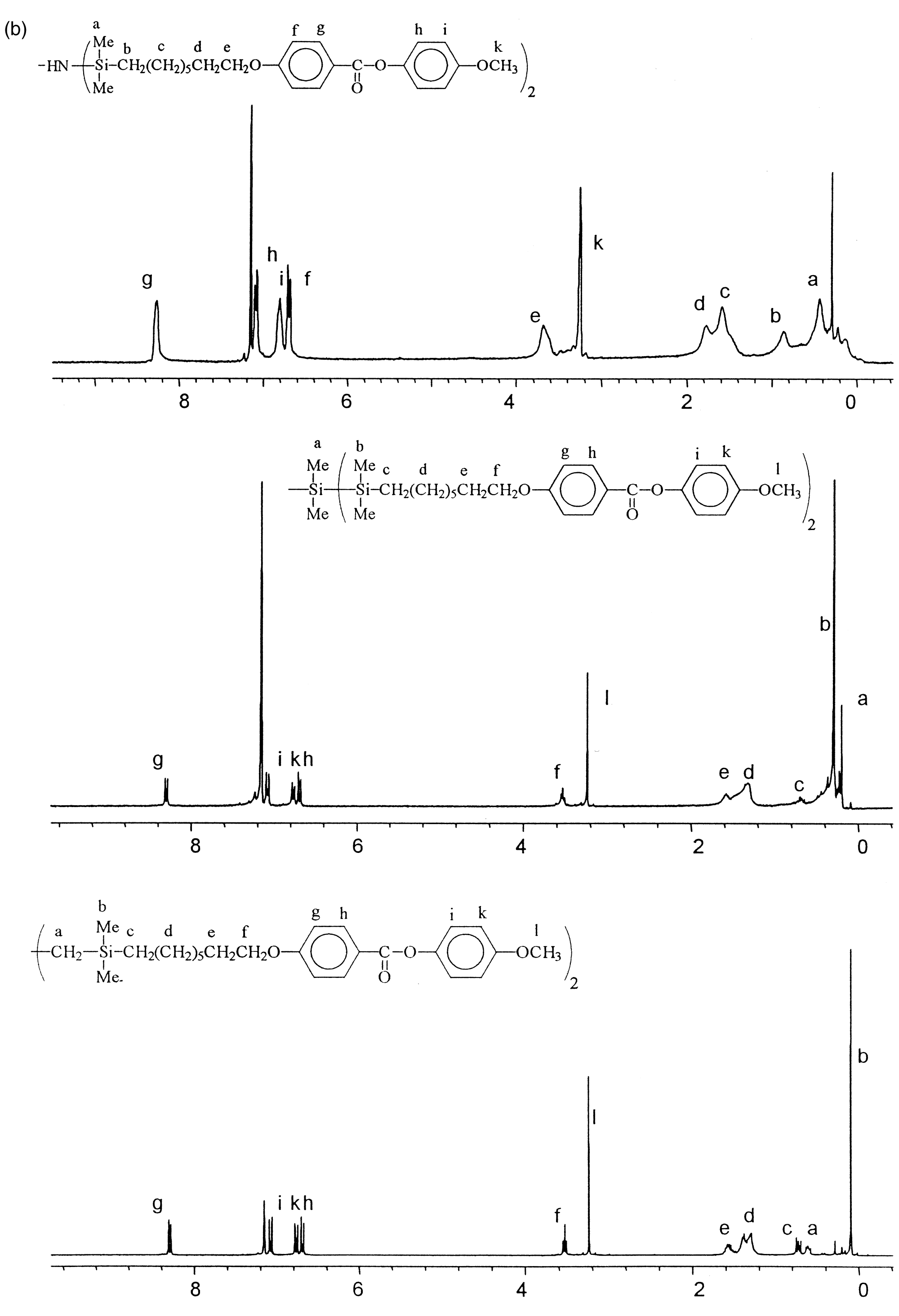

Fig. 3. (*continued*)

exception is the side chain poly(ethylene) in which silicon atoms are in fact parts of the side chains (Fig. 4a). This polymer remains, however, both with the relevant polycarbosilane, an analogue of the dimer with propylene spacer (Fig. 4b and 4c) and it seems worthy to know how far such the comparison can prove justified.

It might have been expected that the liquid crystalline poly(ethylene) should exhibit higher phase transition temperatures, compared to the respective polycarbosilane, with the same number of silicon atoms per monomeric unit. We have shown earlier [15] that polycarbosilane backbone is more flexible than the purely organic one (e.g. polymethacrylate) and that the organic polymer system, bearing the same mesogenic side groups as the equivalent polycarbosilane, shows significantly higher phase transition temperatures (50–70°C).

Table 1
Phase transition temperatures of organosilicon dimers. Comparison with the relevant macromolecular systems

Entry	Polymer/Dimer	Spacer	Transition temperatures (°C)	ΔT (°C)	DP_n
1	D	$-Me_2SiCH_2SiMe_2-$	**C** 25 **SmA** 35 **N** 68 **Iso**[a]	43	
1a	P	$-MeSiCH_2SiMe-$	**T**$_g$ 7 **C** 30 **SmA** 98 **Iso**	68	85
2	D	$-Me_2Si-O-SiMe_2-$	**C** 40 **SmA** 48 **N** 63 **Iso**	23	
2a	P	$-MeSi-O-SiMe-$	**T**$_g$ − 5 **C** 36 **SmA** 92 **Iso**	56	32
3	D	$-Me_2Si(CH_2)_3SiMe_2-$	**C** 62 **SmA** 68 **N** 72 **Iso**	10	
3a	P	$-MeSi(CH_2)_3SiMe-$	**T**$_g$ 1 **C** 49 **SmA** 83 **Iso**	34	460
3b	P	$-Me_2SiCHCH_2CHSiMe_2-$	**T**$_g$ − 119 **C** 28 **SmA** 115 **Iso**	87	75
4	D	$-Me_2SiCH_2CH_2SiMe_2-$	**C** 68 **SmA** 77 **N** 87 **Iso**	19	
5	D	$-Me_2SiSi(Me)_2SiMe_2-$	**C** 65 **Iso**	—	
6	D	$-Me_2Si-NH-SiMe_2-$	**C** 44 **SmA** 53 **N** 66 **Iso**	22	

[a] Monotropic.

In reality, it appears from Table 1 that the polyethylene (entry 3b) with side chains containing silicon atoms shows similar range of phase transition temperatures as polycarbosilanes with propylene (entry 3a) and methylene (entry 1a) spacers. It is certainly because of a significant difference in silicon and carbon atom radii — 117 pm and 77 pm, respectively. The increased, by about 50%, size of silicon atom compared to carbon will have several consequences. The most important ones for its phase behaviour are certainly longer Si–C bonds, ∽ 190 pm compared to 154 pm for C–C and lower barrier to Si–C bond rotation. It has to result in higher flexibility of the side chain polyethylene polymer system, even though, contrary to typical polycarbosilanes, the silicon atoms are not incorporated into the main chain. This observation thus broadens further the dimeric model method for other polymer structures, where organosilicon spacer is not necessarily part of a respective polymer main chain, but occupies both main backbone and partly also the side pendant.

A comparison of the series of dimers with carbosilane spacers, Table 1 (entry 1,3,4) with the two boundary polycarbosilanes 1a and 3a points to an analogy in thermal characteristics of the liquid crystalline phases. There is usually a well marked odd–even effect, observed for dimers, which seems to be the reason for monotropic properties of the dimer with bis(dimethylsilyl)methylene spacer. Its ethylene analogue, with the even number of atoms, exhibits the highest smectic–nematic and nematic–isotropic phase transition temperatures within the carbosilane dimers. One could thus expect the respective polymer poly(l-methyl-l-silapropane) to exhibit better ordered liquid crystalline phase and in a wider temperature range, unfortunately the potential cyclic monomer – l-methyl-l-silacyclopropane is unstable and cannot be taken into account as it rearranges to dimethylvinylsilane [20]

The corresponding polycarbosilanes exhibit an analogous structure to the dimer structure of the smectic phase (S_A), most probably with the same type of the monolayer formation, as *d*/l falls between 1.02 and 1.08 [15] and compares with the values for the dimers i.e. 1.12–1.20 [10]. The results prove as well that the attachment of mesogens to polymer chain generates higher ordering of the mesophase. For all the studied polymers, including side chain polyethylene (entry 3b) and polysiloxane (entry 2a), a nematic phase, shown by the dimers, gives way to smectic S_A in the whole temperature range of the mesophase formation.

The second important aspect that becomes clear from the study of dimers with different spacers, by modelling various polymer systems it is possible to predict properties of polymers that have not been even synthesized.

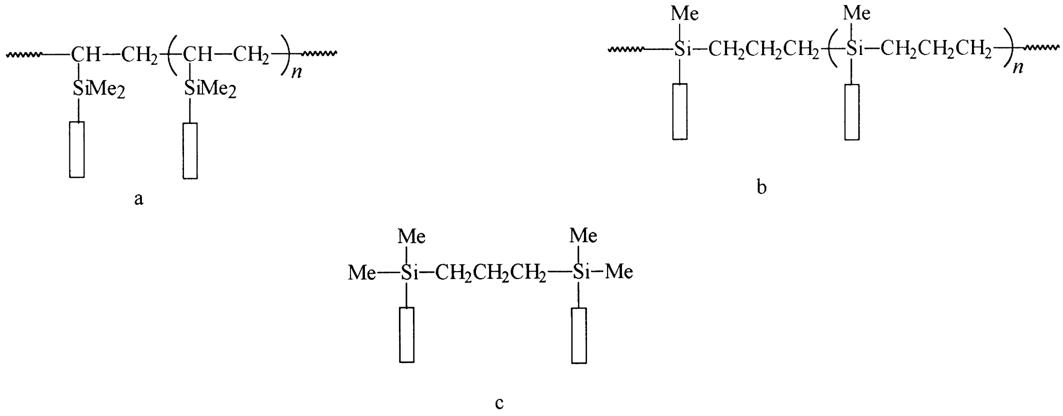

Fig. 4. Polymer analogues (a) polyethylene and (b) polycarbosilane of LC dimer (c) with propylene spacer.

It is well known that poly(silylenes), often referred to as polysilanes, having the polymer backbone made up entirely of silicon atoms, are different from all the other high polymers in the fact that they exhibit sigma electron delocalization [21]. This effect makes them more extended and stiffened compared with e.g. poly(olefins). Certainly as a result of this feature poly(silylenes) form a rather rare type of mesomorphic materials — *condis* crystals (conformationally disordered crystals) [4]. On the other hand, our results show that the respective dimer (entry 5) with trisilylene spacer is not liquid crystalline at all. The relative rigidity of the pure silicon backbone seems to promote only *condis* phase with main chain segments playing the role of rod-like mesogens. Judging from the lack of liquid crystal properties by our dimeric model, one should not expect thermotropic mesomorphism for its side chain mesogenic polymer analogues.

On the contrary, a mesogenic dimer with the silazane link (entry 6), a model of side chain polysilazanes (these were not yet made) promises mesomorphic properties close to that of polysiloxanes with even higher thermal stability which is known to be a characteristic feature of the Si–NH–Si system. The temperature range of mesophase for the polsilazane dimers equals to 22°C compared to 23°C for its siloxane analogue.

This wider method of comparing model low molecular weight dimers with various spacers, in our opinion, forms an useful tool for predicting properties of new polymers, leaving apart problems connected with variable molecular weight and polydispersity. It is much easier to build up a respective dimeric model and verify properties of polymers before starting often complicated synthesis of an equivalent side chain polymer.

4. Conclusions

Mesogenic dimers with various organosilicon spacers are easily prepared by hydrosilylation of mesogenic alkenes with α,ω-Si–H terminated spacers. Comparison of their thermal and structural properties with those of existing liquid crystal polycarbosilanes, polysiloxane, and even polyethylene with silyl containing moieties in the side chains, allows to treat the low molecular liquid crystals as useful models for structurally comparable side chain polymers, avoiding discrepancies as a result of variation in molecular weight and degree of polydispersion. This general method of building low molecular models can be also used to predict liquid crystal properties of new potential macromolecular systems. However, more systematic work in this area is certainly needed to understand all the factors that may affect the dimer–polymer relationship.

Acknowledgements

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