Macromolecules **2000,** *33,* 289−293

Vinylsilanes as Monomers for Side Chain Polymer Liquid Crystals

Tomasz Ganicz and Włodzimierz A. Stańczyk*

Centre of Molecular & Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Łódz, Poland

Natalya K. Gladkova

Lomonosov State University, Vorobiev Hills, II9899 Moscow, Russia

Irma Śledzińska

Institute of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warsaw, Poland

Received April 12, 1999; Revised Manuscript Received September 17, 1999

ABSTRACT: A series of novel side chain polymers−silylated polyethylenes were prepared containing 4′-methoxyphenyl-4-(*ω*-alkenyloxy)benzoate mesogenic groups of the general formula $\{-CH_2-CH[SiMe_2(CH_2)_mOC_6H_4C(O)OC_6H_4OMe]\}_n-$, where $m = 4, 5, 8, 11$. The ones having five and eight carbon atoms in the alkane moiety of a flexible spacer proved to be liquid crystalline, independent of molecular weight (DP = 75, 230). Alternative synthetic pathways have been described starting with anionic polymerization of Me_3SiVi or $Me_2PhSiVi$ in the presence of BuLi, followed by functionalization of side silyl group to give reactive Si−H bonds and hydrosilylation of terminal, mesogenic alkenes. The properties of liquid crystal polyethylenes were compared with those of side chain polycarbosilanes of similar structure. The advantage of polyethylenes, while preserving all important features of polycarbosilanes, is shown by their broad temperature range of mesophase formation and the economically attractive synthesis.

Introduction

In recent years a new group of liquid crystal side chain polymers, based on a polycarbosilane backbone, has been described.[1] The important features of this novel class of the liquid crystalline materials allow for creation of a wide spectrum of thermotropic properties within the same type of main polymer chain, by varying the number of carbon and silicon atoms and thus affecting directly the number of mesogenic units bound to the backbone. Moreover, any architectural changes always lead to uniform sequences along the polymer chain, whereas in other cases (e.g., polysiloxanes), to change the number of mesogens per one main chain atom, one has to resort to random copolymers only.

Until now, compared to the most intensively studied, purely inorganic and organic polymer backbones bearing side chain mesogens (i.e., those based on polysiloxanes and polyacrylates[2]), polycarbosilanes exhibit intermediate phase transition temperatures, covering a useful range of mesophase generation. Depending on the type of mesogens the liquid crystal phase exists typically between 25 and 110 °C, which is attractive from the point of view of applied studies. It is apparent[3] that incorporation of silicon atoms into a carbon polymer skeleton increases the flexibility of the system as a result of a significant difference in carbon and silicon atomic radius, 77 and 117 pm, respectively, leading to longer bonds along the chain and a lower rotation barrier.

Additionally, the advantage of the liquid crystal polycarbosilanes, compared to the recommended polysiloxanes, is that they exhibit higher thermal stability and are resistant to the redistribution process of monomeric units, under basic conditions.[4,5] At present, the disadvantage of this new class of liquid crystal polymers is their relatively high cost, due to low yield in syntheses of the respective monomers−silacyclobutanes,[1] although an intensive work on more efficient synthetic routes is under way.[4] Recently, we have found[3] that almost all the advantages of liquid crystal polycarbosilanes can be preserved in systems comprising a purely organic main chain (e.g., polyethylene) having silicon atoms in the side flexible spacers, separating mesogenic cores from the polymer backbone. In this report we present simple synthetic pathways leading to this attractive new group of mesomorphic polymers.

Experimental Section

Materials. Me_3SiVi (Aldrich) and $PhMe_2SiVi$, made as described in the literature,[6] were distilled twice from potassium mirror prior to use. Me_3SiCl (Aldrich) was distilled twice under argon. $AlCl_3$ and POCl (Aldrich) were used as received. All solvents were purified by standard procedures and, apart from MeOH, were distilled from potassium mirror. Catalysts (*sec*-BuLi and *n*-BuLi), solutions in toluene, were prepared from standard solutions in *n*-hexanes (Aldrich). The syntheses of mesogenic 4′-methoxyphenyl-4-(*ω*-alkenyloxy)benzoates were carried out according to the literature procedures.[7]

Polymerization of Me_3SiVi and $PhMe_2SiVi$. Anionic polymerizations were carried out using a high-vacuum break-seal technique. Thus, in a typical process, $PhMe_2SiVi$ (1.0 g, 61.6 mmol) in toluene (20 mL) was added to an ampule equipped with a magnetic bar and a sidearm break-seal containing an alkyllithium catalyst (6.25×10^{-5} mol of *n*-BuLi in 0.25 mL of toluene) (1.0×10^{-3} mol of *n*-BuLi per 1 mol of $PhMe_2SiVi$). The reaction was initiated by breaking the glass membrane and mixing the catalyst with the solution of monomer. The reaction mixture was stirred at room temperature for 3 h, and then the living polymerization was stopped by addition of methanol (5 mL). The polymer was precipitated by pouring into methanol (50 mL), and then it was centrifuged and dried under vacuum, to give 0.22 g (yield 22%) of poly(vinyldimethylphenylsilane).

---

* Corresponding author.

10.1021/ma990558v CCC: $19.00

Table 1. Polymerization of Me_3SiVi and $Me_2PhSiVi$

					polymer			
run	monomer M	initiator I	[I]/[M]	solvent	yield	M_n	M_w/M_n	DP_n
1	Me_3SiVi	*sec*-BuLi	1.76×10^{-3}	toluene	39	13 900	1.55	140
2	Me_3SiVi	*n*-BuLi	1.40×10^{-4}		78	43 000	2.44	430
3	$Me_2PhSiVi$	*sec*-BuLi	1.34×10^{-3}	toluene	35	15 500	1.78	95
4	$Me_2PhSiVi$	*n*-BuLi	1.00×10^{-3}	toluene	22	18 500	2.20	115
5	$Me_2PhSiVi$	*n*-BuLi	4.76×10^{-4}		45	163 000	2.10	1000

Table 2. Synthesis of Poly(vinyldimethylsilane)

		poly(vinyldimethylsilane)			
substrate	DP_n	yield	M_n	M_w/M_n	DP_n
$[-CH_2CH(SiMe_2Ph)-]_n$	1000	78	21800	2.53	250
$[-CH_2CH(SiMe_3)-]_n$	140	57	6400	1.67	75
$[-CH_2CH(SiMe_3)-]_n$	430	80	20000	2.23	230

^1H NMR of $[-CH_2-CH(SiMe_3)-]_n$ ($CDCl_3$) δ: 1.21−1.45 (m, 2H, $-CH_2-$), 0.41−0.73 (m, 1H, $-CH-$), −0.10 (s, 9H, $Si(CH_3)_3$).

^1H NMR of $[-CH_2-CH(SiMe_2Ph-)]_n$ (C_6D_6) δ: 7.25−7.50 (m, 5H, aromatic protons), 1.35−1.40 (m, 2H, $-CH_2-$), 0.45−0.50 (m, 1H, $-CH-$), 0.29−0.30 (m, 6H, $Si(CH_3)_2$).

Results of the polymerization of vinylsilanes are summarized in Table 1.

Synthesis of Poly(vinyldimethylsilane) $[-CH_2-CH(SiMe_2H)-]_n$. Polymers of various DP (see Table 2) were made by chlorination of poly(vinyldimethylphenylsilane) or poly(vinyltrimethylsilane), followed in both cases by reduction with $LiAlH_4$. Thus, a solution of poly(vinyldimethylphenylsilane) (DP_n = 1000) (15.75 g) in benzene (150 mL) was added dropwise to a suspension of $AlCl_3$ (7.30 g) in 200 mL of benzene at 8 °C (ice bath) during 15 min. Then HCl (gas) was bubbled through the reaction mixture for 1 h at 8 °C and an additional 2 h at room temperature. After that time the ^1H NMR analysis of an evaporated small sample of polymer revealed the disappearance of resonances in the aromatic region and formation of $[-CH_2-CH(SiMe_2Cl)-]_n$ {^1H NMR (C_6D_6) δ: 1.90−2.20 (m, 1H, $-CH-$), 1.20−1.30 (m, 2H, $-CH_2-$), 0.45−0.65 (s, 6H, $Si(CH_3)_2Cl$)}. At this stage POCl (17 mL) was added to the reaction mixture in order to separate the excess of $AlCl_3$, the polymer solution was filtered off, and benzene was removed under vacuum. The solid poly(vinyldimethylchlorosilane) was dissolved in Et_2O (60 mL) and was then added dropwise to the stirred suspension of $LiAlH_4$ (7.2 g) in Et_2O (100 mL), at room temperature for 30 min. The reaction mixture was refluxed under argon for a further 10 h and filtered, and Et_2O was removed from the solution under vacuum. Solid residue was extracted with pentane (100 mL). The polymer solution was filtered, and the solvent was evaporated. The resulting poly(vinyldimethylsilane) $[-CH_2-CH(SiMe_2H)-]_n$ was dried under vacuum for 8 h. 6.5 g (78%) of white powder was obtained (DP_n = 250).

^1H NMR ($CDCl_3$) δ: 3.81 (broad s, 1H, $Si(CH_3)_2H$), 1.15−1.75 (m, 2H, $-CH_2-$), 0.51−1.11 (m, 1H, $-CH-$), −0.07 (m, 6H, $Si(CH_3)_2$ H). ^{13}C NMR (C_6D_6) δ: 31.9 ($-CH_2-CH-$), 29.7 ($-CH_2-CH-$), 2.1 ($Si(CH_3)_2H$). ^{29}Si NMR (C_6D_6) δ: 22.0 ($Si(CH_3)_2H$).

The alternative route, starting from poly(vinyltrimethylsilane), was carried out as follows: $[-CH_2CH(SiMe_3)-]_n$ (DP_n = 430) (6.58 g) was refluxed under argon with $AlCl_3$ (0.5 g) in 50 mL of Me_3SiCl, while the volatile product, tetramethylsilane, was collected in a cold trap. After 24 h the chlorination was completed as judged by the ^1H NMR spectrum (see above). The reaction mixture was filtered under argon, and the excess Me_3SiCl was removed under vacuum. Poly(vinyldimethylchlorosilane) was then dissolved in 30 mL of Et_2O and reduced as described earlier using 3.6 g of $LiAlH_4$ in Et_2O (50 mL) to give 3.75 g (80%) of poly(vinyldimethylsilane) (DP_n = 230).

Exemplary ^1H NMR spectra of polyvinylsilanes before and after modification (poly(vinyltrimethylsilane) and poly(vinyldimethylsilane), respectively) are shown in Figure 1.

Synthesis of Side Chain Liquid Crystal Polyethylenes. The side chain polymers were made via hydrosilylation of mesogenic 4′-methoxyphenyl-4-(ω-alkenyloxy)benzoates ($CH_2{=}CH-(CH_2)_{m-2}OC_6H_4C(O)OC_6H_4OCH_3$, *m* = 4, 5, 8, 11) with poly(vinyldimethylsilane) having polymerization degree of 75 and 230. In a typical hydrosilylation reaction 4′-methoxyphenyl-4-(5-pentenyloxy)benzoate (1.3 g, 4.16 mmol) and 0.322 g (3.74 mmol of $-[CH_2-CH(SiMe_2H)]-$ monomeric units) of poly(vinyldimethylsilane) (DP = 75) were dissolved under nitrogen in dry (sodium mirror) toluene (10 mL) in a Schlenk tube. After addition of a catalyst—10 μL of 3% platinum vinylmethylcyclosiloxane complex solution in vinylmethylcyclosiloxanes (1.6×10^{-4} mol of Pt mol^{-1} of the Si−H)—the reaction was carried out for 24 h, with magnetic stirring, at room temperature. The temperature was then raised, and the process was continued for 82 h at 60−65 °C (the progress of hydrosilylation was followed by IR). The solvent was then evaporated, and the polymer was purified by several dissolutions (methylene chloride) and precipitations (methanol) until it was free from the excess mesogen (TLC). 0.89 g (60%) of side chain polyethylene was obtained.

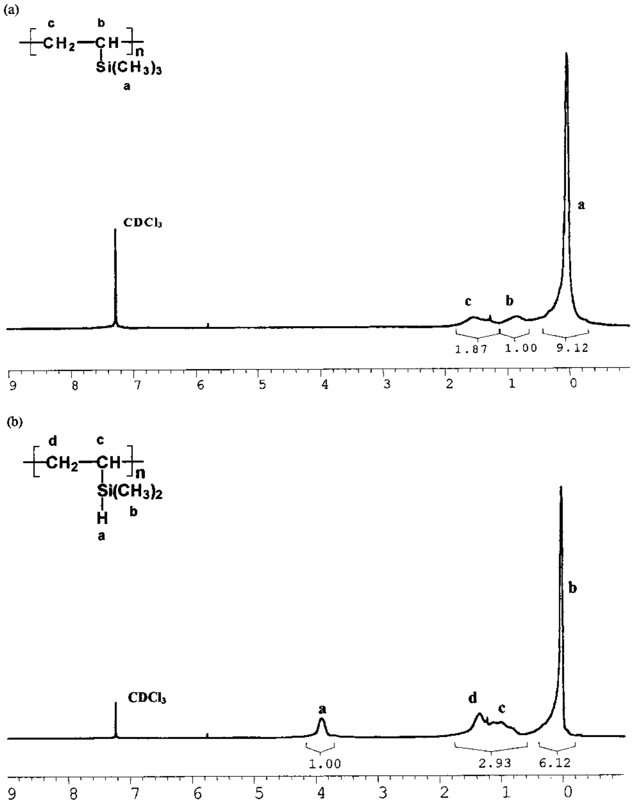
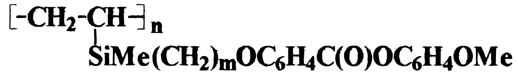


Figure 1. ^1H NMR spectra of (a) poly(vinyltrimethylsilane) and (b) poly(vinyldimethylsilane). Solvent = $CDCl_3$.

^1H NMR (C_6D_6) δ: 6.75−8.30 (m, 8H, aromatic protons), 3.60−3.72 (m, 2H, CH_2O), 3.28 (s, 3H, OCH_3), 1.40−1.85 (m, 6H, CH_2 other than terminal), 0.80−0.95 (m, 3H, CH + $Si-CH_2$), 0.35−0.50 (m, 6H, $Si(CH_3)_2$). ^{13}C NMR (C_6D_6): 115.4−133.2 (aromatic carbon atoms), 76.3 (CH_2O), 68.9 (CH_2CH_2O), 55.7 (OCH_3), 47.2 (CH_2CH), 30.1 ($CH_2CH_2CH_2O$), 25.3 ($Si-CH_2CH_2$), 21.1 ($SiCH_2$), 15.4 (CH_2CH), 2.1 ($Si(CH_3)_2$). ^{29}Si NMR (C_6D_6): −2.0.

Preparation details and thermal phase behavior of liquid crystal polyethylenes, having various polymerization degree and oligomethylene spacers of different length, made according

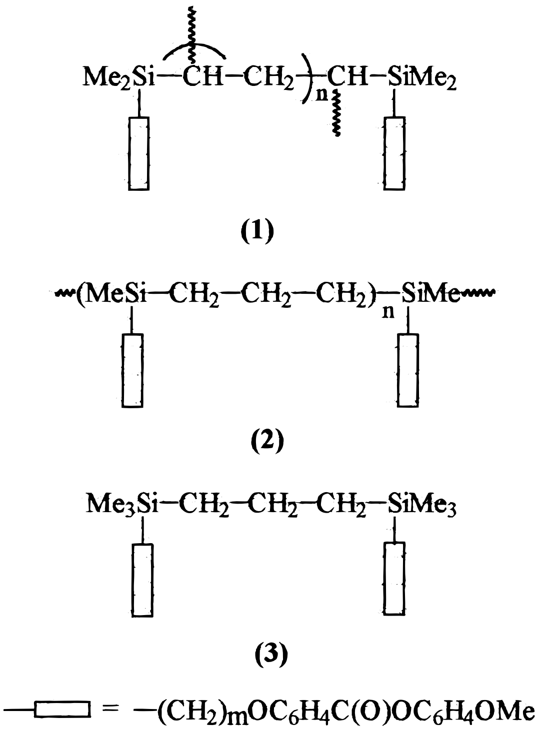
Table 3. Synthesis and Characterization of Side Chain Polyethylenes



$$[-CH_2-\underset{\displaystyle SiMe(CH_2)_mOC_6H_4C(O)OC_6H_4OMe}{\underset{|}{CH}}-]_n$$

m	DP$_n$	hydrosilylation time (h)	catalyst [Pt] (mol/L)	yield	thermal transitions (°C) T_m	T_i
4	75	144	1.0×10^{-4}	58	75	
5	75	106	1.6×10^{-4}	60	65	110
8	75	168	1.6×10^{-4}	41	27	115
11	75	144	6.3×10^{-4}	22	89	
4	230	144	1.0×10^{-4}	58	78	
5	230	120	2.6×10^{-4}	51	63	112
8	230	192	4.7×10^{-4}	41	35	118
11	230	120	5.9×10^{-4}	19	91	

Scheme 1



to this procedure, are shown in Table 3.

Characterization. IR spectra were obtained with an ATI Mattson spectrometer for polymer solutions in sodium dried toluene.

Chemical structures of side chain liquid crystal polyethylenes and of all the chemical intermediates were confirmed by nuclear magnetic resonance using Bruker AC 200 and MSL 300 spectrometers.

Molecular weight and heterogeneity indices were measured by gel-permeation chromatography (GPC) using a Waters system with Wyatt/Optilab 902 interferometric refractometer, calibrated for monodisperse polystyrene standards. The values of M_n were additionally confirmed using a Knauer vapor pressure osmometer.

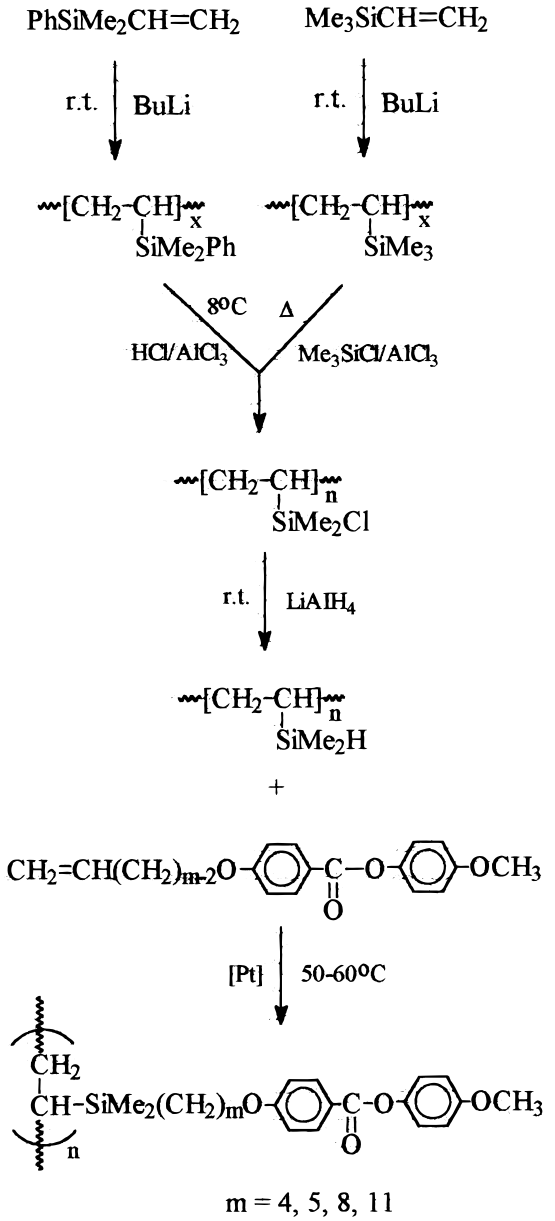
Thermal phase behavior was studied with differential scanning calorimetry (DSC) using a DuPont DSC-910, calibrated with an indium standard. Transitions were verified by optical microscopy. X-ray diffraction measurements were performed in transmission mode using Guinier camera with Co Kα monochromatic radiation. Diffraction patterns of magnetically oriented samples were obtained in a flat camera with Cu Kα radiation. Aligned samples were produced on slow cooling from isotropic melt into mesophase, in a magnetic field of 1 T.

Results and Discussion

Synthesis. Scheme 1 shows the structure of a desired side chain polyethylene (**1**), compared to relevant polycarbosilane (**2**) and their low molecular weight model[3] with the $(CH_2)_3$ spacer (**3**). The polymer (**1**) was designed in order to provide mesomorphic properties similar to traditional polycarbosilanes as they both comprise the same number of carbon and silicon atoms but differ in the structure of the monomeric unit. The methoxyphenylbenzoate type mesogen was chosen to enable direct comparison with other polymers, described earlier,[2] and was attached to substituted polyethylene using a standard hydrosilylation method. The main purpose, though, was to synthesize a polymer equivalent to polycarbosilane by an economic route. On the basis of our studies concerning dimeric liquid crystalline models of polymers (e.g., **3**),[8] we could predict that polymer (**1**) should have similar mesomorphic properties to the equivalent polycarbosilane (**2**). Our attention to a simple route, leading to functionalized, silylated polyethylenes, was attracted by the work of Gladkova et al. on multifunctional carbon-chain polymers.[9] In the present study we used both the originally described substrate − vinyldimethylphenylsilane as well as more readily available vinyltrimethylsilane in anionic polymerization, in the presence of BuLi. The reaction pathways leading to the synthesis of novel side chain liquid crystal polymers are illustrated in Scheme 2. The first, alternative step involves polymerization of vinylsilanes, and as shown in Table 1, independent of the initiator (*n*-BuLi, *sec*-BuLi), the yield and molecular weight of the resulting polymer are usually higher when trimethylvinylsilane is used as a substrate. Next, the two polymers are functionalized to give poly(vinyldimethylsilane) via an intermediate chlorinated polymer. Table 2 reveals that the polymerization degree decreases on functionalization. This effect is more pronounced for poly(vinyldimethylphenylsilane) when the DP of the final product is 4 times lower than it is in the case of poly(vinyltrimethylsilane) (a factor of ∼2). There seems to be no reason why such differences could occur during final reduction with $LiAlH_4$ of the common intermediate, poly(vinyldimethylchlorosilane). On the other hand, it was described in the literature that an isomerization mechanism occurs on polymerization of vinylsilanes with BuLi−tetramethylethylenediamine, leading to branched structures of polycarbosilane type, i.e., with silicon−carbon bonds in the main chain.[10,11] The same authors claim that some of the rearrangement takes place even in the absence of TMEDA. In our case the NMR spectra do not reveal any additional resonances, characteristic for partly rearranged poly(vinylsilane)s. However, it cannot be excluded that few rearranged moieties are present along the chain, well below the spectroscopic accuracy. Silicon−carbon bonds in polycarbosilanes are known to undergo occasional cleavage on chlorination,[2,12] and we believe that it is the chlorination step that is responsible for the decrease of the molecular weight of polyethylenes on their functionalization. The different extent to which the molecular weight is reduced is also well explained by the fact of using two different polymer substrates (poly(vinyldimethylphenylsilane) and poly(vinyltrimethylsilane)) as well as two chlorinating agents ($HCl/AlCl_3$ and $Me_3SiCl/AlCl_3$).

Apart from the desired cleavage of methyl or phenyl groups from silicon and, as described above, also of the

Scheme 2. Synthetic Pathways



individual Si−C bonds in rearranged moieties of the main chain, one has to be sure that the parallel splitting of the silyl groups pendant from the polyethylene chain does not occur. It is well proved, though, by 1:1 integration at 4.25−4.45 and 1.65−1.85 ppm, corresponding to Si−H and −CH− protons in the ^{1}H NMR spectra of poly(vinyldimethylsilane) $[-CH_2CH(SiMe_2H)-]_n$, showing that silyl groups remain intact.

Evaluating the two alternative steps of the synthetic route, it appears that the one involving trimethylvinylsilane as a substrate is more attractive due to lower cost of the monomer, simpler functionalization, and smaller decrease of molecular weight during the latter process.

Characterization of Liquid Crystal Polyethylenes. Properties of this novel group of side chain liquid crystal organosilicon polymers vary, as expected, with the length of a flexible spacer. They tend to crystallize (Table 3) in the case of too short $(CH_2)_4$ or too long $(CH_2)_{11}$ alkane chains, linking the main backbone with mesogenic core, whereas liquid crystal properties are generated for systems involving $(CH_2)_5$ and $(CH_2)_8$. It is interesting that in structurally similar polysilaethylene $\{[-CH_2Si(Me)(R)-)$, R = side mesogenic chain with methoxybenzoate core$\}$,[3] $(CH_2)_4$, and $(CH_2)_{11}$, links do not inhibit liquid crystal properties. However, in the case of polyethylene, silicon atoms are separated by three (not one, as for silaethylene) carbon atoms. Moreover, purely carbon main chain tends to be more rigid.[1] The effect of molecular weight (DP = 75 and 230) does not seem to introduce significant changes into thermal transitions, but it is generally known[12] that the value of DP ∼ 100 is regarded as a limit, above which further increase of the main chain length does not affect liquid crystal properties. From this point of view it is important to stress that, aiming for a proper molecular weight of liquid crystal polyethylenes, one must keep in mind the degradation process that occurs during functionalization of linear polymer precursors (see above). The direct comparison of properties between the silylated polyethylenes (**1**) and polycarbosilanes that possess the main chain organosilicon sequence built up from silabutane monomeric units (**2**) seems to be justified, looking at the common model dimer (**3**) (Scheme 1). The mesomorphic properties are summarized in Table 4. Side chain polyethylenes (**1**) follow the general picture of liquid crystal polymers, enhancing mesomorphic properties (degree of ordering, temperature span of mesophase) compared to low molecular weight systems, represented here by dimer (**3**). For the linking alkane of the same length, the nematic phase exhibited in part by the dimer gives way to the higher ordered smectic one, and the temperature range of the generation of mesophase increases over 8 times. The range is also much wider (∼80 °C) when compared to the relevant polycarbosilane (34 °C) with flexible spacer comprising $-(CH_2)_8-$. The advantage of silylated polyethylenes over their polycarbosilane analogues is even more visible once the shorter, $(CH_2)_5$, alkane chain is used. In such the case the polycarbosilane shows only phase transition from crystal to isotropic liquid, while polyethylenes remain smectic over the range 40−50 °C.

Table 4. Comparison of Liquid Crystal Polyethylenes and Polycarbosilanes Having Common Side Mezogen $[-(CH_2)_mOC_6H_4C(O)OC_6H_4OMe]$, $m = 5, 8$

type of liq crystal (Scheme 1)	m	DP$_n$	type of phase; temp (°C)	ΔT (°C)	d (nm)	d/l
(1)	5	75	C 6.5SmA$_1$110I	45	2.63	1.10
(1)	5	230	C 63SmA$_1$112I	49	2.62	1.10
(2)[a]	5	460	C 61I			
(1)	8	75	C 27SmA$_1$115I	88	3.02	1.09
(1)	8	230	C 35SmA$_1$118I	83	3.01	1.09
(2)[a]	8	460	C 49SmA$_1$83I	34	3.12	1.15
(3)[b]	8	*d*	C 62SmA$_1$68N72I	10	3.36	0.60[c]

[a] From ref 2. [b] From ref 3. [c] Each mesogenic moiety of the dimer belongs to a separate monolayer. [d] Dimer.

For both types of polymers, presented here, the values of the interlayer spacing d and the length l of side chain in the most extended conformation are comparable. It is characteristic of a disordered orthogonal smectic mesophase SmA$_1$ with polymer backbones mostly confined into sublayers between two layers of mesogenic cores.[13] The model dimer also forms the monolayer type SmA$_1$ mesophase, but as each mesogenic core belongs to a separate layer it leads to $d \sim l/2$. One can notice that for polycarbosilane the value of d/l is slightly higher (1.15) than the values found for silylated polyethylenes (1.09 and 1.10), which can be attributed to the presence of a more rigid, purely carbon backbone in the latter polymers. On the other hand, the presence of a silicon atom in each side pendant introduces more flexibility, leading to a broader temperature range of mesophase compared to the case of polysilabutane. It is worth remembering that polycarbosilanes, having silicon atoms in the main chain, exhibit an intermediate flexibility between that of liquid crystal polyacrylates and polysiloxanes.[1] A similar effect is observed here for polyethylenes, once rigidity of a carbon backbone is compensated by higher flexibility in the side chains.

Conclusions

Side chain liquid crystalline polyethylenes with mesogenic moieties attached to the main chain via silicon atom have been synthesized for the first time. The complete synthetic procedure and characterization of the novel polymers having alkane spacers consisting of 4, 5, 8, and 11 methylene groups are presented. Out of two alternative routes starting from dimethylphenylvinylsilane or trimethylvinylsilane, the one using Me_3SiVi as a monomer proves to be more effective. Their properties are compared to that of polycarbosilane (polysilabutane), which can be regarded, judging from the common low molecular weight model dimer, as analogous polymer systems. A mesomorphic phase was observed in a broad temperature range (~85 °C) compared to that (34 °C) for polysilabutane. Both polymer systems with methoxybenzoate type mesogenic core form the same smectic (SmA_l) phases. The interplay between a rigid carbon skeleton and increased flexibility of a pendant, due to the presence of silicon atom in the side group, led to liquid crystal polymers having a composition similar to that of polycarbosilanes. Thus, while all the positive features of polycarbosilanes should be preserved,[1] such as an attractive temperature range of mesophase and high thermal and hydrolytic stability, this novel group of polymers has an advantage of being synthetically more economic. Judging from the present catalog prices of the respective monomers—trimethylvinylsilane and methylsilacyclobutane—as well as from the fact of comparable total yields of chemical transformations, the cost of synthesis of linear polyethylenes with pendant dimethylsilyl groups is ~20 times lower than that of its structural analogue, polycarbosilane.

Acknowledgment. Support from the State Committee for Scientific Research (KBN) through a grant and a fellowship (N.K.G.) from the J. Mianowski Foundation is gratefully acknowledged.

References and Notes

(1) Ganicz, T.; Stańczyk, W. A. *Trends Polym. Sci.* **1997**, *5*, 305−310.
(2) Ganicz, T.; Stańczyk, W. A.; Białecka-Florjańczyk, E.; Śledzińska, *I. Polymer* **1996**, *37*, 4167−4174.
(3) Ganicz, T.; Stańczyk, W. A.; Białecka-Florjarńczyk, E.; Śledzińska, I. *Polymer* **1999**, *40*, 4733−4739.
(4) Interrante, L. V.; Liu, Q.; Rushkin, I.; Shen, Q. *J. Organomet. Chem.* **1996**, *521*, 1−10.
(5) Chojnowski, J.; Stańczyk, W. *Adv. Organomet. Chem.* **1990**, *30*, 243−307.
(6) Jones, P. R.; Lim, T. F. O.; McBee, M. L.; Pierce, R. A. *J. Organomet. Chem.* **1978**, *159*, 99−110.
(7) Mausac, M.; Hardouin, F.; Richard, H.; Archard, M. F.; Sigaud, G.; Gasparoux, H. *Eur. Polym. J.* **1986**, *22*, 13 7−142.
(8) Śledzińska, I.; Ganicz, T.; Stańczyk, W. A.; Białcka-Florjańczyk, E. In *Liquid Crystals: Chemistry and Structure*; Tykarska, M., Dąbrowski, J., Zieliński, J., Eds.; *Proceedings of SPIE*, Washington, 1998; Vol. 3319, pp 220−223.
(9) Gladkova, N. K.; Khodjaeva, V. L.; Guselnikov, L. E. *J. Inorg. Organomet. Polym.* **1995**, *5*, 123−133.
(10) Oku, J.; Hasegawa, T.; Kawakita, T.; Kondo, Y.; Takaki, M. *Macromolecules* **1991**, *24*, 1253−1256.
(11) Oku, J.; Hasegawa, T.; Nakamura, K.; Takeuchi, M.; Takaki, M.; Asami, R. *Polym. J.* **1991**, *23*, 195−199.
(12) *Side Chain Liquid Crystal Polymers*; McArdle, C. B., Ed.; Blackie: Glasgow, 1989.
(13) Davidson, P.; Levelut, A. M. *Liq. Cryst.* **1992**, *11*, 469−517.

MA990558V