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Communications to the Editor

New Chiral Smectic Polysiloxanes from Mesogenic Olefin or Vinyl Ether Monomers

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Ferroelectric, chiral smectic C* (S_{C^*}) polymers have very recently attracted growing interest for electrooptical applications.[1-9] In fact, they exhibit optimal values of spontaneous polarization[4] and response time[9] comparable to those of small-molecule liquid crystals.[10] In addition, they already show that they can successfully compete even with monomeric ferroelectric liquid crystals for high information screens. Moreover, the novel electroclinic effect has lately been described[8,9,11,12] for the smectic A (S_A) phase of a few chiral liquid crystal polymers. In such chiral orthogonal smectic phases an induced molecular tilt can be originated, with a resultant induced polarization, when an electric field is applied along the smectic layers.[13] Specific features of this electroclinic effect are the linear electrooptical response and the extremely fast switching time.

Most side-chain liquid crystal polymers are comprised of a highly flexible polysiloxane backbone and mesogenic side-chain substituents of various structures.[14] Long aliphatic spacer segments are typically used for connecting the mesogenic side chains to facilitate substantial decoupling of the main chain and side chains. These polymers are currently prepared by a polymer-analog reaction of hydrosilylation of mesogen-containing α-olefins with poly(hydrogenmethylsiloxane)s as catalyzed by platinum complexes.[14]

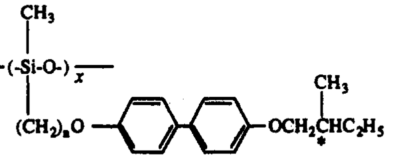
The main objective of this work was the synthesis of chiral liquid crystal polysiloxanes exhibiting a variety of chiral smectic mesophases that could then be used for studies of their ferroelectric and electroclinic properties. As one further objective, the feasibility of a new synthetic procedure for the preparation of liquid crystal polysiloxanes using mesogenic vinyl ethers in addition to the conventional use of α-olefins was also successfully explored. Three different chiral polymer structures **1**–**3** were synthesized, and their liquid crystal properties were studied with particular reference to the incidence of chiral smectic mesophases.

Vinyl monomers **5a**–**d**, **6**, and **7** which were the precursors of polymers **1a**–**d**, **2**, and **3**, respectively, were synthesized according to a general scheme,[15] and all the experimental details will be given elsewhere. They exhibit liquid crystal behavior which is greatly dependent on the total number of skeletal atoms (y = 4, 5, 8, or 11) in the alkenyl substituent in the 4-position of the 4,4′-biphenylyldioxy group (Table I). It is important, however, to recognize the intrinsic smectogenic character of the molecular structure chosen. This tendency is evidently greatly reinforced in going to their polymeric analogs.

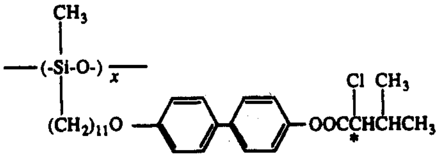
Table I
Liquid Crystalline[a] Characteristics of Mesogenic α-Olefin (5a–d and 6) and Vinyl Ether (7) Monomers

monomer	y^b	$[\Phi]^{25}{}_D{}^c$ (deg)	phase transitions (in K)[d] (with transition enthalpy (in kJ mol^{-1}))
5a	4	+25.4	k 373 (21) I
5b	5	+23.0	k 380 (23) I
5c	8	+22.0	k 352 (17) I
5d	11	+21.2	k [345 (6) S_G*] 346 (26) S_C* 347 (3) S_A 349 (8) I
6	11	+5.5	k 341 (36) S_A 343 (3) I
7	11	+24.6	k [344 (3) S_E] 345 (39) S_A 348 (8) I

[a] By DSC. [b] Total number of skeletal atoms in the alkenyl substituent. [c] Molar optical rotation, in chloroform. [d] k, crystalline; S, smectic; I, isotropic. Monotropic transitions are given in square brackets.



1a-d



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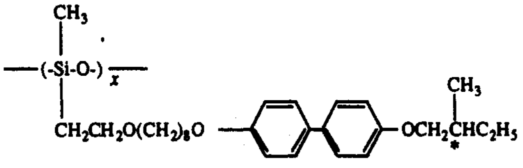

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1	a	b	c	d
n	4	5	8	11

Polymers **1a**–**d**, **2**, and **3** were prepared[14] by grafting the vinyl monomers on the preformed poly(hydrogenmethylsiloxane) (**4**; $DP_n \approx 35$, from Petrarch). The grafting reaction of the vinyl ether **7** was performed in toluene solution at 50 °C with a **4** (repeat unit)/**7** mole ratio of 1/1.1 in the presence of the platinum divinyltetramethyldisiloxane (DVTMS) catalyst (**7**/DVTMS ≈ 1000 mole ratio; Scheme I). During the reaction, FT-IR monitoring of the progressive disappearance of the Si–H stretching absorption at 2168 cm^{-1} and the vinyl stretching absorption at 1642 cm^{-1} (α-olefin) or at 1610 cm^{-1} (vinyl ether) was carried out to ensure quantitative grafting of the terminal alkene monomer to produce the liquid crystal side-chain polysiloxanes. In this way, the reaction appeared to be completed after 4 h, but it was maintained for an additional 10 h. Under these conditions, no side reactions took place

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Scheme I
Grafting of Vinyl Ether 7 onto Poly(hydrogenmethylsiloxane) (4)

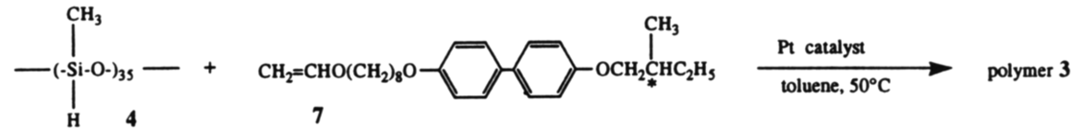


Table II
Physicochemical and Liquid Crystalline Characteristics of Polysiloxanes 1–3

polymer	y^a	$[\Phi]^{25}{}_D{}^b$ (deg)	$M_n \times 10^{-3\,c}$	MWD^c	T_g (K)	T_x (K)	ΔH_x (kJ mol^{-1})	$T_{S_{C^*}-S_A}$ (K)	$\Delta H_{S_{C^*}-S_A}$ (kJ mol^{-1})	T_{S_A-I} (K)	ΔH_{S_A-I} (kJ mol^{-1})
1a	4	+26.3	9.2	2.2	314	386	2.4			405	5.0
1b	5	+20.3	9.2	2.3	321	404	3.9	412	1.3	429	7.4
1c^d	8	+23.8	12.0	2.1	319	399	3.4	414	0.9	428	6.0
1d^d	11	+25.3	12.6	2.0	319	370	1.3	397	0.7	429	7.5
2	11	+1.0	14.7	2.1	311	359	2.5	373	nd	439	5.7
3^d	11	+13.2	12.4	1.7	318	373	0.8	398	0.8	418	7.5

[a] Total number of skeletal atoms in the spacer. [b] Molar optical rotation, in chloroform. [c] By SEC, in tetrahydrofuran. [d] The noted samples displayed an additional ordered smectic mesophase in the ranges 399–405 (**1c**), 370–387 (**1d**), and 373–389 K (**3**) (see text for details).

nor was appreciable crosslinking observed. The molecular weights and molecular weight dispersities of the polymers were determined by size-exclusion chromatography (SEC) as calibrated against polystyrene standards using both refractive index and ultraviolet absorption detectors. It was not possible to use the universal calibration method, and the measured molecular weights were not corrected for the different responses with the styrene and siloxane repeat units. This may be reflected in somewhat scattered values of the molecular weight and degree of polymerization values ($DP_n \approx 25$–30). Unreacted species were easily removed by fractionation with diethyl ether and methanol. The hydrosilylation reaction is well established in organic chemistry,[16] but vinyl ethers were never used before in polymer synthesis, one exception being the reaction of oligomeric hydrogensiloxanes with vinyl ethers of poly(ethylene glycol) or poly(propylene glycol) for the preparation of nonmesogenic block copolymers.[17] In this work we also used *n*-butyl vinyl ether for quantitative grafting onto the same poly(hydrogenmethylsiloxane) (**4**) for the preparation of the corresponding polysiloxane (**8**) (M_n = 4600, M_w/M_n = 3.8). These examples suggest that this reaction can be of very general utility in organic polymer synthesis, and we are extending it to various different mesogenic substrates for the synthesis of unconventional liquid crystal polymer structures.

The main features of the liquid crystal properties of the polysiloxanes prepared are summarized in Table II. The phase behavior between the glass transition temperature (T_g) and the transition temperature noted as T_x is rather complex and consistent with the presence of ordered smectic or semicrystalline states. It needs to be further investigated as to ascertain the nature of the intermediary phases between T_g and T_x. The S_A and S_{C^*} phases were easily identified by the appearance of unambiguous focal-conic textures with fans and broken fans, respectively, and by their X-ray diagrams (Figure 1). On cooling the S_{C^*} phase, an additional smectic phase occurs in polymers **1c** at 405 K, **1d** at 387 K, and **3** at 389 K (Table II) which exists down to T_x. Its paramorphotic patterns display more broken and truncated fans, suggesting the formation of an ordered tilted mesophase with a better correlation of the smectic layers along their normal. It resembles very much the textures of the smectic I (S_I).[18] The formation of tilted mesophases is also demonstrated by the X-ray diffraction diagrams of oriented fibers pulled in the smectic mesophase or in the isotropic liquid of the samples (tilt angle $\theta \approx 15°$ at room temperature) (Figure 2). The phase sequence S_A–S_C–S_I occurring with decreasing temperature is rather rare in polymers but is more common in small-molecule liquid crystals[18] and is found, on cooling from the isotropic liquid, in, e.g., the standard material terephthalylidenebis(4-*n*-decylaniline).[19] The transition enthalpies (in kJ mol^{-1}) from the S_{C^*} phase to this new phase are 3.0 for **1c**, 2.5 for **1d**, and 2.8 for **3**, suggesting the occurrence of a weakly first-order transition. In contrast, the S_{C^*}–S_A transition ($\Delta H_{S_{C^*}-S_A}$ = 0.7–1.3 kJ mol^{-1}) appears to be second order in character, whereas the isotropization transition (ΔH_{S_A-I} = 5.0–7.5 kJ mol^{-1}; ΔS_{S_A-I} = 12.0–18.0 J mol^{-1} K^{-1}) is strongly first order. Note that on increasing the length of the flexible spacer segment the stability of the mesophase is enhanced and the number of the identified smectic phases above T_x increases. Thus, polymer **1a** (n = 4) shows an S_A phase, whereas **1b** (n = 5) presents S_A and S_{C^*} phases, and **1c** (n = 8) and **1d** (n = 11) present three mesophases. Finally, we compare polymers **1d** and **3** incorporating spacer segments of different chemical nature but the same number of skeletal atoms (y = 11). The two polymers exhibit essentially identical liquid crystal behavior (Table II), one minor difference being detected in their isotropization temperature (T_{S_A-I} = 429 K for **1d** and 418 K for **3**) but not in their isotropization enthalpy (ΔH_{S_A-I} = 7.5 kJ mol^{-1} for both). Apparently, the replacement of a methylene group

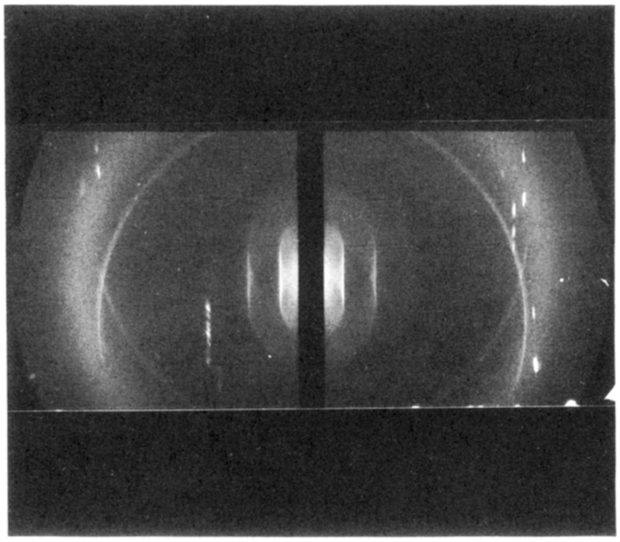


Figure 1. X-ray diffraction diagram of the S_A mesophase of polymer **1d** at 417 K (interlayer distance d = 33.4 Å; intermolecular distance $D \approx 4.4$ Å; length of the side chain in the fully extended conformation $L \approx 33$ Å).

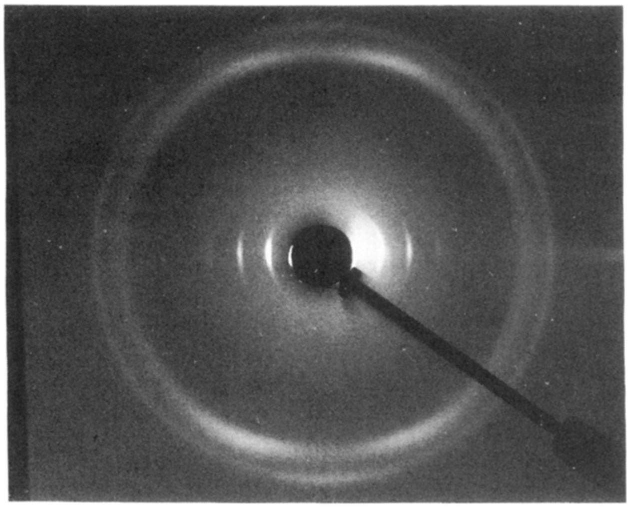
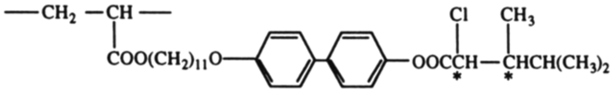


Figure 2. X-ray diffraction pattern (fiber vertical axis) at room temperature of a fiber of polymer **1d** pulled from the isotropic liquid at 430 K (interlayer distance d = 32.3 Å; intermolecular distances a = 4.5 Å and b = 4.0 Å; tilt angle $\theta \approx 15°$).

γ to the polysiloxane backbone with an oxygen atom does not alter the molecular framework of the comparable side chains, thus permitting the formation of equally stable smectic phases.

In previous work[12] we have studied the electroclinic effect in the S_A phase of a closely structurally related polyacrylate (**9**). In particular, it was found that the response time was as short as 17 μs (applied voltage U_{pp} = 130 V; f = 100 Hz) at the S_A–I transition at 117 °C, with however an induced tilt angle of only some tenths of a degree. Therefore, we anticipate observing an improved electroclinic response in polymers **1–3** which possess a greatly enlarged S_A temperature range. In addition, the presence of the underlying S_{C^*} phase should make it possible to study the purely ferroelectric mode in this phase. Investigations are under way and will be reported in due course.[20]



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In conclusion, we have synthesized new chiral polymer structures that intrinsically possess a strong smectic tendency, with the smectic A and smectic C* phases encompassing a very broad range of temperatures. They may be suitable model systems for investigations of the electroclinic and ferroelectric effects in chiral liquid crystal polymers. It has also been shown that the synthesis of polysiloxanes from vinyl ether monomers can be a new, complementary procedure for the preparation of liquid crystal polymers, especially when reacting more easily accessible mesogenic vinyl ethers than corresponding α-olefins.

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