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Comb-shaped liquid crystalline stereoregular cyclolinear methylsiloxane copolymer containing lactic acid derivative as chiral mesogenic side group

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Comb-shaped liquid crystalline (LC) stereoregular cyclolinear methylsiloxane copolymers with mesogenic chiral lactic side group were synthesized. X-ray study showed that tacticity of the main cyclolinear methylsiloxane chain influences intra- and intermolecular ordering in LC state.

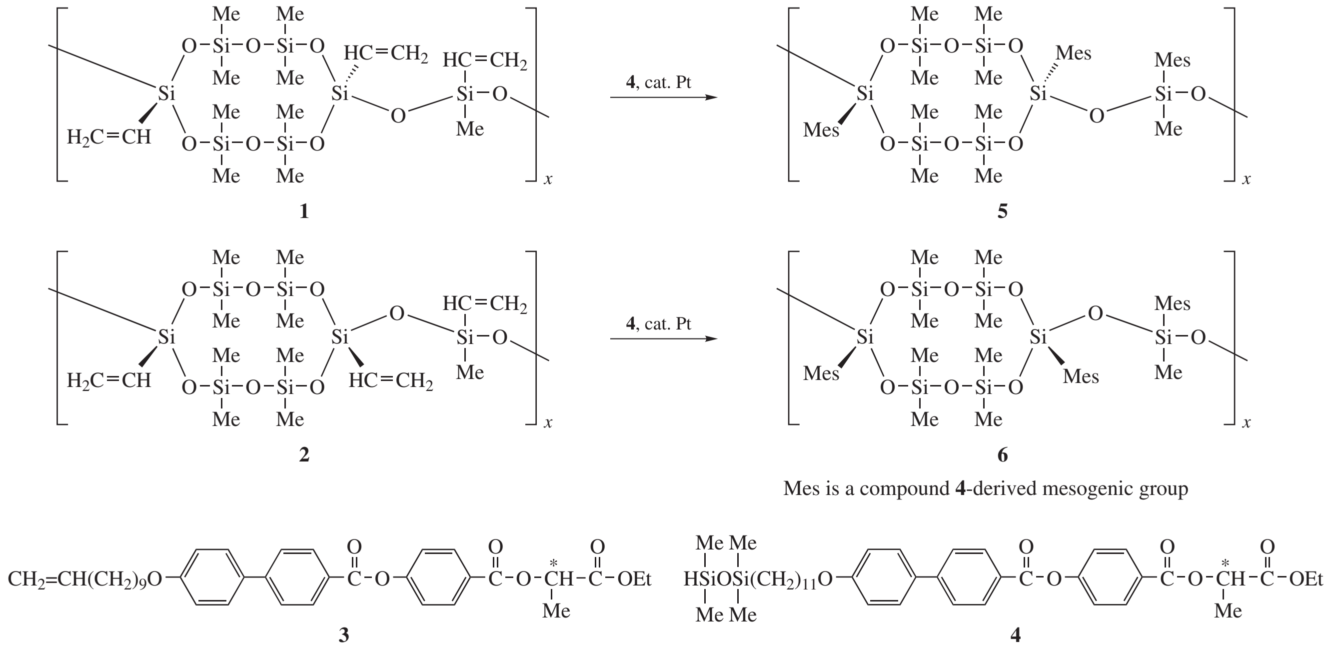
Hitherto, there are only few articles concerning the influence of the structure of stereo isomers of organocyclosiloxanes containing mesogenic groups on the property and ordering in liquid crystalline (LC) state suggesting existence of a few order types: cylinder,[1–3] disc-like and bundle model.[4] The formation of different textures in LC state[5] was found due to the comparison of properties of *trans*-, *cis*-isomers of LC cyclohexasiloxane with two mesogenic groups. *cis*-Isomeres of cyclotetra- and cyclohexasiloxanes with mesogenic cyanobiphenyl groups also demonstrate various types of ordering in LC state.[6] Earlier, the results of investigation of four stereo isomers of LC tetraphenylcyclotetrasiloxanes with cyanobiphenyl groups by SAXS and optical polarizing microscopy (POM) were reported. It was demonstrated that a decisive factor in the molecule possibility to crystallize and form different types of LC-phases[7] is the orientation of mesogenic groups. Recently, synthesis of comb-shaped LC stereo regular cyclolinear methylsiloxane copolymers containing cyanobiphenyl side groups was reported. Using SAXS it was found that the values of interlayer distances of syndio- and isotactic LC copolymer differ in ~4.7 Å at 20 °C and that enthalpy of phase transition of isotactic LC copolymer is higher than that of syndiotactic ones.[8]

The aim of this work was the preparation of comb-shaped LC stereoregular cyclolinear (CLLC) polymethylsiloxanes with side mesogenic chiral groups and terminal lactic ones as well as the study of the influence of tacticity of mesogenic chain on the formation of ferroelectric SmC* phase and type of ordering in LC state.

Stereoregular cyclolinear (CL) methylsiloxanes copolymers **1** and **2** with three vinyl groups were prepared by the published methods.[8,†] The vinyl-terminated mesomorphic precursors **3** and mesogen-containing fragments with a SiH terminal group **4** were synthesized as described.[9,†]

Data on the temperatures of the phase transitions of the compounds **3** and **4** are summarized in Table 1.

Comb-shaped stereoregular CLLC methylsiloxanes copolymers **5** and **6** with mesogenic chiral side groups were obtained by hydrosilylation reaction of copolymers **1** and **2**, respectively, with mesogen compounds **4** in the presence of the Karstedt catalyst (Scheme 1).[‡]



Scheme 1

Table 1 Characteristics of the vinyl and siloxane terminated monomeric precursors **3** and **4**.

Compound	$T_{\text{SmC-SmA}}$/°C		$T_{\text{SmA-I}}$/°C	
	DSC	Optical microscopy	DSC	Optical microscopy
3^a	112	125	143	150
4^b	120	124	133	136

^{a}The temperature phase transition $T_{\text{SmC*-Cr}_2}$ = 43 °C, $T_{\text{Cr}_2\text{-Cr}_1}$ = 35 °C. ^{b}The temperature glass transition $T_g \approx -10$ °C.

Table 2 Thermal behaviour of copolymers **5** and **6**.

Copolymer	Temperature ramp	T_g/°C	$T_{\text{SmC*-SmA}}$/ °C	$\Delta H_{\text{SmC*-SmA}}$/ J g^{-1}	$T_{\text{SmA-I}}$/ °C	$\Delta H_{\text{SmA-I}}$/ J g^{-1}
5	cooling	–7	150	1.5	177	7.3
	heating	–6	155	1.0	180	6.5
6	cooling	–12	152	0.6	176	7.2
	heating	–11	156	0.6	180	5.5

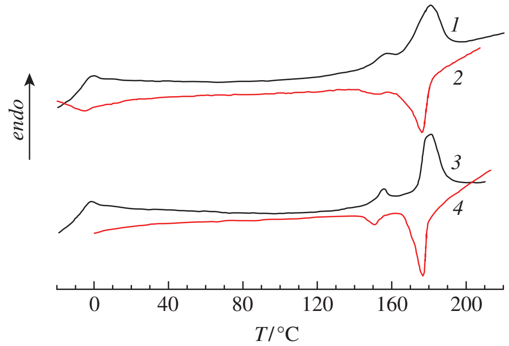


Figure 1 DSC curves corresponding to (*1*,*3*) heating and (*2*,*4*) cooling ramps of copolymers (*1*,*2*) **5** and (*3*,*4*) **6** at a rate of 20 K min^{-1}.

The degree of completion of the hydrosilylation reaction was determined by the disappearance of the signals from the protons of the CH$_2$=CH group in the ^{1}H NMR spectra in the 5.85–6.35 ppm range as well as the signals at 4.50–4.85 ppm for the hydride protons of the HMe$_2$SiO fragment of substance **4**. The molecular structure of all the comb-shaped LC stereoregular CL copolymers extracted was confirmed by ^{1}H and ^{29}Si NMR and IR spectroscopy.

The phase behaviour of comb-shaped stereoregular CLLC copolymers **5** and **6** in the bulk state was studied using DSC, optical polarizing microscopy (OPM) and X-ray analysis.[†]

Heating and cooling scans of samples **5** and **6** reveal two main endothermic effects (Figure 1, Table 2), which correspond to isotropization of the mesophase. The DSCs *1* and *2* exhibit the polymesomorphic transitions. CLLC copolymers **5** and **6** form a mesophase upon heating or cooling, enantiotropic polymesomorphism was absent. The high-temperature transition at 176–180 °C with high enthalpy corresponds to the isotropization. The transition at 155–156 °C recorded on heating with lower enthalpy is assigned to transition smectic SmC*-SmA.

Our OPM study showed that CLLC copolymers **5** and **6** possess enantiotropic thermotropic mesomorphism. These transitions are observed more clearly on slow cooling at 0.1 K min^{-1}. The textures of LC copolymers **5** and **6** formed on cooling from isotropic melt are shown in Figure 2. The growth of initially formed bâtonnets into a confocal texture of smectic A (SmA) phase depends on the cooling rate and the time of exposing in isotropic melt state and does not depend on the tacticity of copolymers. Cooling of the isotropic melt of the samples **5** and **6** leads to the formation of SmA type of the mesophase [Figure 2(*a*) and 2(*c*)]. Formation of the SmA texture and its destruction for copolymer **5** occur at the narrow region 185–172 °C on repeated heating and cooling [Figure 2(*a*),(*b*)]. Destruction of the texture of sample **6** on further cooling begins at 182 °C with complete transformation into SmC* at 175 °C (Figure 2).

X-ray diffraction analysis in small and wide angles revealed that sample **6** possesses smectic structure at room temperature. Four orders of reflection corresponding to interlayer distance of 48.5 Å are observed. Note that the length of compound molecule in totally extended conformation is 39.8 Å. Thus, substantial interdigitation of aliphatic parts of the molecule should take place. Another possibility is chevron structure of the layer in

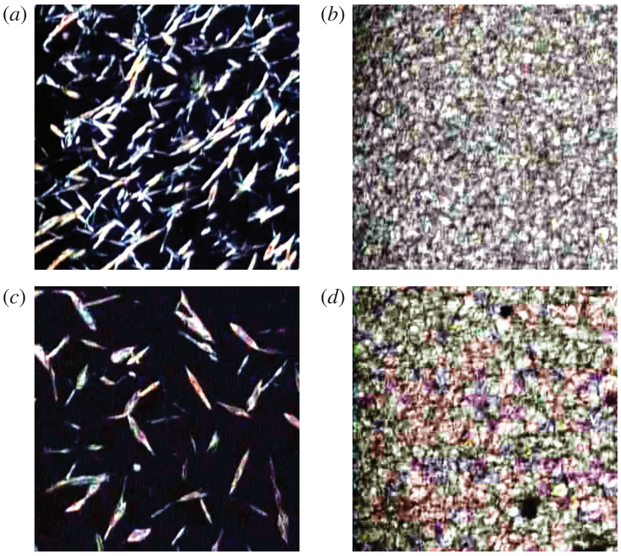


Figure 2 Textures of copolymers (*a*),(*b*) **5** and (*c*),(*d*) **6** in crossed nicoles at (*a*) 198, (*b*) 180, (*c*) 203 and (*d*) 180 °C.

[†] For details, see Online Supplementary Materials.

[‡] *General procedure for the preparation of comb-shaped stereoregular CLLC methylsiloxane copolymers* **5** and **6**. A three-necked flask with two taps for input and output of argon, a condenser and a magnetic stirring bar was filled with argon and evacuated to 1 Torr. This procedure was repeated three times. After that, a solution of copolymer **1** (7 mg, 0.013 mmol) and substance **4** (0.031 mg, 0.043 mmol) in 0.13 ml of anhydrous toluene was placed in the flask under argon flow. After complete dissolution of the substances, 0.20 µl of the Karstedt catalyst was added under argon, and the argon flow was stopped. After 70 h of heating the reaction mixture at 45 °C, no protons for the H–Si and CH$_2$=CHSi groups were detected in the ^{1}H NMR spectrum. The reaction product was dissolved in 0.12 ml of benzene. A white precipitate formed after addition of methanol (0.24 ml), which was reprecipitated twice and evacuated at 60 °C/1 Torr.

Copolymer **5**: yield 32 mg (91%), $\eta_{\text{sp}\,1\%}$ = 0.18 at 20 °C, M_w = 44 000, M_w/M_n = 1.58, T_g = –11 °C, T_i = 180 °C. ^{1}H NMR (C$_6$D$_6$) δ: 0.13 (br. s, 36 H, Me$_2$SiOSiMe$_2$ linear), 0.18 [m, 24 H, (Me$_2$SiO)$_2$ cycle], 0.54 [m, 6 H, (CH$_2$)$_2$SiO$_{1.5}$], 1.39 [m, 48 H, (CH$_2$)$_8$], 1.50 (m, 6 H, CH$_2$), 1.66 (d, 9 H, *Me*CH), 1.88 (m, 6 H, CH$_2$CH$_2$O), 4.08 (m, 6 H, CH$_2$O), 4.33 (t, 6 H, *Me*CH$_2$), 5.34 (q, 3 H, *Me*CH), 7.04 (d, 6 H), 7.42 (d, 6 H), 7.75 (d, 12 H), 8.27 (d, 12 H). ^{29}Si NMR (C$_6$D$_6$) δ: 8.28 and 7.74 [2s, (CH$_2$)$_2$Me$_2$SiO and OMe$_2$Si(CH$_2$)$_{11}$], –22.03 (s, 4 Si, Me$_2$SiO cycle), –66.79 and –67.29 [s, Si, Me(CH$_2$)$_2$SiO and br. s, 2 Si, (CH$_2$)$_2$SiO$_{1,5}$].

Copolymer **6** was prepared similarly to copolymer **5** using copolymer **2** (40 mg, 0.016 mmol) and substance **4** (0.39 mg, 0.054 mmol) in 0.16 ml of toluene, 0.30 µl of the Karstedt catalyst.

Copolymer **6**: yield 37 mg (84%), $\eta_{\text{sp}\,1\%}$ = 0.13 at 20 °C, T_g = –7 °C, T_i = 180 °C. ^{1}H NMR (C$_6$D$_6$) δ: 0.10 (br. s, 36 H Me$_2$SiOSiMe$_2$ linear), 0.12 [m, 24 H, (Me$_2$SiO)$_2$ cycle], 0.52 (m, 12 H, CH$_2$CH$_2$SiO$_{1.5}$), 1.30 [m, 48H, (CH$_2$)$_8$], 1.50 (m, 6 H, CH$_2$), 1.73 (d, 9 H, *Me*CH), 1.80 (m, 6 H, C*H*$_2$CH$_2$O), 2.45 (m, 6 H, CH$_2$O), 4.00 (t, 6 H, OCH$_2$), 4.27 (q, 6 H, MeC*H*$_2$), 5.28 (q, 3H, MeC*H*) 6.92 (d, 6 H), 7.54 (d, 6 H), 7.65 (d, 12 H), 8.18 (d, 12 H). ^{29}Si NMR (C$_6$D$_6$) δ: 8.34 and 7.79 [2s, (CH$_2$)$_2$Me$_2$SiO and OMe$_2$Si(CH$_2$)$_{11}$], –21.95 (s, Me$_2$SiO cycle), –67.55 [br. s, 2 Si, (CH$_2$)$_2$SiO$_{1.5}$ and 1Si, Me(CH$_2$)$_2$SiO].

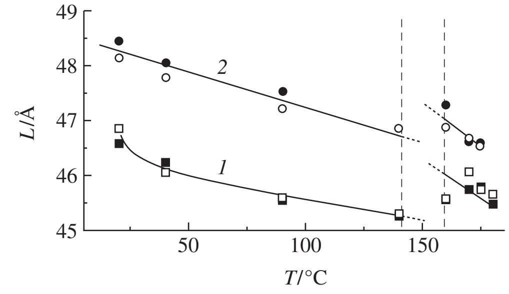


Figure 3 Temperature dependence of smectic interlayer distance for copolymers (*1*) **5** and (*2*) **6**. Region between dashed lines corresponds to SmC* → SmA transition.

which mesogen groups are tilted relatively to layer director. With increasing temperature interlayer distance decreases to 46.9 Å at 140 °C (Figure 3).

Such a change corresponds to negative thermal expansion coefficient $\beta = -2.75\times10^{-4}$ K^{-1} which is rather common for smectic type mesophases. Wide-angle scattering pattern of the compound contains only an amorphous halo of complex shape (Figure 4). Further heating leads to phase transition manifesting itself in the jump of interlayer distance of about 0.5 Å due to additional degree of freedom of mesogen groups in high-temperature SmA phase and corresponding decrease of effective molecular tilt angle. In the temperature range of SmA mesophase the material also possesses negative expansion which is much stronger ($\beta = -8.5\times10^{-4}$ K^{-1}) than that of the SmC* phase.

In contrast to compound **6**, wide-angle X-ray patterns of as-received samples of compound **5** reveal two rather narrow reflections corresponding to *d*-spacings $d_1 = 5.461$ Å and $d_2 = 4.454$ Å. The size of the regions of coherent scattering calculated from the Selyakov–Sherrer equation, is *ca.* 100 Å. Smectic structure manifests itself in three reflections of the first, second and fourth orders corresponding to interlayer distance $L = 46.6$ Å. Specific distribution of electron density along the layer normal results in the negligible intensity of the third order reflection. Temperature behaviour of the material is very close to that of **6**. Interlayer distance decreases with negative temperature expansion coefficient of $\beta = -2.5\times10^{-4}$ K^{-1} (45.2 Å at 140 °C). At temperatures higher than 165 °C SmA mesophase is observed, with L changing from 45.9 Å at 170 °C to 45.6 Å at 180 °C ($\beta = -6.5\times10^{-4}$ K^{-1}). However, at 160 °C interlayer distance observed corresponds neither to SmC* nor to SmA phase. It also has comparatively large half-width. We suppose that at 160 °C coexistence of two smectic phases is observed with corresponding reflections not resolved.

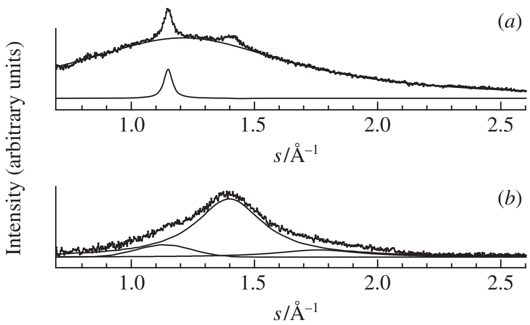


Figure 4 WAXS patterns and their resolution for copolymers (*a*) **5** and (*b*) **6**.

The above mentioned properties of copolymers **5** and **6** characterized by different stereoregularity demonstrate that the change of tacticity of the main CL methylsiloxane chain leads not only to the change of interlayer distances but also to the increase in both intra- and intermolecular ordering for syndiotactic copolymer **6** which is confirmed by the arising of four reflexes in the small angle range and two ones in the region of wide angles.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2013.11.015.

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