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Polymesomorphism in a smectic SmC* phase in a comb-shaped liquid crystalline stereoregular cyclolinear methylsiloxane copolymer with the 4,4′-bisphenylene fragment at terminal lactic acid derivative in mesogenic group

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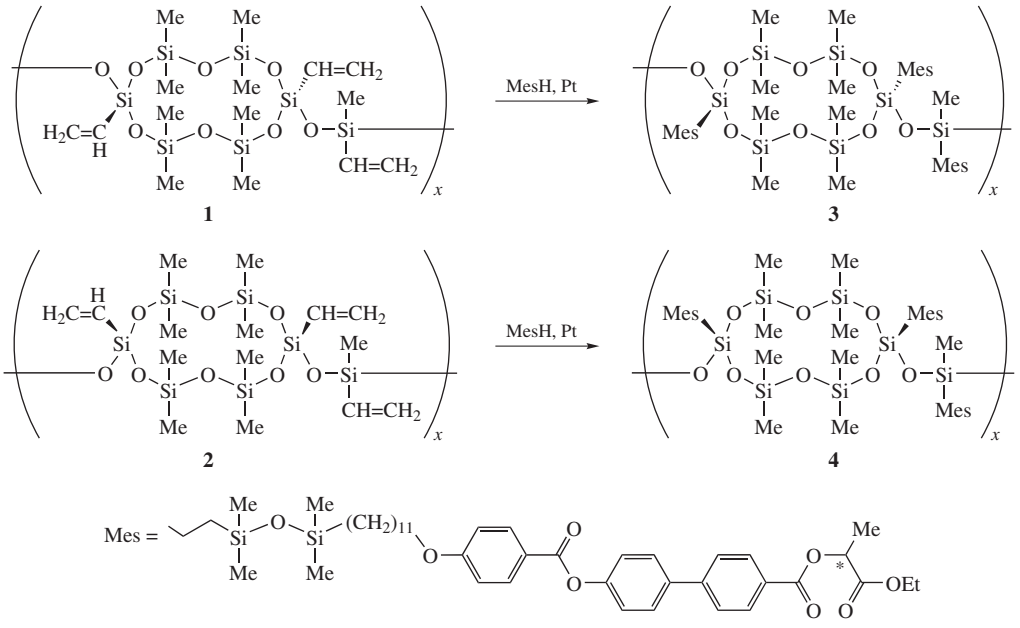
Comb-shaped liquid crystalline stereoregular cyclolinear methylsiloxane copolymers containing a lactic terminal group at the 4,4′-bisphenylene fragment were synthesized. The polymesomorphism of a smectic SmC* phase is influenced by the tacticity of the main chain, as found by X-ray analysis and DSC.

Liquid crystalline (LC) compounds containing to three chiral centers at the lactic terminal group have attracted attention because of the formation of ferro- and antiferroelectric SmC* phases. Monomers of LC compounds containing lactic groups of different design were prepared with ether[1,2] or ester[3,4] bonds between a mesogenic core and the lactic group, with various locations of phenylene and bisphenylene groups in mesogen,[2,11] long alkenyl spacer, HMe_2SiOMe_2Si groups[5,6,11] and with different numbers of chiral centers in the lactic group.[2–10] Mesogens containing lactic acid derivatives with one or two chiral centers were used for the preparation of comb-shaped homo- and copolymers with a main methylsiloxane chain.[1] A study of the physical properties of LC polymers with terminal lactic derivatives revealed the formation of a ferroelectric SmC* phase. However, the influence of the molecular structure on the stabilization of ferro- and antiferroelectric phases remains unknown.[1] Using a derivative of lactic acid, LC elastomers, which form the chiral SmA* phase, were obtained.[12] Chiral mesogen compounds, ethyl (*S*)-lactate derivatives, were introduced as terminal groups in carbosilane ferroelectric LC dendrimers from the first to fifth generations. Variation of a mesogen core structure leads to the stabilization of intra- and intermolecular interactions of mesogen groups (at a chiral center in the case of bisphenylene groups), which is proved by an increase in the temperature interval of SmC* phase existence.[11,13] Earlier, we prepared comb-shaped LC stereoregular methylsiloxane (MS) copolymers with side mesogen cyanobisphenyl groups.[14] Depending on the tacticity of the main chain, the variation in interchain distances was 4.7 Å at 20 °C when three mesogen groups were introduced into the unit.[14] At the same time, the stereoregularity of ferroelectric and antiferro-



Scheme 1

electric polymers is of interest, and the influence of the molecular structure on the stabilization of ferroelectric and antiferroelectric phases is not still fully understood: antiferroelectric phases arise due to intermolecular dipole-dipole interactions, a conformation order of the main chain or other reasons.

The aim of this work was to prepare a comb-shaped liquid crystalline cyclolinear (CL) MS copolymer with lactic terminal groups in the side mesogens and to examine the main chain tacticity effect on the formation of a ferroelectric SmC* phase and the type of order in a LC state.

Stereoregular CL MS copolymers **1**, **2** with three vinyl groups were synthesized according to published procedures.[14] Mesogen-containing precursor MesH with a Si–H terminal group was prepared according to a method described elsewhere.[11] Comb-shaped LC stereoregular CL MS copolymers **3**, **4** with mesogenic chiral side groups were prepared by the hydrosilylation of copolymers **1**, **2** with mesogen compound MesH in the presence of the Karstedt catalyst (Scheme 1).†

The degree of completion of the hydrosilylation reaction was determined by the disappearance of signals from the protons of the CH_2=CH groups in the ^{1}H NMR spectra in the range of 5.80–6.30 ppm and the signals at 4.40–4.80 ppm for the hydride protons of the HMe_2SiO fragment of MesH. The molecular structure of products **3**, **4** extracted was confirmed by ^{1}H and ^{29}Si NMR and IR spectroscopy.‡

Extended singlets are present in the ^{1}H NMR spectra of CL copolymers **3**, **4** in the δ range of 0.01–0.17 ppm. They are related to the protons of methyl groups in the Me_2SiO fragments in cyclohexasiloxane and tetramethyldisiloxane spacers between the backbone and the side chain and the protons of $Me(CH_2)_2SiO$ groups. Multiplets at 0.38–0.56, 0.91, 1.27–1.35 and 1.86 ppm for protons in $MeSi(CH_2)_2O$ and $Si(CH_2)_2O_{1.5}$, $OSiCH_2(CH_2)_7$, $(CH_2)_7$, CH_2CH_2CO groups, respectively, and multiplets at 6.98–7.30 and 7.65–8.16 ppm for protons in aromatic fragments are also present in the ^{1}H NMR spectra and for the proton of terminal lactic groups at 1.45–1.69, 4.32, 5.38 for *Me*CH, $MeCH_2$ and MeC*H*, respectively. In the ^{1}H NMR spectra of copolymers **3** and **4** in the range of 5.80–6.30 ppm 5–7 and 15–17% of CH_2=CH groups remained, respectively.

In the ^{29}Si NMR spectra of copolymers **3**, **4**, the signals for the Si atoms of $Me(CH_2$=$CH)SiO$ and CH_2=$CHSiO_{1.5}$ groups are absent and the signals for the silicon atoms at –22.00 and –66.00 to –67.50 ppm for MeMesSiO and $MesSiO_{1.5}$ groups, respectively, appear. Nevertheless, the ^{1}H NMR spectra of copolymers showed that the hydrosilylation reaction of compounds **1** and **2** with MesH occurred with a conversion of 83–95%. Earlier, analogous results were published for the banana-shaped side chain of LC linear methylsiloxanes.[15]

The phase behaviour of copolymers **3**, **4** in the bulk state was studied using DSC, optical polarization microscopy (OPM) and X-ray analysis (for details, see Online Supplementary Materials).

The heating of the samples of **3** and **4** was accompanied by a glass transition characterized by a small endothermic effect corresponding to the isotropisation of the mesophase (Figure 1). DSC curves *1* and *3* do not exhibit polymesomorphic transitions. LC CL copolymers **3** and **4** form a mesophase upon heating or cooling characterized by the absence of enantiotropic mesomorphism. Moreover, upon cooling copolymer **3** (curve *2*) from isotropic melting, an exothermic peak arises at 106 °C with a very low enthalpy. The similar polymesomorphism in SmC* was observed for comb-shaped polymethylsiloxane with side mesogenic groups and a terminal lactic derivative with two chiral centers but with the different position of 4,4′-bisphenylene in the mesogen core. It was confirmed that the polymesomorphism of the SmC* phase (SmC* → SmC^*_A or SmC* → SmC^*_γ) took place with a very low enthalpy.[1]

Our OPM study showed that LC CL copolymers **3** and **4** underwent an enantiotropic transition. These transitions are observed more clearly upon slow (0.1 K min^{-1}) cooling. The textures of copolymers **3** and **4** were prepared upon cooling the isotropic melt (Figure 2), which leads to the formation of growing network texture at 179 and 169 °C for copolymers **3** and **4**, respectively. The characteristic texture for SmA phase upon cooling copolymers **3** and **4** was not obtained. The further cooling produced the confocal broken type texture [Figure 2(*b*),(*d*)] and a great number of microdomains, which did not allow us to prepare a more clear texture.

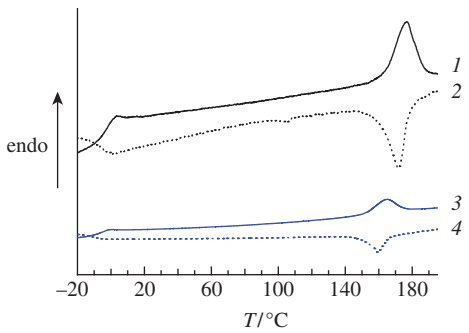


Figure 1 (*1*),(*3*) Heating and (*2*),(*4*) cooling DSC traces of copolymers (*1*),(*2*) **3** and (*3*),(*4*) **4**. Heating rate, 20 K min^{-1}.

† Syndio- (**1**) and isotactic (**2**) cyclolinear poly[oxy-(2,8-divinyl-4,4,6,6,10,10,12,12-octamethylcyclohexasiloxane-2,8-diyl)]methylvinylsiloxanes were synthesized as reported elsewhere.[14]

Copolymer **1**: $[\eta]$ = 0.11 dl g^{-1}, M_w = 12700, M_w/M_n = 1.3, T_g = –98 °C. ^{29}Si NMR (C_6D_6) δ: –21.02 (s, Me_2SiO_{cycle}), –34.98 [s, $Me(H_2C$=$CH)SiO$], –81.07 (s, H_2C=$CHSiO_{1.5}$).

Copolymer **2**: $[\eta]$ = 0.11 dl g^{-1}, M_w = 10900, M_w/M_n = 1.4, T_g = –94 °C. ^{29}Si NMR (C_6D_6) δ: –21.08 (d, Me_2SiO_{cycle}), –35.06 [s, $Me(H_2C$=$CH)SiO$], –81.10 (s, H_2C=$CHSiO_{1.5}$).

The Karstedt catalyst (Pt^0–1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex), a 3 wt% solution in xylenes (Aldrich), was used in the hydrosilylation reaction.

‡ *Synthesis of copolymers* **3**, **4**. A three-necked flask with a condenser and a magnetic stirring bar was filled with argon and evacuated to 1 Torr three times. After that, a solution of copolymer **1** (17 mg, 0.03 mmol) and MesH (70 mg, 0.043 mmol) in 0.30 ml of anhydrous toluene was placed in the flask under argon. After the complete dissolution of substances, 0.20 μl of the Karstedt catalyst was added. After heating the reaction mixture at 45 °C for 160 h, no protons of the H–Si and H_2C=CHSi groups were detected in the ^{1}H NMR spectrum. The reaction product was dissolved in 0.30 ml of benzene. A white precipitate was formed after adding methanol (0.25 ml). After double reprecipitation, the product was evacuated at 60 °C and 1 Torr. Yield of copolymer **3**, 40 mg (47%), M_w = 44000, M_w/M_n = = 1.58, T_g = –2 °C, T_i = 177 °C. ^{1}H NMR ($CDCl_3$) δ: 0.08 (br. s, 36H $Me_2SiOSiMe_{2\ linear}$), 0.12–0.13 [m, 24H, $(Me_2SiO)_{2\ cycle}$], 0.18 [br. s, 3H, $MeSi(CH_2)_2O$], 0.49–0.56 (m, 6H, CH_2SiMe_2O), 1.35 [m, 54H, $(CH_2)_8$], 1.64 (d, 9H, *Me*CH), 1.86 (m, 6H, CH_2CH_2O), 4.07 (t, 6H, CH_2O), 4.32 (q, 6H, $MeCH_2$), 5.33 (q, 3H, MeC*H*), 6.98 (d, 6H), 7.30 (d, 6H), 7.67 (d, 12H), 8.16 (d, 12H). ^{29}Si NMR (C_6D_6) δ: 8.34 (s), 7.79 (s) [$(CH_2)_2SiMe_2O$ and $OSiMe_2(CH_2)_{11}$], –21.95 (s, Me_2SiO_{cycle}), –22.00 [s, 1Si, $Me(CH_2)_2SiO$], –66.79 – –67.55 [br. s, $(CH_2)_2SiO_{1.5}$].

Copolymer **4** was prepared in a similar manner to copolymer **3**. Copolymer **2** (40 mg, 0.074 mmol), MesH (185 mg, 0.255 mmol) in 0.5 ml toluene, 0.40 μl of the Karstedt catalyst; 50 °C, 50 h. Yield of copolymer **4**: 90 mg (45%), M_w = 34900, M_w/M_n = 1.40, T_g = –13 °C, T_i = 165 °C. ^{1}H NMR ($CDCl_3$) δ: 0.01 (br. s, 36H, $Me_2SiOSiMe_{2\ linear}$), 0.06–0.09 [d, 24H, $(Me_2SiO)_{2\ cycle}$ + 3H, $MeSi(CH_2)_2O$], 0.38–0.50 [m, 4H, $(CH_2)_2SiMe_2O$ + 8H, $(CH_2)_2SiO_{1.5}$], 1.27 [m, 48H, $(CH_2)_8$], 1.45 (d, 9H, *Me*CH), 1.80 (m, 6H, CH_2CH_2O), 4.05 (t, 6H, CH_2O), 4.23 (q, 6H, $MeCH_2$), 5.32 (q, 3H, MeC*H*), 5.80–6.05 (m, 3H, H_2C=CH), 6.98 (d, 6H), 7.31 (d, 6H), 7.65 (d, 12H), 8.14 (d, 12H). ^{29}Si NMR (C_6D_6) δ: 8.31 (s), 7.71 [s, $(CH_2)_2SiMe_2O$ and $OSiMe_2(CH_2)_{11}$], –21.42 (br. s, 4Si, Me_2SiO_{cycle}), –22.16 [s, 1Si, $Me(CH_2)_2SiO$], –67.34 [br. s, 2Si, $(CH_2)_2SiO_{1.5}$].

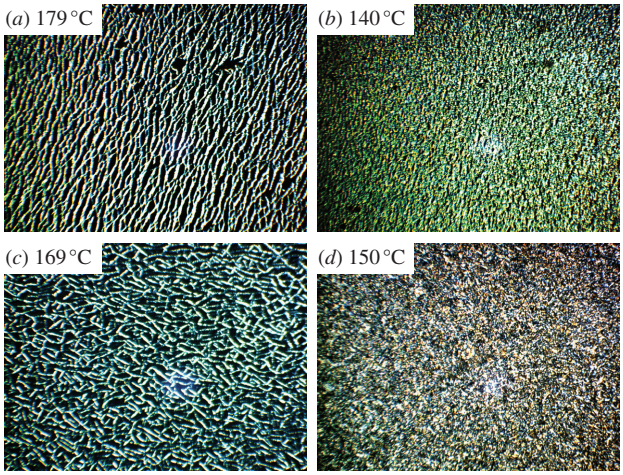


Figure 2 Textures of copolymers (*a*),(*b*) **3** and (*c*),(*4*) **4** in crossed nicols.

The small-angle X-ray diffraction patterns of the as-received samples of copolymer **3** also reveal two orders of reflections corresponding to the interlayer distance L = 45.2 Å. The size of coherent scattering regions calculated from the Selyakov–Scherrer equation, is about 100 Å. Interlayer distance decreases with the negative temperature expansion coefficient $\beta = -1.7\times10^{-4}$ K^{-1} (44.6 Å at 100 °C). At temperatures higher than 100 °C, the SmC* mesophase is observed.

X-ray diffraction analysis in small and wide angles revealed that both of the test samples possess a disordered smectic structure at room temperature. Two orders of reflection corresponding to an interlayer distance of 47.4 Å are observed for copolymer **4**. Note that the length of a molecule in a totally extended conformation is 39.8 Å. Thus, substantial interdigitation of the aliphatic parts of the molecule should take place. Another possibility is the chevron structure of the layer in which mesogen groups are tilted relatively to a layer director. The interlayer distance decreases with temperature to 46.7 Å at 90 °C (Figure 3).

Such a change corresponds to the negative thermal expansion coefficient $\beta = -2.1\times10^{-4}$ K^{-1}, which is rather common for smectic type mesophases. Further heating leads to a phase transition manifesting itself in the jump of interlayer distance of about 0.7 Å due to an additional degree of freedom of mesogen groups in the high-temperature SmC^*_A phase and a corresponding decrease in the effective molecular tilt angle. In the temperature range of the SmC^*_A mesophase, the material also possesses negative expansion, which is much stronger ($\beta = -1.1\times10^{-3}$ K^{-1}) than that of the SmC* phase.

Wide-angle scattering pattern of the compound contains only an amorphous halo of a complex shape (Figure 4).

Thus, the DSC and X-ray study of the phase transition of copolymers **3** and **4** characterized by different tacticity of the

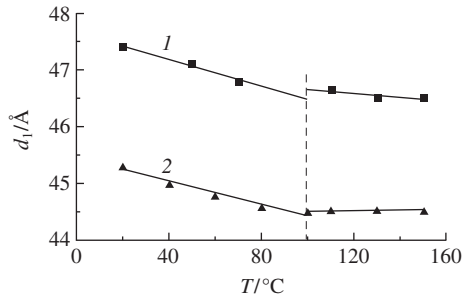


Figure 3 Temperature dependence of the smectic interlayer distance for LC CL copolymers (*1*) **4** and (*2*) **3**. Dashed line corresponds to the $SmC^*_A \rightarrow$ SmC* transition.

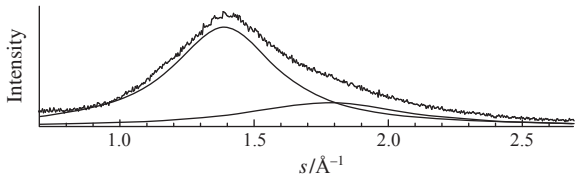


Figure 4 WAXS pattern and its resolution for LC CL copolymer **3**.

main CL MS chain showed that the SmC* phase exists in a wide temperature range regardless of the main chain tacticity. For syndiotactic copolymer **3**, additional transition to either SmC^*_A or SmC^*_γ phases arises unlike for LC dendrimers of 1–5 generations with an analogous mesogenic core (with a 4,4′-bisphenylene fragment at the terminal lactic group), for which a transition in the SmC* phase was not observed.[13] In comb-shaped stereoregular CL MS copolymers with a 4,4′-phenylene fragment at the terminal lactic group, the polymesomorphic transition in the smectic SmC* phase was also not found.[16] The above results for stereoregular polymers **3** and **4** and the data published for stereoregular CL MS polymers with another design of mesogonic core[16] lead to the conclusion that not only a tacticity of the main polymer chain but dipole-dipole intermolecular interactions of side mesogenic groups are responsible for the transition in the smectic SmC* phase.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2013.12.020.

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