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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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Experimental

^{1}H and ^{29}Si NMR spectra were recorded using AV-400 spectrometer (Bruker, USA) at 20°C in $CDCl_3$+CCl_4 solutions. Infrared (IR) spectra were recorded on a Specord M-82 spectrophotometer (Carl Zeiss Jena, Germany) in KBr pellets. The temperatures and the enthalpies of the phase transitions were measured by differential scanning calorimetry (DSC) using a DSC-7 calorimeter (Perkin-Elmer, USA). The heating rate was 20 K min^{-1} (T_g is the glass transition temperature, T_i is the isotropization temperature). DSC scans were recorded after cooling from the isotropic melt at a rate of 20 K min^{-1}. Mesomorphic properties were studied by optical polarization microscopy using an Axiolab Pol microscope (Carl Zeiss, Germany) equipped with a hot stage (Linkam, UK). The samples represented thin films about 10 μm thick placed between two cover glasses.

X-Ray diffraction patterns in small and wide angle scattering regions were obtained using S3-Micropix system (Hecus company), CuK$_\alpha$-radiation, λ = 1.5406 Å with Xenocs Genix source (working voltage and current were 50 kV and 1 mA, respectively). Pilatus 100K detector was employed, as well as linear PSD 50M gas detector (Ar/Me mixture at $8 \cdot 10^5$ Pa). Pinhole collimation system Fox 3D with Kratky collimation slits of 0.1 mm and 0.2 mm width was used, allowing the stable measurements in wave vector interval from s = 0.003 Å^{-1} to s = 1.9 Å^{-1} where $s = 4\pi\sin\theta/\lambda$, 2θ is scattering angle. To get rid of the scattering of X-rays on air molecules, Goebbel mirrors and scattering path were vacuumed at pressures 2.6 ÷ 5.0 Pa. Exposure times were varied from 600 to 5000 s. Temperature behavior of samples was studied using Peltier and Joule attachments at low (-5˚C - 120˚C) at Joule and high (23˚C - 300˚C) temperatures, respectively. Transmission X-ray diffraction patterns at wide angles were also recorded at Bruker D8 Advance powder diffractometer (CuK_α radiation, λ = 1.5406 Å, Vantec 2D detector).

Accelrys Materials Studio® program set was employed for molecular modelling of compounds studied. We used two sets of potentials, which allow taking into account non-covalent interactions of mesogenic groups in liquid-crystalline mesophases: COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) and UFF (Universal Force Field). The COMPASS set is suitable for modelling of isolated molecules and condensed phases of mainly organic, polymeric and of some inorganic compounds, it also allows to parametrize partial charges and valency *ab initio* with subsequent system optimization. To prove the results of modelling, we applied UFF potentials, used for calculation of geometry of organic molecules containing metal-organic complexes, as well as it does not have any limitation on the chemistry of compounds involved.

Syndio- (**1**) and isotactic (**2**) cyclolinear poly[oxy(2,8-divinyl-4,4,6,6,10,10,12,12-octamethyl-cyclohexasiloxane-2,8-diyl)]methylvinylsiloxanes were synthesized as reported. [8] Copolymer **1**: [η]=0.11 dl g^{-1}, T_g=-98^{o}C. ^{29}Si NMR (C_6D_6,) δ: -21.02 (s, $(CH_3)_2SiO_{cycle}$); -34.98 (s, $CH_3(CH_2=CH)SiO$); -81.07 (s, $CH_2=CHSiO_{1.5}$).`Copolymer **2**: [η]=0.11 dl g^{-1}, T_g=-98^{o}C. ^{1}H NMR ($CDCl_3+CCl_4$,) δ: 0.10-0.14 (2s, 12H $(CH_3)_2SiO_{cycle}$); 0.22 (s, 3H $CH_3(CH_2=CH)SiO$); 5.88-6.00 (m, 9H $(CH_2=CH)_3$). ^{29}Si NMR (C_6D_6,) δ: -21.08 (d, $(CH_3)_2SiO_{cycle}$); -35.07 (d, $CH_3(CH_2=CH)SiO$); -81.11 (d, $CH_2=CHSiO_{1.5}$).

Mesogen **3** with terminal chiral groups and mesogen H-Si derivative **4** were synthesized according to the published procedure,[9] using ethyl (S)-(−)lactate. The Karstedt catalyst [Pt(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex] 3 wt% solution in xylenes (Aldrich, USA) was used in the hydrosilylation reaction.