Supporting Information

Phase Behavior of Side-Chain Liquid-Crystalline Polymers Containing Biphenyl Mesogens with Different Spacer Lengths Synthesized via Miniemulsion Polymerization

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Synthesis and characterization of 6-MLCM:

\textbf{Ethyl-4-(4-hydroxy)phenyl Benzoate (2, Scheme 1):} The solution of 4'-hydroxy-4-biphenylcarboxylic acid (1) (10 g, 46.65 mmol) in 100 ml of ethanol (99.99%) and 100 ml of benzene containing a catalytic amount of H\textsubscript{2}SO\textsubscript{4} was refluxed for 24 h. The reaction mixture was cooled and poured into distilled water, and then extracted twice with CH\textsubscript{2}Cl\textsubscript{2}. The organic phase was separated and washed with distilled water, dried
with Na₂SO₄, filtered, and evaporated. The yellow-white powder was dissolved in CHCl₃, where unreacted 1 precipitated. The CHCl₃ solution was filtered and evaporated resulting in a white crystalline powder, yield 9.49 g (84%). ¹H NMR (CDCl₃, 400 MHz) δ 1.43 (t, 3H, -CH₂CH₃), 4.42 (q, 2H, -CH₂CH₃), 6.96 (d, 2H, 3'-H and 5'-H), 7.54 (d, 2H, 2'-H and 6'-H), 7.64 (d, 2H, 2-H and 6-H), 8.11 (d, 2H, 3-H and 5-H).

**Ethyl 4'-(6-bromohexyl)oxy-[1,1'-biphenyl]-4-carboxylate (3, Scheme 1):** The mixture of 2 (8.33 g, 34.38 mmol), 1,6-dibromohexane (83.81 g, 344 mmol) and potassium carbonate (34.23 g, 258.3 mmol) were refluxed with stirring in acetone (380 ml) for 24 h. The reaction mixture was filtered hot, the residue washed with acetone, and the acetone removed by rotating evaporation. Light petroleum or hexane (40-60 °C) was added to the concentrated organic extracts and the resulting precipitate collected and dried. The crude product was recrystallised from ethanol with hot filtration to ensure the complete removal of the dimeric side-product. Yield 8.816 g (64.1%). ¹H NMR ((CD₃)₂CO, 400 MHz) δ 1.27-1.45 (m, 5H, -CH₂CH₃, O(CH₂)₃CH₂(CH₂)₂Br), 1.57 (t, 2H, -O(CH₂)₂CH₂), 1.85 (t, 2H, -OCH₂CH₂), 1.93 (t, 2H, -CH₂CH₂Br), 3.55 (t, 2H, -CH₂Br), 4.1 (t, 2H, -OCH₂), 4.38 (q, 2H, -CH₂CH₂), 7.08 (d, 2H, 3′-H and 5′-H), 7.7 (d, 2H, 2′-H and 6′-H), 7.78(t, 2H, 2-H, and 6-H), 8.08 (d, 2H, 3-H, and 5-H).

**Ethyl 4'-(6-(methacryloyloxy)hexyl)oxy-[1,1'-biphenyl]-4-carboxylate (4, Scheme 1):** Methacrylic acid (2.242 g, 27.91 mmol), was reacted with potassium hydrogen carbonate (3.189 g, 31.85 mmol) at room temperature for 5 min to form potassium methacrylate. The solution of 3 (8.816 g, 22.03 mmol) and hydroquinone (0.063 g, 2.203 mmol) in N,N'- dimethylformamide (120 ml) was added to potassium methacrylate salt and the resulting mixture was stirred at 100°C for 24 h. The reaction mixture was allowed to cool and was poured into water (ca. 1000 ml). The resulting precipitate was filtered, dried and dissolved in dichloromethane. The organic solution
was washed with 5% aqueous sodium hydroxide and then water. The solvent evaporated and the solid monomer filtered and washed with water. The crude product was recrystallized from ethanol. Yield: 7.48 g (83%). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 1.44 (t, 3H, -CH$_2$CH$_3$), 1.54 (m, 4H, O(CH$_2$)$_2$ CH$_2$CH2), 1.77 (m, 2H, - CH$_2$CH$_2$OC(O)), 1.86 (m, 2H, -OCH$_2$CH$_2$), 1.98 (s, 3H, -C(CH$_3$)=CH$_2$), 4.04 (t, 2H, -CH$_2$OC(O)), 4.2 (t, 2H, -OCH$_2$), 4.42 (q, 2H, -CH$_2$CH$_3$), 5.58 (s, 1H, CH$_2$=C- cis), 6.13 (s, 1H, CH$_2$=C- trans), 7.01 (d, 2H, 3'-H and 5'-H), 7.59 (d, 2H, 2'-H and 6'-H), 7.64 (d, 2H, 2-H, and 6-H), 8.11 (d, 2H, 3-H, and 5-H).
Fig. S1. $^1$H NMR spectrum of 6-MLCM (a) and 6-PMLCM obtained from solution (b) and miniemulsion (c) polymerization.
**Fig. S2.** $^1$H NMR spectrum of 5-MLCM (a) and 5-PMLCM obtained from solution (b) and miniemulsion (c) polymerization

**Fig. S3.** $^1$H NMR spectrum of 4-MLCM (a) and 4-PMLCM obtained from solution (b) and miniemulsion (c) polymerization
Fig. S4. $^1$H NMR spectrum of 3-MLCM (a) and 3-PMLCM obtained from solution (b) and miniemulsion (c) polymerization.

Fig. S5. DSC curves of n-MLCMs during the second heating scan at a rate of 10 °C min$^{-1}$ under nitrogen atmosphere. For clarity, 6 W/g was added to the scan of the sample n=3; 4 W/g to that of sample n=4 and 2 W/g was added to the scan of the sample n=5.
Fig. S6. TGA curves of n-PMLCMs at a rate of 10 °C/min under nitrogen atmosphere
**Fig. S7.** Transition temperatures (a) and entropies (b) associated with the thermal transitions of high molar mass n-PMLCMs (solid symbols), low molar mass n-PMLCMs (empty symbols) and poly[ω-(4´-methoxybiphenyl-4-yloxy)alkyl methacrylate]s in reference 3 (cross symbols) as function of the number of methylene units in the spacer. The thermal transitions were extracted from second heating scans.
Fig. S8. Position of the maxima attributed to the long-range order periodicity as function of the assigned reflection order index obtained for the high-molar mass samples: (a) 3-PMLCM; (b) 4-PMLCM; (c) 5-PMLCM; (d) 6-PMLCM. Results from SAXS are represented by squares and results from WAXS by circles. Continuous lines are linear regression fits $Q_{i}^{**} = iQ_{1}^{**}$ with the value indicated $Q_{1}^{**}$-values.
Fig. S9. Temperature dependence of the positions of the different peaks identified in the XR-patterns (empty symbols: SAXS; filled symbols: WAXS) of the high-molar mass 3-PMLCM sample. For the peaks centered at $Q_{1}^{**}$ and $Q_{1}^{*}$ and selected temperatures, the lines represent the width of the peak at its half maximum. Note that for the peak at $Q_{1}^{**}$, at temperatures below the clearing point this width is of the order of the size of the point, and therefore cannot be resolved in the plot.
Fig. S10. Temperature dependence of the positions of the different peaks identified in the XR-patterns (empty symbols: SAXS; filled symbols: WAXS) of the high-molar mass 4-PMLCM sample. For the peaks centered at $Q_1^{**}$ and $Q_3^*$ and selected temperatures, the lines represent the width of the peak at its half maximum. Note that for the peak at $Q_1^{**}$, at temperatures below the clearing point this width is of the order of the size of the point, and therefore cannot be resolved in the plot.
Fig. S11. Temperature dependence of the positions of the different peaks identified in the XR-patterns (empty symbols: SAXS; filled symbols: WAXS) of 5-PMLCM sample. For the peaks centered at $Q_{1}^{**}$ and $Q^{*}$ and selected temperatures, the vertical lines represent the width of the peak at its half maximum. Note that for the peak at $Q_{1}^{**}$, at temperatures below $T_{II}$ this width is of the order of the size of the point, and therefore cannot be resolved in the plot.
Fig. S12. Temperature dependence of the positions of the different peaks identified in the XR-patterns (empty symbols: SAXS; filled symbols: WAXS) of the high-molar mass 6-PMLCM sample. For the peaks centered at $Q_{1}^{**}$ and $Q_{1}^{*}$ and selected temperatures, the lines represent the width of the peak at its half maximum. Note that for the peak at $Q_{1}^{**}$, at temperatures below the clearing point this width is of the order of the size of the point, and therefore cannot be resolved in the plot.
**Fig. S13.** Region of $^1$H NMR spectrum (left) and $^{13}$C NMR spectrum (right) for n-PMLCMs showing the peaks associated with the α-methyl.

**Table S1.** Tacticities$^a$ of high molecular weigh n-PMLCMs.

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<th>sample</th>
<th>mm</th>
<th>mr</th>
<th>rr</th>
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<tr>
<td>4-PMLCM</td>
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<td>0.54</td>
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<tr>
<td>5-PMLCM</td>
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<td>6-PMLCM</td>
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$^a$mass fraction of isotactic (mm), heterotactic (mr) and syndiotactic (rr). The reported values are the average of tacticities calculated from $^1$H NMR and $^{13}$C NMR spectra.
Fig. S14. WAXS patterns on 5-PMLCM at 30°C (red), 115°C (blue) and 150°C (green).

Table S2. Thermal properties of the low molar mass n-PMLCMs. Results obtained from the first cooling DSC scan are denoted with the subscript ‘c’, and from the second heating, with subscript ‘h’.

<table>
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<tr>
<th>n</th>
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<th>T_{II,a}</th>
<th>T_{I,h}</th>
<th>T_{II,h}</th>
<th>$\Delta H_{I,h}$</th>
<th>$\Delta H_{II,h}$</th>
<th>$\Delta S_{I,h}/R$</th>
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<td>1.2</td>
<td>1.55</td>
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<td>284</td>
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$^a$ Smectic E (Smectic E or Smectic C) – Smectic A, and $^b$ Smectic A – Isotropic transitions, as identified by PLM and XR. $^c$ Temperatures at 5% weight loss of the samples in TGA.
Fig. S15. WAXS-results at the temperatures indicated. (a) and (b): 3-PMLCM; (c) and (d): 4-PMLCM; (e) and (f): 5-PMLCM; (g) and (h): 6-PMLCM. Panels on the left: high molar mass samples; panels on the right: low molar mass samples.
Fig. S16. SAXS-results at the temperatures indicated. (a) and (b): 3-PMLCM; (c) and (d): 4-PMLCM; (e) and (f): 5-PMLCM; (g) and (h): 6-PMLCM. Panels on the left: high molar mass samples; panels on the right: low molar mass samples.