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:

Ethyl-4-(4-hydroxy)phenyl Benzoate (2, Scheme 1): The solution of 4'-hydroxy-4biphenylcarboxylic 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_2SO_4 was refluxed for 24 h. The reaction mixture was cooled and poured into distilled water, and then extracted twice with CH₂Cl₂. 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,-CH₂CH₃), 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%). ¹H NMR (CDCl₃, 400 MHz) δ 1.44 (t, 3H, -CH₂CH₃), 1.54 (m, 4H, O(CH₂)₂ CH₂CH2), 1.77 (m, 2H, - CH₂CH₂OC(O)), 1.86 (m, 2H,-OCH₂CH₂), 1.98 (s, 3H, -C(CH₃)=CH₂), 4.04 (t, 2H, -CH₂OC(O)), 4.2 (t, 2H, -OCH₂), 4.42 (q, 2H,-CH₂CH₃), 5.58 (s, 1H, CH₂=C- cis), 6.13 (s, 1H, CH₂=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. ¹H NMR spectrum of 6-MLCM (a) and 6-PMLCM obtained from solution (b) and miniemulsion (c) polymerization



Fig. S2. ¹H NMR spectrum of 5-MLCM (a) and 5-PMLCM obtained from solution (b) and miniemulsion (c) polymerization



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



Fig. S4. ¹H 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 $Q_i^{**}=i^*Q_1^{**}$ with the value indicated Q_1^{**} -values.



Fig. S9. Temperature dependence of the positions of the different peaks identified in the XRpatterns (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 XRpatterns (empty symbols: SAXS; filled symbols: WAXS) of the high-molar mass 4-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. S11. Temperature dependence of the positions of the different peaks identified in the XRpatterns (empty symbols: SAXS; filled symbols: WAXS) of 5-PMLCM sample. For the peaks centered at Q₁** and Q* and selected temperatures, the vertical lines represent the width of the peak at its half maximum. Note that for the peak at Q₁**, 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 XRpatterns (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 ¹H NMR spectrum (left) and ¹³C NMR spectrum (right) for n-PMLCMs showing the peaks associated with the α -methyl.

sample	mm	mr	rr
3-PMLCM	0.00	0.38	0.62
4-PMLCM	0.00	0.46	0.54
5-PMLCM	0.00	0.30	0.70
6-PMLCM	0.00	0.39	0.61

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

^amass fraction of isotactic (mm), heterotactic (mr) and syndiotactic (rr). The reported values are the average of tacticities calculated from ¹H NMR and ¹³C 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'.

n	T _{I,c} ^a (°C)	T _{II,c} ^b (°C)	T _{I,h} ª (°C)	T _{II,h} ^b (°C)	ΔH _{I,h} (kJ/mol)	ΔH _{II,h} (kJ/mol)	$\Delta S_{I,h}/R$	$\Delta S_{II,h}/R$	T _g (°C)	T _d ° (°C)
3	129	187	133	194	3.30	5.34	0.97	1.36		287
4	109	155	112	162	2.53	4.57	0.78	1.26		280
5	132	194	137	201	5.07	7.68	1.49	1.84	93	267
6	99	157	104	161	3.76	5.63	1.2	1.55	81	284

^a Smectic **E** (Smectic **E** or Smectic **C**) – Smectic **A** and ^bSmectic **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.