New Journal of Chemistry

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

Supplementary Information

Influence of Main-chain and Molecular Weight on the Phase Behaviors of Side-Chain Liquid Crystalline Polymers without the Spacer

Ni Bin, Luo Yongbin, Liu Yujie, Chen Sheng*, Zhang Hailiang*

Key Laboratory of Polymeric Materials and Application Technology of Hunan Province, Key Laboratory of Advanced Functional Polymer Materials of Colleges and Universities of Hunan Province, College of Chemistry, Xiangtan University, Xiangtan 411105, Hunan Province, China

.

4-methoxy-4'-hydroxybiphenyls: Dimethyl sulfate (68g, 0.54 mol) was added dropwise to a water (400 mL) solution of 4,4'-dihydroxybiphenyl (100 g, 0.54 mol) and NaOH (43 g, 1.08 mol) at room temperature. The reaction process produced lots of solid. After 1 hour, the resulting precipitate was collected by filtration, washed with NaOH solution and hot water, neutralized by aqueous HC1, and dried under vacuum. The product was purified by recrystallization from ethanol.

4-alkyloxy-4'-hydroxybiphenyls: 4-Alkyloxy-4-hydroxybiphenyls were synthesized by standard methods from 4,4'-biphenyldiol with bromoalkanes in the presence of K_2CO_3. The mixture was heated for 12 h in 55 ^oC, next the reaction mixture poured into a large amount of water to precipitate products. The products were purified by precipitation in water from THF solution three times. At last, the crude products were purified by column chromatograph (silica gel, CH_2Cl_2). The final product of 4-alkoxybiphenol was white powder.

4, 4'-alkoxybiphenyl acrylate: 0.3mol acryloyl chloride and 1.5 mol TEA were dissolved in 200mL THF. Under intense stirring at 0 ^oC, 0.1 mol 4-alkyloxy-4-hydroxybiphenyls was slowly added into the above solution over a period of 2 h. The mixture was further stirred at room temperature for 12 h, the mixture was filtered in order to remove inorganic salts. Then the reaction mixture was precipitated into a large amount of water, and was filtered. At last, the crude products were purified by column chromatograph (silica gel, CH_2Cl_2/ petroleum ether=10/1). The characterization data of monomers were as follows:

MBiA-1: ^{1}H NMR ($CDCl_3$): 3.80-3.89 (s, 3H, -O-CH_3), 6.02-6.05 (d, H, =CH_2), 6.32-6.39 (q, H, -CH=), 6.61-6.66 (d, H, =CH_2), 6.97-7.55 (m, 8H, Ar-H). Mass Spectrometry (MS) (m/z) [M] Calcd for $C_{16}H_{14}O_3$, 254.09.; found, 254.12.

MBiA-4: ^{1}H NMR ($CDCl_3$): δ = 0.86-1.83 (m, 7H, alkoxy H), 3.99-4.03 (t, 2H, -O-CH_2-), 6.01-6.04(d, H, =CH_2), 6.38-6.31 (q, H, -CH=), 6.65-6.61 (d, H, =CH_2). 6.96-7.71 (m, 8H, Ar-H), Mass Spectrometry (MS) (m/z) [M] Calcd for $C_{19}H_{20}O_3$, 296.14.; found, 296.27.

MBiA-6: ^{1}H NMR ($CDCl_3$): δ = 0.81-1.81 (m, 11H, alkoxy H), 3.98-4.01 (t, 2H, -O-CH_2-), 6.01-6.04(d, H, =CH_2), 6.31-6.38 (q, H, -CH=), 6.61-6.65 (d, H, =CH_2), 6.98-7.57 (m, 8H, Ar-H). Mass Spectrometry (MS) (m/z) [M] Calcd for $C_{21}H_{24}O_3$, 324.17.; found, 324. 68.

MBiA-10: ^{1}H NMR ($CDCl_3$): δ = 0.81-1.81 (m, 19H, alkoxy H), 3.99-4.1 (t, 2H, -O-CH_2-), 6.0-6.03(d, H, =CH_2), 6.30-6.37 (q, H, -CH=), 6.60-6.63 (d, H, =CH_2), 6.9-7.6 (m, 8H, Ar-H). Mass Spectrometry (MS) (m/z) [M] Calcd for $C_{25}H_{32}O_3$, 380.24.; found, 380.386.

MBiA-18: ^{1}H NMR ($CDCl_3$): δ = 0.81-1.81 (m, 35H, alkoxy H), 4.01-3.98 (t, 2H, -O-CH_2-), 6.01-6.04 (d, H, =CH_2), 6.31-6.38 (q, H, -CH=), 6.60-6.65(d, H, =CH_2), 6.98-7.57 (m, 8H, Ar-H). Mass Spectrometry (MS) (m/z) [M] Calcd for $C_{33}H_{48}O_3$, 492.36.; found, 492.41.

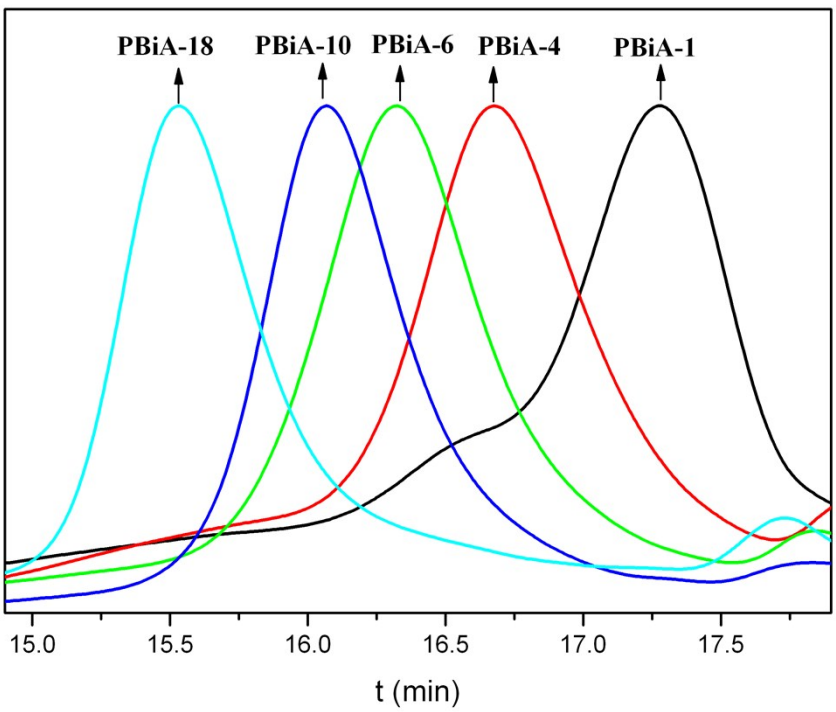

Figure S1 GPC trace of PBiA-m with low M_n.

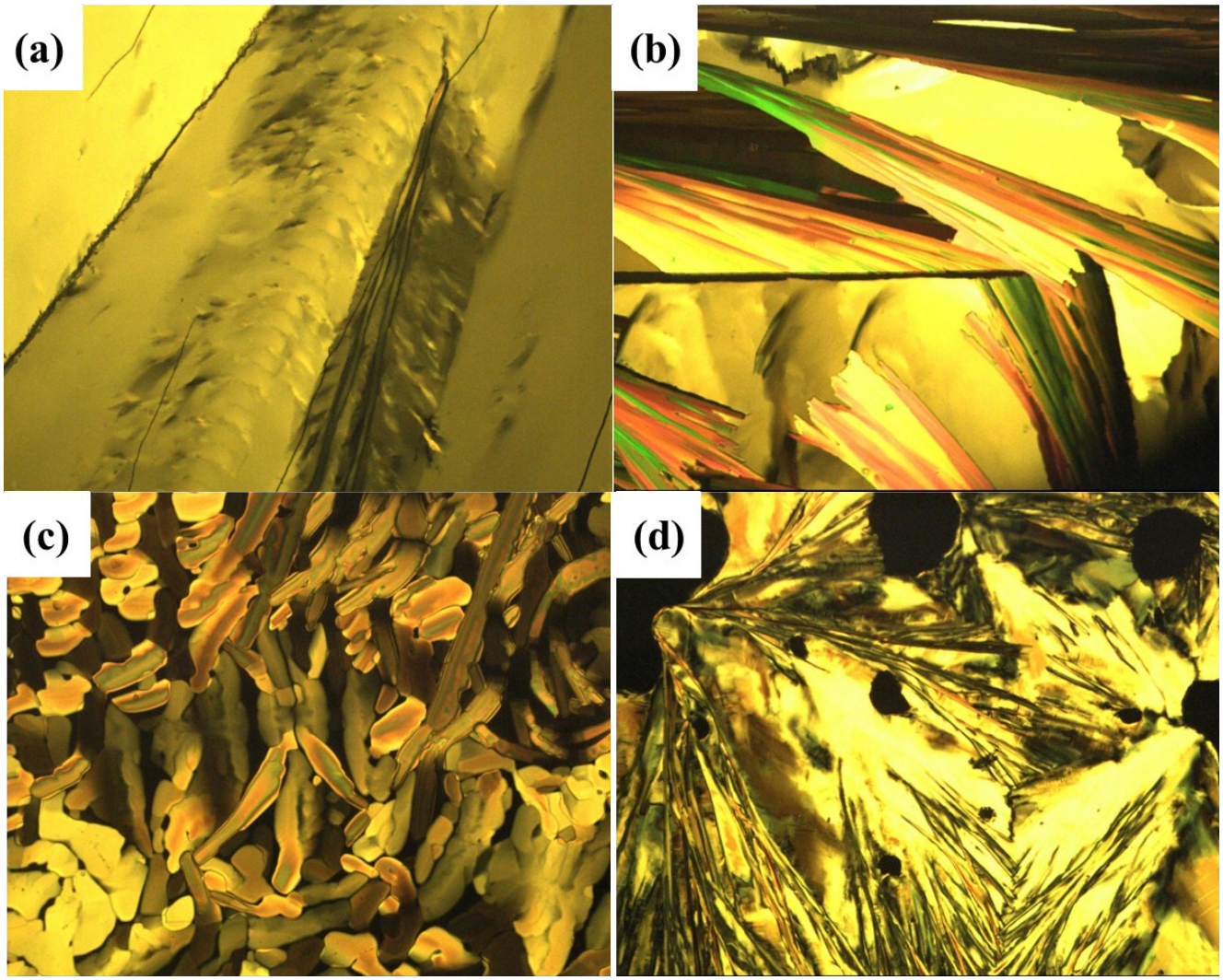

Figure S2 Representative POM images of the texture of the MBiA-1 (a), MBiA-4 (b), MBiA-6 (c) and MBiA-18 (d) maintained at 25°C (b) (Magnification: ×200).

Table S1 Properties of PBiA-m (m = 1, 4, 6, 10, 18) with low M_n

Sample	M_n($\times 10^3$)[a]	PDI[a]	T_i (°C)[b]
PBiA-1	1.2	1.15	210
PBiA-4	2.4	1.15	300
PBiA-6	3.7	1.13	282
PBiA-10	5.1	1.12	275
PBiA-18	9.0	1.13	280

a. Relative M_n and PDI were measured by GPC using PS standards.

b. The transition temperature from liquid crystalline phase to isotropic phase measured by POM at a

heating rate of 10 °C min^{-1} during the second heating process.

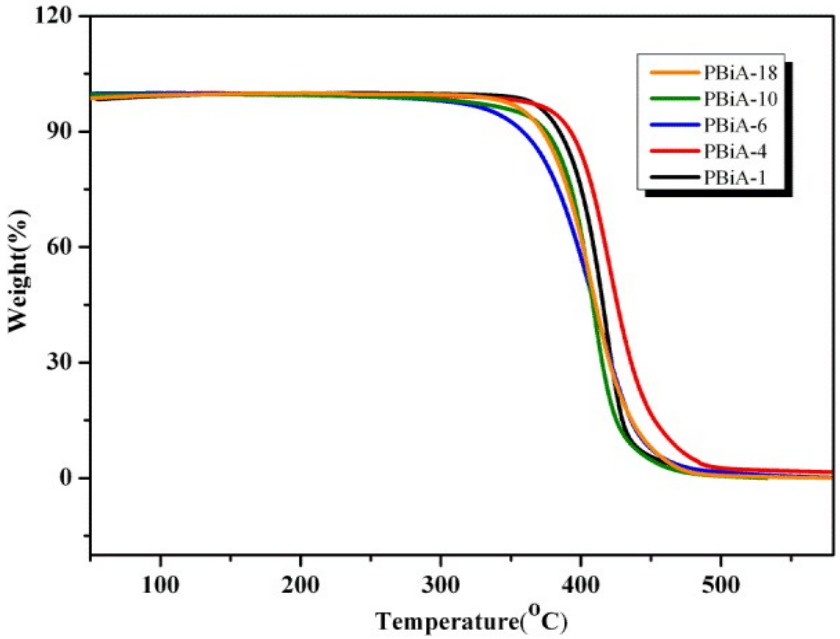

Figure S3 TG curse of PBiA-m at a rate of 20 °C min^{-1} under nitrogen atmosphere.

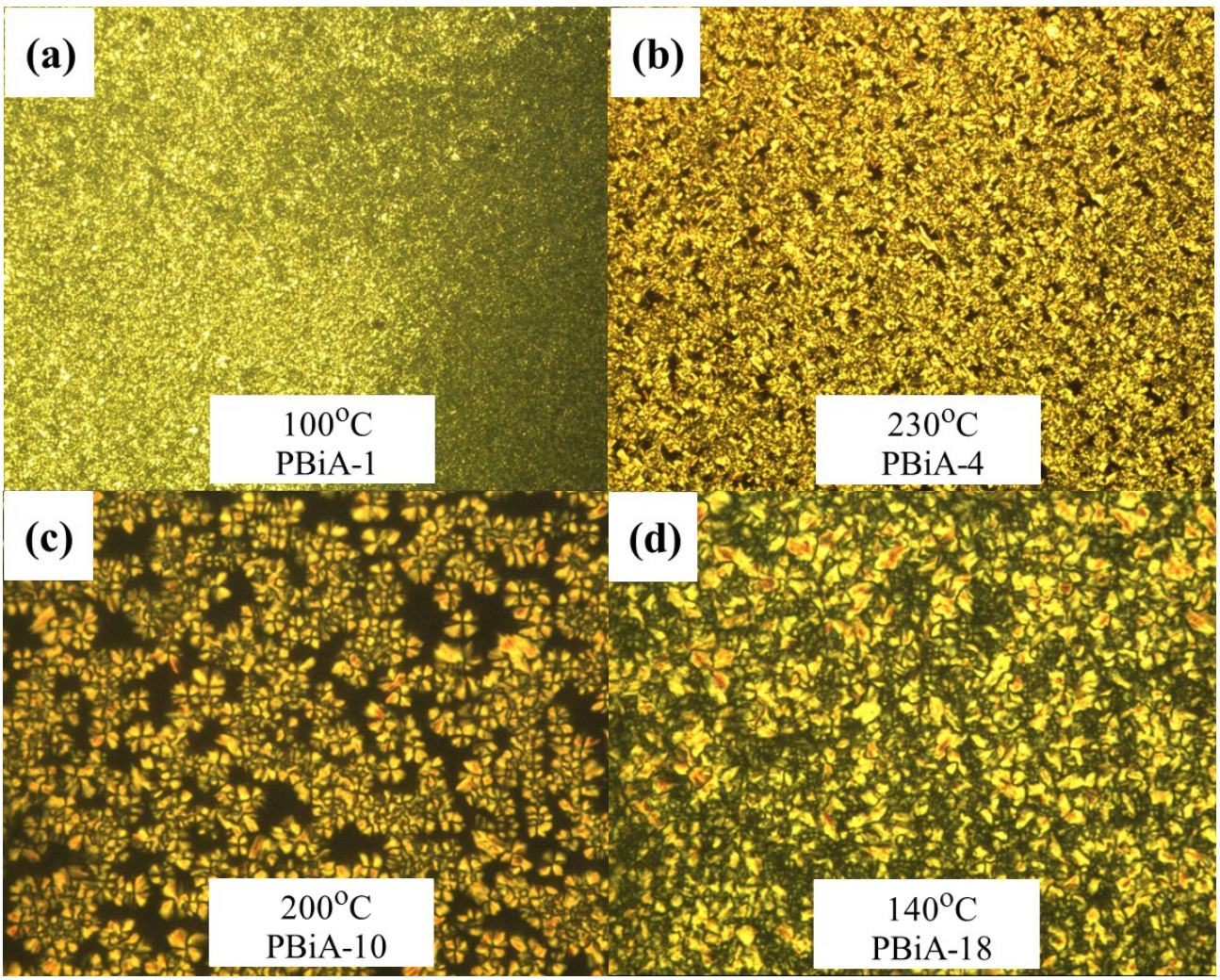

Figure S4 Representative POM images of the texture of the PBiA-1 (a), PBiA-4 (b), PBiA-10 (c) and PBiA-18 (d) with low M_n (Magnification: ×200).

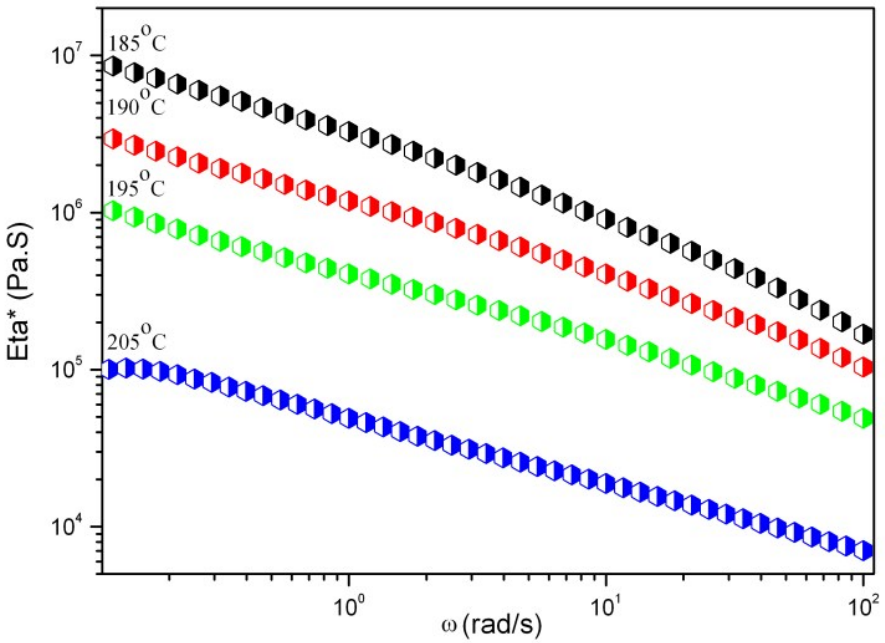

Figure S5 Viscosity versus shear rate at various temperatures.