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Bistable mesomorphism and supramolecular stereomutation in chiral liquid crystal azopolymers

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Synthesis of monomers

Compounds **1**-**6** were synthesized according to the methods previously described for **1S**, **3S** and **5S.**[50] Characterization data are given below (main characterization data of the R-enantiomer of the synthetic intermediates have been selected for simplicity).

(R)-4-Methylpropyloxynitrobenzene **1(R)**. Yellowish oil (92 % yield).^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.12 (d, J = 9.3 Hz, 2H), 6.88 (d, J = 9.3 Hz, 2H), 4.46-4.33 (m, 1H), 1.80-1.55 (m, 2H), 1.30 (d, J = 6.1 Hz, 3H), 0.94 (t, J = 7.5 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 163.43, 140.77, 125.74, 115.04, 75.84, 28.81, 18.77, 9.42. IR (Nujol, cm^{-1}): 2975, 2936, 2879, 1605, 1592, 1512, 1496, 1380, 1262, 1110, 846.

(R)-4-Methylheptyloxynitrobenzene **2(R).** Yellowish oil (89 % yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.13 (d, J = 9.3 Hz, 2H), 6.88 (d, J = 9.3 Hz, 2H), 4.50-4.40 (m, 1H), 1.79-1.66 (m, 1H), 1.63-1.51 (m, 1H), 1.49-1.16 (m, 11H), 0.84 (t, J = 6.9 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 163.44, 140.79, 125.78, 115.01, 74.75, 36.05, 31.60, 29.03, 25.20, 22.42, 19.28, 13.89. IR (Nujol, cm^{-1}): 2929, 2855, 1605, 1592, 1512, 1495, 1379, 1261, 1109, 846.

(R)-4-Methylpropyloxyaniline **3(R).** Yellow oil (91 % yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.74 (d, J = 8.7 Hz, 2H), 6.63 (d, J = 8.7 Hz, 2H), 4.15-4.07 (m, 1H), 3.55-3.18 (s broad, 2H), 1.75-1.50 (m, 2H), 1.24 (d, J = 6.1, 3H), 0.97 (t, J = 7.4, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 151.20, 140.17, 117.90, 116.39, 76.41, 29.24, 19.41, 9.90. IR (Nujol, cm^{-1}): 3428, 3357, 3220, 2969, 2920, 2876, 1603, 1541, 1508, 1462, 1232.

(R)-4-Methylheptyloxyaniline **4(R).** Yellow oil (92 % yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.74 (d, J = 8.8 Hz, 2H), 6.64 (d, J = 8.8 Hz, 2H), 4.23-4.12 (m, 1H), 3.57-3.25 (s broad, 2H), 1.75-1.63 (m, 1H), 1.57-1.21 (m, 12H), 0.88 (t, J = 6.8, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 151.25, 139.98, 117.87, 116.42, 72.20, 36.04, 31.60, 29.35, 25.60, 22.63, 19.88, 14.11. IR (Nujol, cm^{-1}): 3435, 3360, 3218, 2956, 2929, 2857, 1624, 1509, 1465, 1233, 823.

(R)-4-Methylpropyloxy-4'-hydroxyazobenzene **5(R).** Yellow-orange crystalline leaflets (75 % yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.89 (d, J = 9.0 Hz, 2H), 7.82 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 9.0, 2H), 6.88 (d, J = 8.8, 2H), 4.47-4-36 (m, 1H), 1.86-1.60 (m, 2H), 1.34 (d, J = 6.1, 3H), 1.02 (t, J = 7.5, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 160.38, 158.19, 146.88, 146.57, 124.50, 124.34, 115.91, 115.81, 75.37, 29.14, 19.16, 9.70. IR (KBr, cm^{-1}): 3383 (broad), 2972, 2933, 1595, 1499, 1247, 1146, 842.

(R)-4-Methylheptyloxy-4'-hydroxyazobenzene **6(R).** Yellow-orange crystalline leaflets (68 % yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.85 (d, J = 9.0 Hz, 2H), 7.82 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 9.0, 2H), 6.92 (d, J = 8.8, 2H), 4.49-4-40 (m, 1H), 1.84-1.71 (m, 1H), 1.66-1.54 (m, 1H), 1.51-1.21 (m, 11H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 160.44, 157.71, 147.14, 146.57, 124.52, 124.40, 115.78, 115.75, 74.23, 36.39, 31.77, 29.24, 25.46, 22.58, 19.70, 14.07. IR (KBr, cm^{-1}): 3388 (broad), 2955, 2928, 1597, 1501, 1247, 1146, 842.

(R)-4-Methylpropyloxy-4'-(6"-hydroxyhexyl-1"-oxy)azobenzene **7(R)** A mixture of *(R)*-4-methylpropyloxy-4'-hydroxyazobenzene **5(R)** (2.07 g, 7.66 mmol), 6-chloro-1-hexanol (1.15 g, 8.42 mmol), finely ground potassium carbonate (1.59 g, 11.49 mmol) and potassium iodide (0.25g, 1.53 mmol) in DMF (50.00 mL) was heated under reflux overnight. The reaction mixture was cooled to room temperature, water was added and the product extracted with hexane/ethyl acetate. The combined organic extracts were washed with water, dried over anhydrous MgSO4 and evaporated to dryness. The crude product was purified by flash chromatography using hexane/ethyl acetate (4:1) to yield the required product as a yellow solid. Yield: 85%. H NMR (400 MHz, $CDCl_3$, δ): 7.85 (dd, J = 9.0 Hz, J = 2.3 Hz, 4H), 6.98 (dd, J = 9.0, J = 2.1 Hz, 4H), 4.43-4-33 (m, 1H), 4.02 (t, J = 6.5 Hz, 2H), 3.65 (t, J = 6.5 Hz, 2H), 1.87-1.35 (m, 10H), 1.33 (d, J = 6.1, 3H), 0.99 (t, J = 7.5 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 161.00, 160.28, 146.90, 146.71, 124.27, 124.23, 115.73, 114.58, 75.23, 68.08, 62.74, 32.59, 29.12, 29.08, 25.81, 25.49, 19.16, 9.70. IR (KBr, cm^{-1}): 3384 (broad), 2943, 2855, 1593, 1493, 1242, 1143, 841.

(R)-4-Methylheptyloxy-4'-(6"-hydroxyhexyl-1"-oxy)azobenzene **8(R).** Prepared from **6(R)** according to the procedure described for **7(R).** Yellow powder (83 % yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.85 (dd, J = 9.0 Hz, J = 3.0 Hz, 4H), 6.98 (dd, J = 9.0, J = 5.8 Hz, 4H), 4.47-4-40 (m, 1H), 4.04 (t, J = 6.5 Hz, 2H), 3.67 (t, J = 6.5 Hz, 2H), 1.88-1.72 (m, 3H), 1.67-1.22 (m, 18H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 161.02, 160.32, 146.96, 146.75, 124.30, 124.25, 115.75, 114.62, 74.17, 68.12, 62.88, 36.40, 32.68, 31.77, 29.24, 29.17, 25.86, 25.53, 25.46, 22.58, 19.13, 14.07. IR (KBr, cm^{-1}): 3382 (broad), 2940, 2857, 1590, 1499, 1253, 1143, 842. Anal. Found (calcd): C 73.04% (73.20), H 8.94% (8.98), N 6.56% (6.57).

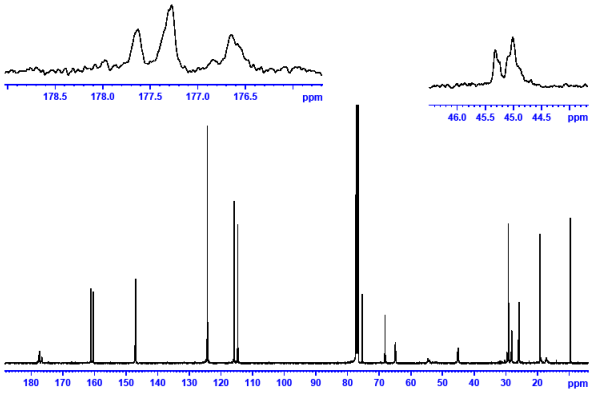
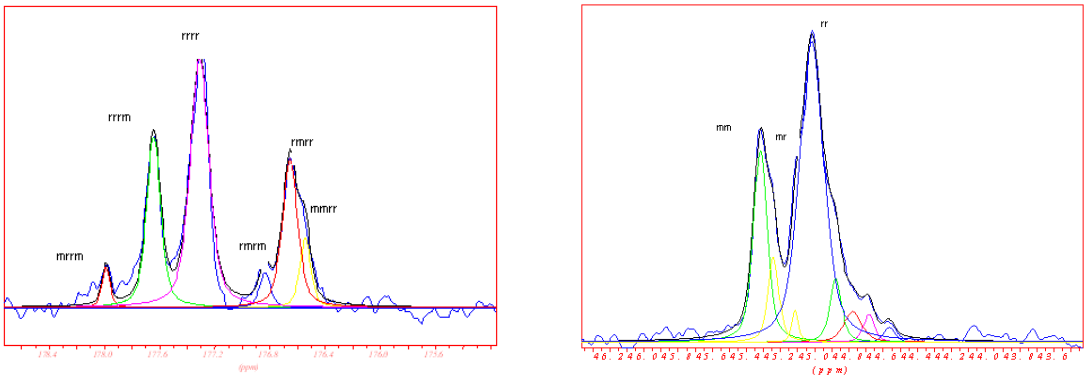


Figure S1. ^{13}C NMR of the polymer P4S. Inset of the region corresponding to C=O and CH_2 (methylenic chain group) is included.



No.	Pos. [ppm]	Int. (abs.)	Width [Hz]	G/L	Integral (abs.)
1	177.9880	19694	6.76	0.50	2.568729e+005
2	177.6418	82546	12.18	0.50	1.939907e+006
3	176.5425	33535	9.47	0.50	6.127537e+005
4	176.8350	16948	9.47	0.50	3.096750e+005
5	177.3090	120828	16.23	0.50	3.783762e+006
6	176.6538	72187	13.17	0.50	1.834351e+006
7	45.3177	108095	9.76	0.50	2.035603e+006
8	45.2412	47700	7.70	0.50	7.086745e+005
9	44.5625	8149	7.70	0.50	1.210876e+005
10	44.6824	15544	7.70	0.50	2.309834e+005
11	44.7768	17126	12.32	0.50	4.071876e+005
12	44.8763	35835	8.21	0.50	5.679930e+005
13	45.1136	17917	4.62	0.50	1.597480e+005
14	45.0166	169520	16.94	0.50	5.541791e+006

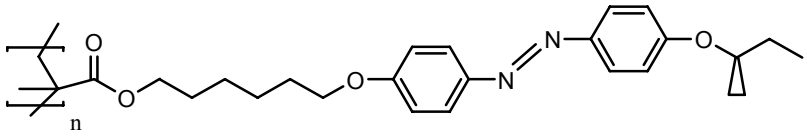


Figure S2. Deconvolution of the ^{13}C NMR signals corresponding to the C=O and CH_2 (chain) groups of P4S (see chemical structure).

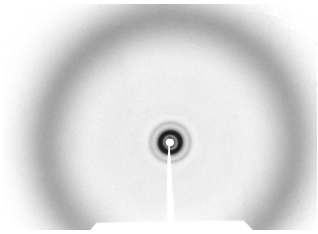


Figure S3. X-Ray pattern of a sample of P8S cooled at 1ºC/min.

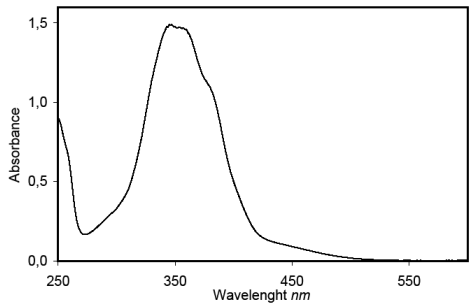


Figure S4. UV- vis spectrum of a film of P8S cooled at 20ºC/min.

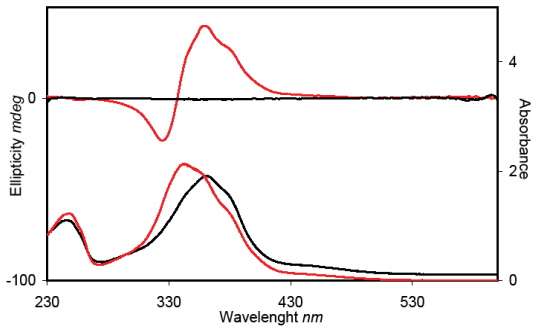


Figure S5. UV-vis (down) and CD spectra (up) of P8R in DCM solution (——) and in DCM/hexane solution (——).

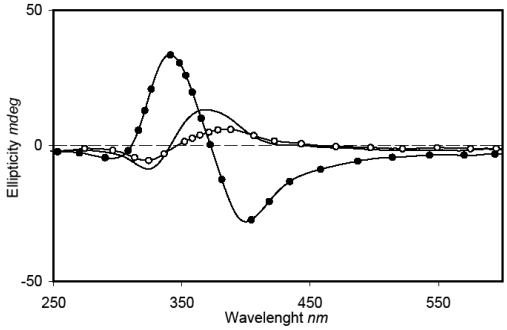


Figure S6. CD spectra of P8R as prepared film (——), and annealed at isotropic temperature and after cooled down at 10ºC/min (—O—) and 1.2ºC/min (—●—).