

Synthesis

Synthesis of the mesogens

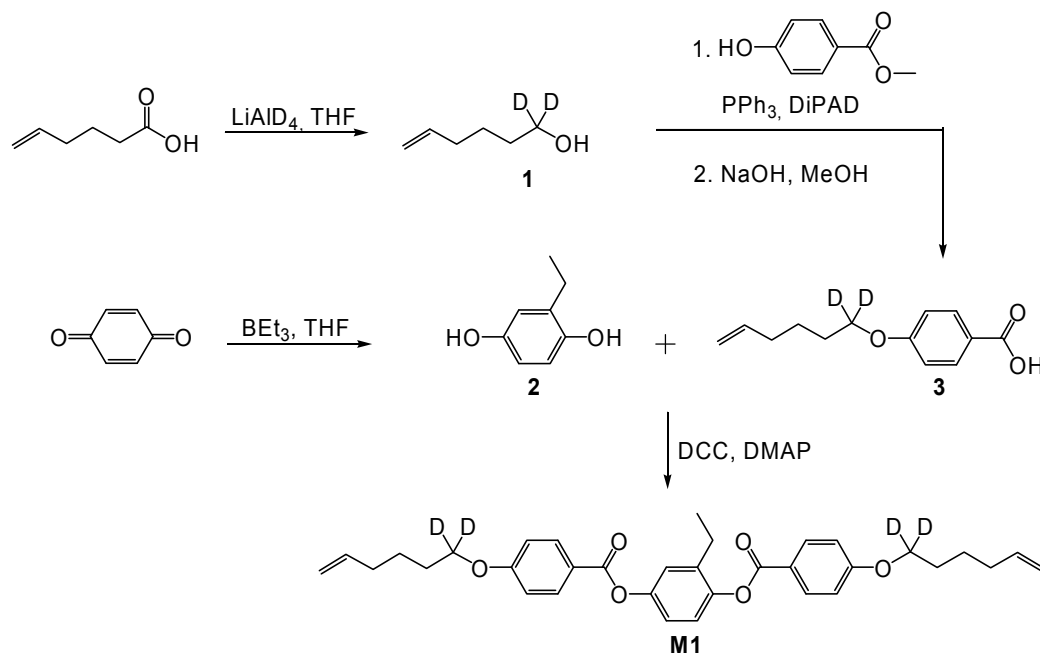


FIG. S1: Synthesis of the deuterated mesogen **M1**.

1D,1D-Hex-5-ene-1-ol, 1

LiAlD₄ (3.52 g, 84 mmol, 1 eq.) was suspended in freshly distilled tetrahydrofuran (THF) (40 ml) under argon atmosphere and cooled with an ice bath. Hex-5-ene acid (10 ml, 9.60 g, 84 mmol) was added drop wise during 1.5 h and the mixture was stirred at room temperature over night. Then, water (5 ml) and successively aqueous NaOH (15%, 3.7 ml) was added to eliminate excess of LiAlD₄. The white solid was filtered off and washed with Et₂O. After washing the ethereal phase with water (3 × 20 ml) it was dried over MgSO₄ and distilled two times at ambient pressure (T(oil bath) = 192 °C). The deuterated alcohol **1** was isolated as a colourless liquid (4.3 g, 42 mmol, 50%).

$^1\text{H-NMR}$ (300 MHz, CDCl_3): δ = 1.37-1.56 (m, 4H, 3- CH_2 and 4- CH_2), 2.02-2.09 (m, 2H, 2- CH_2), 2.65 (bs, 1H, OH), 4.91-5.01 (m, 2H, 6- CH_2), 5.72-5.85 (m, 1H, 5-CH).

2-Ethylbenzene-1,4-diol, 2

A three neck flask with thermometer, dropping funnel and argon supply was equipped with triethylborane (1 M solution in THF, 100 ml, 0.1 mol, 1.1 eq.) under argon atmosphere and a solution of 1,4-benzoquinone (9.8 g, 0.091 mol, 1.0 eq.) in THF (100 ml) was slowly added under ice-cooling. The mixture was stirred at 0°C for 15 min and another 3 h at room temperature. Degassed water (10 ml) was added and the mixture was stirred over night at room temperature. Then the mixture was poured into brine (500 ml) and extracted with Et_2O (4×100 ml).

The organic phases were washed with brine (2×100 ml) and aqueous NaHCO_3 solution (10%, 4×100 ml) and subsequently dried over MgSO_4 . After evaporation of the solvent the product **2** was dried *in vacuo* and obtained as a yellow powder (7.8 g, 57 mmol, 62%). The following reaction steps were done without further purification.

$^1\text{H-NMR}$ (300 MHz, acetone- d_6): δ = 1.15 (t, 3H, $-\text{CH}_3$), 2.55 (q, 2H, CH_2 -), 6.47 (dd, 1H, 5-H), 6.61 (dd, 1H, 6-H), 6.65 (d, 1H, 3-H).

4-(1'D,1'D-Hex-5'-enoxy)benzoic acid, 3

4-Hydroxybenzoic acid methyl ester (6.4 g, 42 mmol), the deuterated alcohol **2** (5.2 g, 51 mmol, 1.2 eq.) and triphenylphosphine (PPh_3) (15.9 g, 63 mmol, 1.5 eq.) were dissolved in dry THF (100 ml). A solution of diazocarboxylic acid diisopropyl ester (DiPAD) (12.5 ml, 12.5 g, 63 mmol, 1.5 eq.) in THF (20 ml) was added under ice cooling during 2 h. Et_2O was added to the reaction mixture, the mixture was cooled over night and the precipitated triphenylphosphine oxide was filtrated off. For the saponification, the solvent was evaporated

and NaOH (3.4 g, 84 mmol, 2 eq.) dissolved in methanol (100 ml) and water (50 ml) was added. After heating under reflux for 2 h, the mixture was stirred over night at room temperature. Afterwards, concentrated HCl was added carefully until $pH = 1$ was reached. The precipitate was filtered, washed with water and recrystallised from methanol and *iso*-hexane to give a colourless crystalline solid (5.6 g, 25.1 mmol, 60%).

$^1\text{H-NMR}$ (300 MHz, acetone- d_6): $\delta = 1.33$ (tt, 2H, 3'-CH₂), 1.94-1.98 (m, 2H, 4'-CH₂), 2.30 (t, 2H, 2'-CH₂), 5.05-5.17 (m, 2H, 6'-CH₂), 5.77-5.91 (m, 1H, 5'-CH), 6.84-6.89 (m, 2H, 2-CH and 3-CH), 7.96-8.01 (m, 2H, 1-CH and 4-CH), 11.50 (bs, 1H, COOH).

Deuterated mesogenic monomer, **M1**

Ethylhydroquinone **3** (5 g, 36.2 mmol), the benzoic acid **2** (17.7 g, 79.6 mmol, 2.2 eq.) and 4-(dimethylamino)-pyridine (DMAP) (9.7 g, 79.6 mmol, 2.2 eq.) were dissolved in dry CH₂Cl₂ (300 ml) and *N,N'*-Dicyclohexylcarbodiimide (DCC) (16.4 g, 79.6 mmol, 2.2 eq.) dissolved in CH₂Cl₂ (50 ml) was added over 1 h at room temperature. After stirring over night at room temperature, the precipitated urea was filtered off and the raw product was filtrated over silica gel using CH₂Cl₂ as a solvent. The solvent was evaporated from the filtrate and the remaining white solid was recrystallised from *iso*-hexane to yield **M1** as colourless crystals (17 g, 31 mmol, 86%).

$^1\text{H-NMR}$ (300 MHz, CDCl₃): $\delta = 1.15$ (t, 3H, -CH₃), 1.53 (m, 4H, 2 x 2''-CH₂), 1.77 (tt, 4H, 2 x 3''-CH₂), 2.08 (td, 4H, 2 x 4''-CH₂), 2.55 (q, 2H, CH₂-), 4.90-5.02 (m, 4H, 2 x 6''-CH₂), 5.70-5.84 (m, 2H, 2 x 5''-CH), 6.88-6.93 (m, 2 x 3'-CH and 2 x 4'-CH), 7.00-7.13 (m, 3H, 2-CH, 3-CH and 4-CH), 8.06-8.11 (m, 4H, 2 x 2'-CH and 2 x 5'-CH).

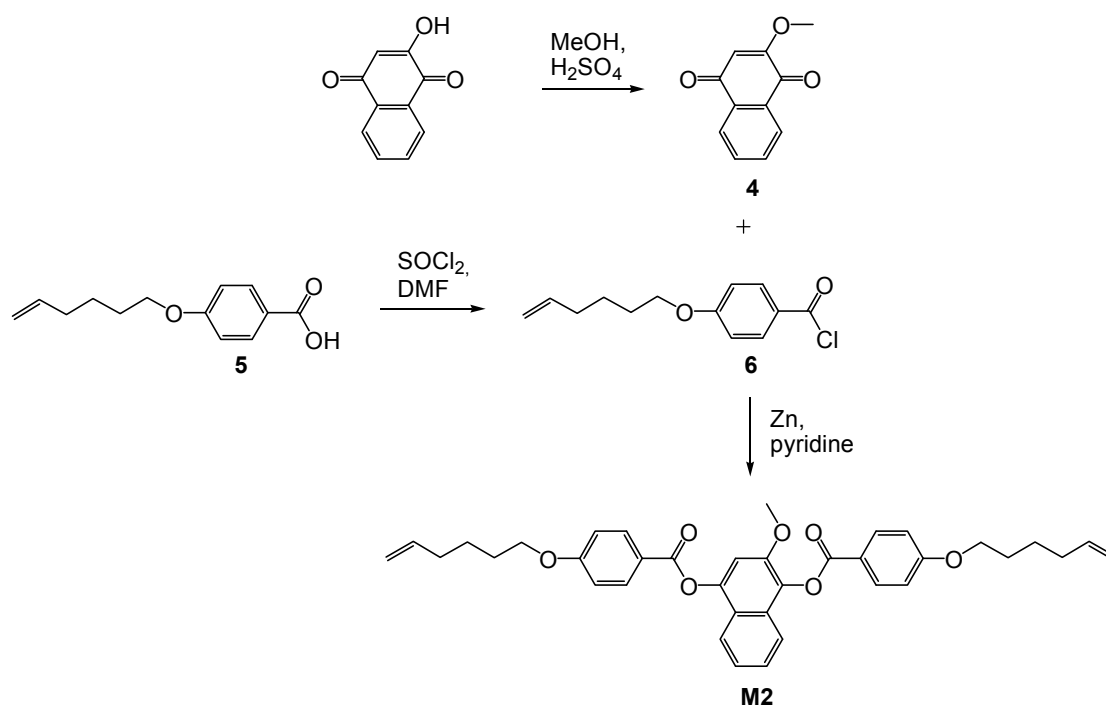


FIG. S2: Synthesis of the naphthalene mesogen **M2**.

1-Methoxynaphthoquinone, **4**

1-Hydroxynaphthoquinone (7.8 g, 45 mmol) was suspended in methanol (400 ml). Concentrated sulfuric acid (95%, 2 ml) was added and the mixture heated to reflux over night. After raising the *pH* to 7 using aqueous NaOH, the solvent was removed in vacuo and the residues were recrystallised twice from methanol (7.9 g, 40.7 mmol, 91%).

¹H-NMR (250 MHz; CDCl₃): δ = 3.84 (s, 3H, -OCH₃), 6.11 (s, 1H, 3-H), 7.60-7.72 (m, 2H, 6-H and 7-H), 8.00-8.09 (m, 2H, 5-H and 8-H).

Mesogenic naphthalene monomer, **M2**

Freshly distilled thionyl chloride (6.5 ml, 10.6 g, 82.5 mmol, 15 Äquiv.) and *N,N*-dimethyleformamide (DMF, catalytic) were added to the undeuterated benzoic acid derivative **5** (1.21 g, 5.5 mmol, 1.1 eq., synthesised analogous to **3**, starting with undeuterated reactants)

and heated to reflux under argon atmosphere for 4 h. Afterwards, the excess of thionyl chloride was removed *in vacuo*.

Zinc powder (8.0 g, 122 mmol) was stirred in aqueous HCl (3%, 30 ml) at room temperature for 20 min. Subsequently, the zinc was filtrated, washed with water (20 ml) and acetone (20 ml) and dried *in vacuo* (80°C, 20 mbar) over night.

The quinone **4** (0.48 g, 2.5 mmol, 1 eq.) was dissolved in dry pyridine (20 ml, dried over 4 Å molecular sieves), the activated zinc (0.55 g, 8.3 mmol, 1.7 eq.) was added and the mixture was stirred for 30 min. The chloride **6** was dissolved in dry pyridine (20 ml) and added to the quinone solution over 1 h. The mixture was stirred over night, the solvent was evaporated and the residues were dissolved in ethyl acetate (100 ml). The organic phases were washed with aqueous HCl (3%, 3 × 30 ml) and water (3 × 30 ml) and the aqueous phases were successively extracted with ethyl acetate (3 × 50 ml). The organic phases were dried over MgSO₄ and the solvent was evaporated. Purification by column chromatography (15 cm, silica, cyclohexane:ethyl acetate 5:1, 50 ml per fraction) and recrystallisation from methanol yielded the mesogen **M2** as colourless crystals (0.66 g, 1.1 mmol, 44%).

¹H-NMR (250 MHz; CDCl₃): δ = 1.55 (tt, 4H, 2 × 3''-CH₂), 1.80 (tt, 4H, 2 × 2''-CH₂), 2.09 (tdt, 4H, 4''-CH₂), 3.87 (s, 3H, -OCH₃), 4.02 (t, 4H, 1''-CH₂), 4.91-5.03 (m, 4H, 2 × 6''-CH₂), 5.76 (ddt, 2H, 2 × 5''-CH), 6.93-6.99 (m, 4H, 2 × 3'-CH and 2 × 5'-CH), 7.25-7.42 (m, 3H, 3-CH and 6-CH u. 7-CH), 7.80 (ddd, 2H, 5-CH and 8-CH), 8.18-8.24 (m, 4H, 2 × 2'-CH and 2 × 6'-CH).

Synthesis of the linear polymers

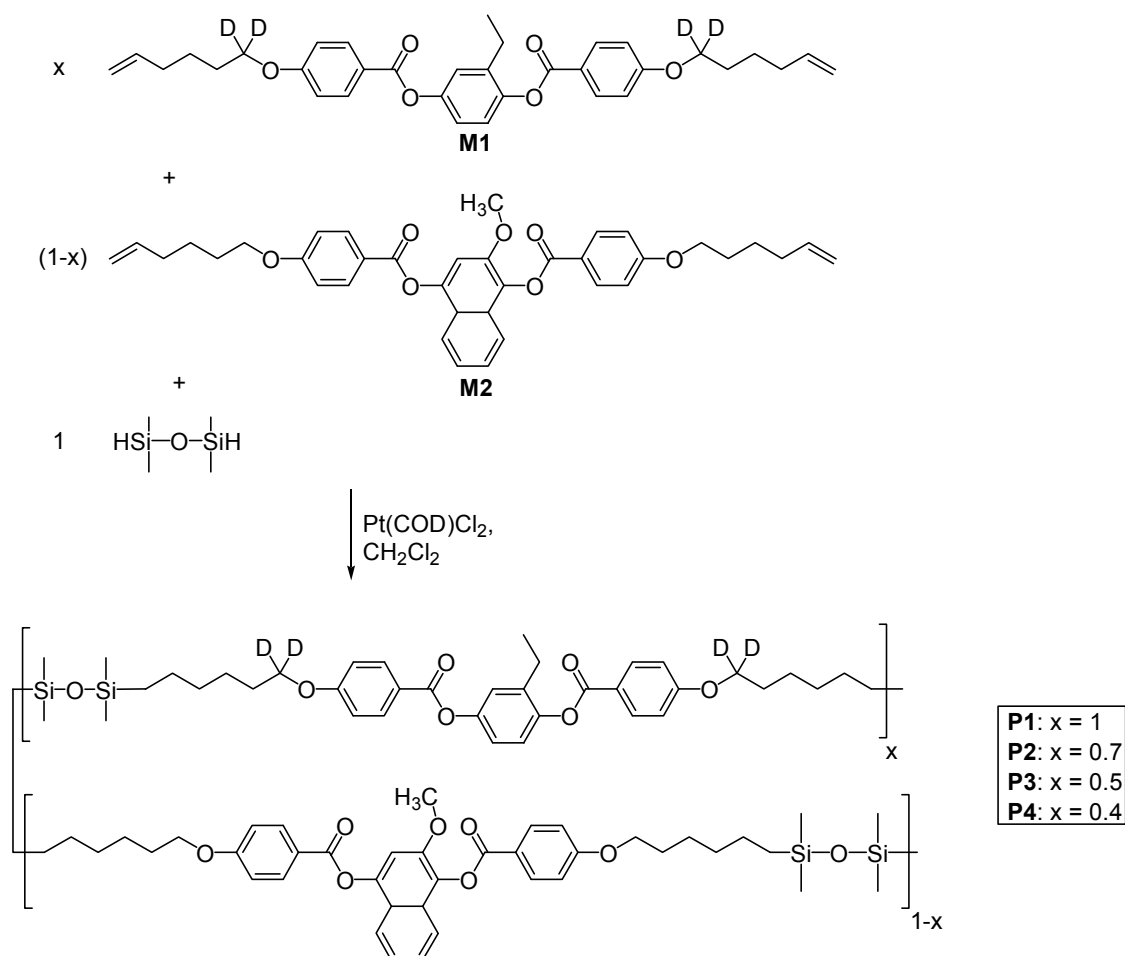


FIG. S3: Synthesis of the investigated polymers **P1-P4**.

The mesogens **M1** and **M2** were placed into a glass vessel and the volatile comonomer dihydrotetramethyldisiloxane (TMS) was added in slight excess and left to evaporate until stoichiometric conditions were reached. The solvent and the catalyst (30 μl , 1 % w/w Pt(COD)Cl_2 in CH_2Cl_2) were added quickly and the reaction mixture was stirred for 4 days at 60°C. The quantities of the reactants used for the polymers can be found in Table S1.

The copolymers were precipitated four times from different solvents (a mixture of Et_2O and methanol for **P2-P4** and pure methanol in the case of **P1**) and dried *in vacuo*.

The linear polymers exhibit degrees of polymerisation between $\overline{DP} = 32$ and $\overline{DP} = 11$ (Table S2). The polydispersity of the copolymers **P2-P4** is lower than that of **P1** because they were precipitated from a mixture of Et₂O and methanol, in which oligomeric compounds are also soluble.

The relation in which the mesogens **M1** and **M2** were incorporated into the copolymers **P2-P4** were measured by comparing the intensities of characteristic peaks for the two mesogens (**M1**: q at $\delta = 2.54$, 2H, ethyl-CH₂; **M2**: s at $\delta = 3.87$, 3H, methyl-CH₃) in the ¹H-NMR spectra of the copolymers. Thereby deviations from the given quantities were found and the fraction of **M2** was higher than expected. Hence, **M2** seems to be inserted preferably into the copolymers and it seems to have a higher reactivity (possibly due to a higher purity of the monomer) as compared to **M1**.

TABLE S1: Quantities of the reactants and solvent used for the synthesis of the polymers **P1-P4**

	fraction of M1 in reaction mixture	x	M1	M2	TMS	solvent
P1	1	1	385.3 mg, 0.7 mmol		95 mg, 0.7 mmol	thiophene-free toluene (1.7 ml)
P2	0.7	0.5	535.4 mg, 0.98 mmol	250.4 mg, 0.42 mmol	187.7 mg, 1.4 mmol	CH ₂ Cl ₂ (1.5 ml)
P3	0.5	0.4	382.2 mg, 0.70 mmol	417.4 mg, 0.70 mmol	187.7 mg, 1.4 mmol	CH ₂ Cl ₂ (1.5 ml)
P3	0.4	0.3	305.9 mg, 0.56 mmol	500.9 mg, 0.84 mmol	187.7 mg, 1.4 mmol	CH ₂ Cl ₂ (1.5 ml)

TABLE S2: Number- and weight-average molecular weight M_n and M_w , polydispersities PD and average degree of polymerization \overline{DP} of the polymers **P1-P4** as measured by means of GPC.

	x	M_w (g/mol)	M_n (g/mol)	PD	\overline{DP}
P1	1	68000	22000	3.2	32
P2	0.5	13000	8000	1.6	11
P3	0.4	17000	10000	1.7	14
P4	0.3	19000	10000	1.9	14

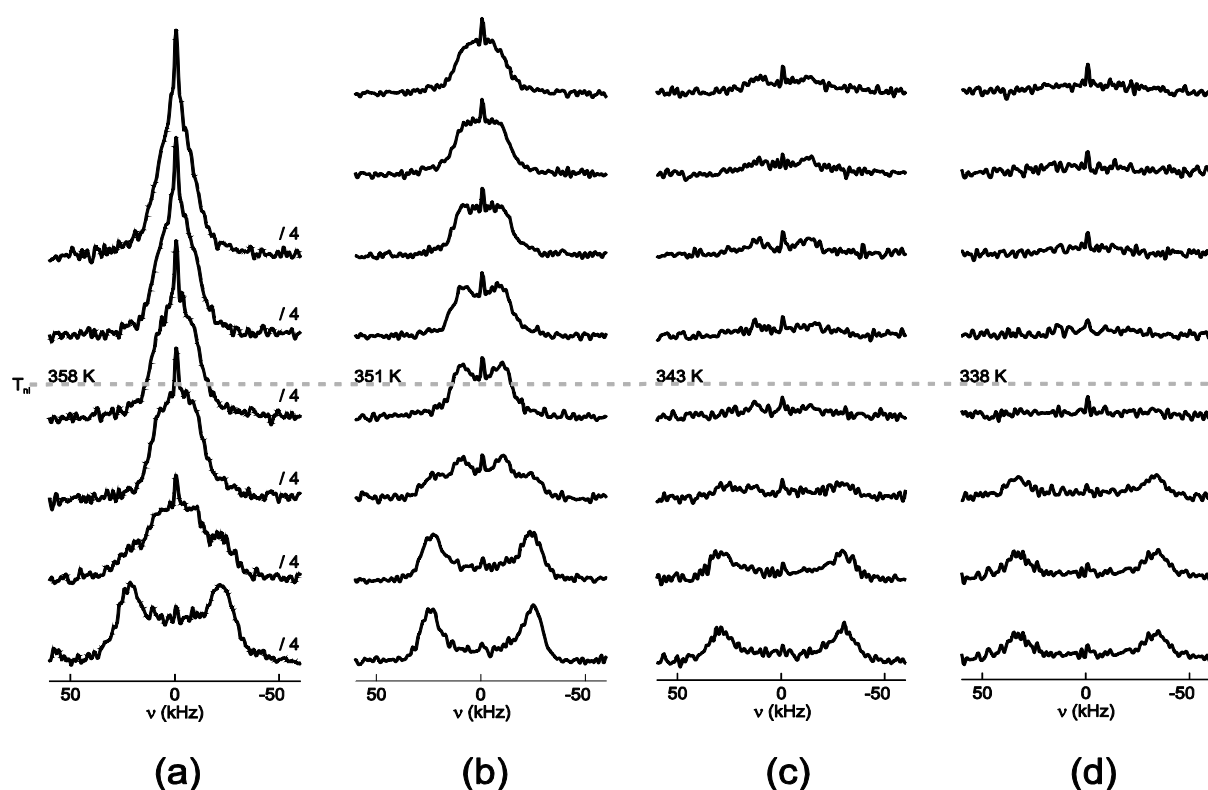
Methods

Number- (M_n) and weight-average (M_w) molecular weights and polydispersities ($PD = M_w/M_n$) were determined by gel permeation chromatography (GPC) versus polystyrene standards. The GPC measurements were carried out at 303 K in chloroform with PSS-SDV columns (8.0 mm x 30 mm, 5 mm particles, 103, 104, 105, 106 Å pore size). For detection, a refractive index detector was used.

Transition temperatures were determined by differential scanning calorimetry (DSC) using a Perkin Elmer DSC-7 instrument. Thermal properties were determined from extrapolation to zero heating rate using heating runs of 5, 10, 20 and 40 K·min⁻¹.

²H-NMR experiments were performed on a Bruker Avance 500 solid-state NMR spectrometer ($B_0 = 11.7$ T, $\nu(^2\text{H}) = 76.8$ MHz). Angle steps were controlled by a servomotor triggered by pulses from the NMR console. Solid echo experiments were performed with 90° pulses of 4 μs length and 43 μs spacing and acquisition times of 8.24 ms. The spectra were recorded with various numbers of scans ranging from 14k to 1k. Typically, to save experimental time less scans were used at higher temperatures leading to lower SNR. To compare the signal intensity all spectra were then normalised to the number of scans - any additional scaling factors are given in the spectra.

^2H -NMR spectra at temperatures around T_{ni}



S4: ^2H -NMR spectra of the polymers **P1-P4** (a)-(d) measured in 1 K steps at temperatures around T_{ni} . The spectra were recorded with the first director oriented parallel to the magnetic field of the experiment.

The homopolymer **P1** and the copolymer **P2** exhibit a subcritical transition from the isotropic to the nematic state, as indicated by the biphasic spectra observed at temperatures around T_{ni} (Fig. S4a-b). For the copolymers **P3** and **P4**, with a direct transition from the isotropic to the biaxial-nematic phase, the intensity of the spectra in the isotropic phase is extremely low because of the slow molecular dynamics (Fig. S4c-d). It is therefore not possible to conclude from the ^2H -NMR spectra whether the phase transition is of first or, as might be expected, of second order.

The spectra of the copolymers **P2** and **P3** show a clear splitting in the isotropic phase (Fig. S4b-c) which is superimposed by an isotropic peak at higher temperatures. For the homopolymer **P1** the isotropic spectrum at temperatures close to T_{ni} is also unusually broad and it seems plausible that an underlying duplet is also present (Fig. S4a).

A splitting of the ^2H -NMR spectra in the isotropic phase is often observed for the paranematic phase of crosslinked LC polymers.^[1] However, all investigated polymers are viscous melts in the isotropic phase, appearing completely black under crossed polarisers, also after several heating and cooling runs. They also remain soluble in *e. g.* chloroform (DSC samples, 4 heating and cooling runs with heating and cooling rates from 40 to 5 K min⁻¹ from -50 to 150 °C). Furthermore, all spectra were recorded starting from the isotropic phase and cooling to the nematic phase, where the mesogens were able to orient in the magnetic field, which would not have been possible if they were crosslinked in the isotropic phase. Hence, there is no sign of thermally induced crosslinking of the polymers which could explain the development of a broad paranematic phase.

It can be assumed that the magnetic field of the NMR experiment can induce a paramagnetic phase. Gramsbergen *et al.*^[2] calculated for typical values of $|\Delta\chi_{\text{max}}| = 10^{-7}$ and a magnetic field of $B = 15$ T an induced nematic order at T_{ni} of $S \approx 10^{-5}$ - 10^{-4} compared to $S \approx 0.3$ in the nematic phase. This is much smaller than what we observe here as judged from the relation of the splittings in the nematic and the isotropic state of the copolymer **P2** ($\Delta v_n / \Delta v_i \approx 2.5$).

It is known from observations of the molecular dynamics of nematic main-chain polymers and elastomers that the rotation of the mesogens around their short axes sets in at temperatures around T_{ni} .^[3] As the mesogenic moieties are connected to each other via flexible spacers, it might be speculated that this rotation is quite uniform and leads to a preferred average orientation of the mesogens with respect to the magnetic field although the mesogens show overall isotropic behaviour. Especially since only the fraction of mesogens whose dynamics is

already faster than the time-scale of the NMR experiment are observed in this temperature range, this might be possible explanation of the effect.

To finally explain the splitting of the isotropic spectra more detailed NMR experiments are necessary which will probably be complicated by the low signal intensity.

[1] A. Lebar, G. Cordoyiannis, Z. Kutnjak und B. Zalar, *Advances in Polymer Science*, 2012, 1-39, DOI: 10.1007/12_2010_103.

[2] E. F. Gramsbergen, L. Longa and W. H. de Jeu, *Physics Reports*, **4**, 195 (1986).

[3] F. Brömmel, W. Stille, H. Finkelmann, and A. Hoffmann, *Soft Matter* **7**, 2387 (2011).