Supplementary Information

Mesomorphism and Shape-Memory Behavior of Main-Chain Liquid-Crystalline Co-Elastomers:

Modulation by the Chemical Composition

Alfonso García-Márquez,[1] Benoît Heinrich,[1] Nicolas Beyer,[1] Daniel Guillon,[1] and Bertrand Donnio[*,1,2]

1. *Institut de Physique et de Chimie des Matériaux de Strasbourg (IPCMS), UMR 7504 (CNRS-Université de Strasbourg), 23 Rue du Loess BP 43, 67034 Strasbourg Cedex 2, France.* *Bertrand.Donnio@ipcms.unistra.fr*

2. *Complex Assemblies of Soft Matter Laboratory (COMPASS), UMI 3254 (CNRS-Solvay-University of Pennsylvania), CRTB, 350 George Patterson Boulevard, Bristol, PA 19007, USA.*

Table of content

1. Materials and Methods

1.1. Instrumentation

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 300 (300 MHz) spectrometer. The internal references of the spectrum correspond to the peak of the solvent CDCl$_3$ (ppm).

Elemental analyses were realized at the Charles Sadron Institute Strasbourg (France).

Polymers were characterized using Gel Permeation Chromatography (GPC), obtained using a Waters Chromatographer.

The optical textures of the mesophases were studied with a Leitz optical polarizing microscope equipped with a Mettler FP82 hot-stage and a Mettler FP80 central processor.

The thermal properties were investigated using a differential scanning calorimetry (DSC) with a TA Instruments DSC-Q1000 instruments operated at scanning rates in a range from 2 to 10°C.min^{-1}.

The TGA measurements were carried out on a SDTQ 600 apparatus at scanning rate of 10°C min^{-1}, under air.

The oriented SAXS patterns were recorded by using a pinhole Cu-Kα (λ = 1.542 Å) parallel beam from a sealed-tube generator (900 W) equipped with a home-mounted Kirkpatrick-Baez optics, the detector to sample distance being 107.3 mm. Phosphor imaging screens were used for detection, scanned with a Storm820 scanner of Molecular Dynamics and analyzed using homemade ImageJ plug-ins. A piece of the elastomeric film was placed in a home-made heating apparatus. During the experiment, the temperature was controlled within ±0.03°C.

Elastomer films were prepared with a Sigma 3-16 centrifuge (Fisher Scientific Bioblock). The rotor was replaced by a home-built cylindrical PTFE Cell and surrounded by a specially designed molded resistance (Cetal). PT100 sensors were placed in cavities of the heating element and of the rotor axis top; the calibration of the thermal path allowed the control of the cell temperature within a few degrees. Temperature control and measurements were performed by using a 3208N-7100A PID module (Eurotherm) and a Nokeval 2021 meter (Dimelco). See images section 7.

Elongation measurements were performed with a home-built glass heat exchanger connected to a Unistat silicone oil-circulating bath (Huber), in which the elastomer film was suspended and eventually loaded with a mass. A PT100 sensor close to the film and connected to a Nokeval

2021 meter allowed film temperature control within one degree. Pictures of the film were registered with a digital camera (Fuji S1Pro) and treated with the ImageJ software to calculate the elongation ratio.

1.2. Materials

1.2.1. Chemicals were used as purchased, without further purification

4-benzyloxybenzoic acid (99 %), methyl 4-hydroxybenzoate, 4-benzyloxyphenol (99 %), 4-dimethylaminopyridine (DMAP, 99 %) were purchased from Alfa-Aesar. 4-Vinyloxybutanol (99 %), triphenylphosphine (PPh_3, 99 %), diisopropyl azodicarboxylate (DIAD, 94 %) were obtained from Acros. Methyl-hydroquinone (98 %), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI.HCl), $PtCODCl_2$ (98 %) and tetramethyldisiloxane (TMDS, 97 % pure) were purchased from Aldrich. DCC (N,N-dicyclohexylcarbodiimide) (99 %) and Pd/C catalyst (99 %) were obtained from Lancaster. 1,1,3,3,5,5-Hexamethyltrisiloxane (HTMS) and 2,4,6,8,10-pentamethyl-1,3,5,7,9,2,4,6,8,10-pentaoxapentasilecane (HD5) were purchased from ABCR.

1.2.2. All solvents were distilled before use

Dimethylformamide (DMF) was obtained from Normapur (99.8 % pure). Hexane and cyclohexane were obtained from Carlo-Erba (>99.9 % pure). Methanol (MeOH), obtained from Carlo Erba (>99.9 % pure), was dried over magnesium turnings and iodine before distillation. Dichloromethane (CH_2Cl_2), obtained from Carlo Erba (stabilized with amylene, 99.8 % pure), was distilled over calcium chloride prior to chemical reactions and N_2-chromatography columns. Tetrahydofuran (THF), obtained from Ridel-de-Haën (> 99 % pure), was dried over potassium hydroxide, and distilled over sodium wire and before use. Toluene, purchased from Alfa Aesar (99.5 % pure), was first extracted with concentrated sulfuric acid until the acidic phase was colorless, then washed with brine and dried over sodium sulfate and finally distilled over sodium wire and stored over 3Å molecular sieves. HCl was obtained from Normapur (37 % pure).

2. Synthesis

2.1. Monomers Synthesis

2-Methyl-1,4-phenylene bis(4-(benzyloxy)benzoate), **1**
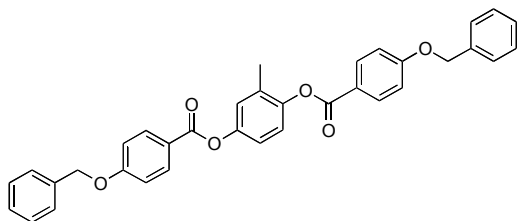
In a 500 mL three-necked, round-bottom flask, 6.00 g (26.3 mmol) of 4-benzyloxybenzoic acid, 1.65 g (13.3 mmol) of 4-hydroxy-2-methylphenol (methylhydroquinone) and 0.43 g (3.5 mmol) of 4-(*N,N*-dimethylamino)pirydine (DMAP) were added, dried in vacuum with a heating gun and then dissolved in 100 mL of dry dichloromethane. Argon was added and the emulsion cooled to 0° C. 7.30 g (38.1 mmol) of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI.HCl) were added and the reaction mixture was magnetically stirred for 5h. The resulting solution was extracted with brine (2x 500 mL) and the organic phase was then recovered and concentrated in vacuum. The residue was purified by chromatography column (SiO$_2$, dichloromethane) to yield 5.80 g of a white solid (67 %). ^{1}H-RMN (300 MHz, CDCl$_3$) δ (ppm): 2.26 (3H, s, CH$_3$), 5.19 (4H, s, BnCH$_2$O), 7.08 (2H, d, ^{HH}J=8.8 Hz, *m*-Ar''), 7.10 (2H, d, ^{HH}J=9.0 Hz, *m*-Ar'), 7.19 (3H, m, Ar [a]), 7.47 (10H, m, Ph-H), 8.18 (2H, d, ^{HH}J=7.9 Hz, *o*-Ar''), 8.21 (2H, d, ^{HH}J=8.5 Hz, *o*-Ar'). Both Ar' and Ar'' rings are unequivalent due to the methyl substituent in the central ring (Ar), which reduces the overall-symmetry of the molecule.

2-Methyl-1,4-phenylene bis(4-hydroxybenzoate), **2**
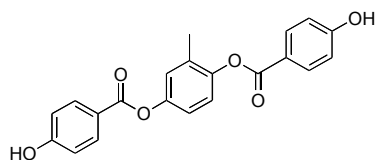
In a 500 mL two-necked, round-bottom flask, 4.50 g (8.26 mmol) of **1** were dissolved in 250 mL of dry tetrahydrofuran (THF) and the solution flushed with argon. 25 mg of palladium in charcoal (10%) were slightly added and placed in a specially designed hydrogenation system. The mixture

was stirred at room temperature until the starting product was consumed. The black suspension was filtered on Celite ® and the solvent evaporated in vaccuo to give 2.88 g of a white solid (96 %). ^{1}H-RMN (300 MHz, $(CD_3)_2CO$) δ (ppm): 2.22 (3H, s, CH_3), 6.99 (2H, d, ^{HH}J=8.6, m-Ar''), 7.01 (2H, d, ^{HH}J=8.6 Hz, m-Ar'), 7.18 (3H, m, Ar), 8.05 (2H, d, ^{HH}J=8.5 Hz, o-Ar''), 8.08 (2H, d, ^{HH}J=8.5 Hz, o-Ar'). Both Ar' and Ar'' rings are unequivalent due to the methyl substituent in the central ring (Ar), which reduces the overall-symmetry of the molecule.

2-Methyl-1,4-phenylene bis(4-(4-vinyloxy)butoxy)benzoate), monomer **N1**
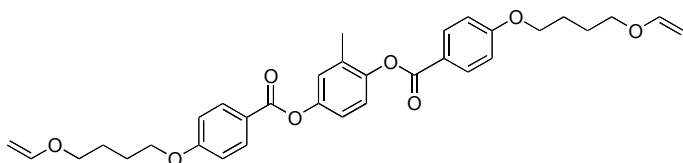
In a three-necked, round-bottom flask, 2.78 g (7.63 mmol) of **2** and 4.80 g (18.3 mmol) of triphenylphosphine (PPh_3) were added. An argon flush was performed and the solids were dissolved in 150 mL of anhydrous THF. The mixture was stirred and cooled down to 0ºC. Then 2.27 mL (18.3 mmol) of 4-vinyloxybutanol were added followed by 3.34 mL (16.0 mmol) of diisopropylazodicarboxylate (DIAD), added dropwise. The reaction mixture was kept at 0ºC for 1 h and left to warm up to room temperature for 8 h. The resulting solution was concentrated to dryness and redissolved in a minimum quantity of a mixture of dichloromethane-cyclohexane (1:3) and purified by chromatography column (triethylamine-neutralized SiO_2, dichloromethane-cyclohexane (1:3)). The crude product was dried and crystallized from anhydrous methanol (white crystals 3.3 g, 77 %). Elemental analysis for $C_{33}H_{36}O_8$ (MW = 560.63 g.mol^{-1}): Calcd: C% 70.70, H% 6.47; Found: C% 71.19, H% 6.34. ^{1}H-RMN (300 MHz, $CDCl_3$) δ (ppm): 1.91 (8H, m, C$\underline{H}_2$-CH_2O), 2.25 (3H, s, CH_3), 3.78 (4H, t, ^3J=5.9 Hz, CH_2O), 4.02 (2H, dd, ^{2gem}J=2.0 Hz; ^{3cis}J=6.0 Hz, C$\underline{H}_2$=CH-O), 4.11 (4H, t, ^3J=4.6 Hz, CH_2-O), 4.21 (2H, dd, ^{2gem}J=2.0 Hz; $^{3trans}J$=12.0 Hz, C$\underline{H}_2$=CH-O), 6.50 (2H, dd, ^{3cis}J=6.8 Hz; $^{3trans}J$=7.4 Hz, CH_2=C$\underline{H}$-O), 6.98 (2H, d, ^2J=6.8 Hz, m-Ar''), 6.99 (2H, d, ^{HH}J=6.8 Hz, m-Ar'), 7.11 (3H, m, Ar), 8.14 (2H, d, ^{HH}J=7.8 Hz, o-Ar''), 8.17 (2H, d, ^{HH}J=7.9 Hz, o-Ar'). ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm): 16.4 (CH_3), 22.0 (CH_2), 25.6 (CH_2), 25.8 (CH_2), 67.4 ($\underline{C}H_2OCH$=CH_2), 67.5 ($\underline{C}H_2OCH$=CH_2), 67.7 (CH_2OAr''), 67.8 (CH_2OAr'), 86.4 (CH=$\underline{C}H_2$), 114.2 (m-ArH), 120.0 (o-Ar'H), 121.5 (Ar''$_{ipso}$COO), 121.8 (Ar'$_{ipso}$COO), 122.5 (2C, o'-Ar''H), 131.7 (Ar$_{ipso}CH_3$) 132.2 (o-ArH), 147.0 (Ar'$_{ipso}$OCO), 148.4 (Ar''$_{ipso2}$OCO), 151.8 ($\underline{C}H$=CH_2), 163.3 ($ArOCH_2$), 164.5 (Ar''$\underline{C}OOAr$), 164.9 (Ar'$\underline{C}OOAr$). Both Ar' and Ar'' rings are unequivalent due to the methyl substituent in the central ring (Ar), which reduces the overall-symmetry of the molecule.

4-(Benzyloxy)phenyl 4-(benzyloxy)benzoate, **3**
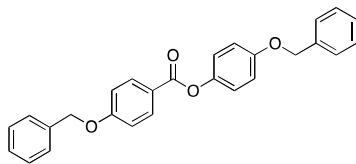
In a three-necked, round-bottom flask, 5.75 g (24.4 mmol) of 4-benzyloxybenzoic acid, 4.89 g (24.4 mmol) of 4-benzyloxyphenol and 0.36 g de DMAP were dried in vacuum with a heating gun and then dissolved in 100 mL of dry dichloromethane. Argon was added and the emulsion cooled to 0ºC. 5.61 g (29.3 mmol) of EDCI were added and the reaction mixture was magnetically stirred for 12h. The resulting solution was extracted with brine (2x 200 mL). The organic phase was then recovered and concentrated in vacuum. The residue was purified by chromatography column (SiO$_2$, dichloromethane) to give 8.28 g of a white solid (83 %). ^{1}H-NMR (300 MHz, CDCl$_3$): δ (ppm): 5.07 (2H, s, PhC$\underline{H}_2$), 5.17 (2H, s, PhC$\underline{H}_2$), 7.00 (2H, d, [HH]J=8.5 Hz, m-Ar), 7.05 (2H, d, [HH]J=8.9 Hz, m-Ar'), 7.12 (2H, d, [HH]J=8.9 Hz, o-Ar), 7.39 (10H, m, $\underline{Ar}$CH$_2$), 8.15 (2H, d, [HH]J=8.5 Hz, o-Ar'). ^{13}C-NMR (75 MHz, acetone-d_6): δ (ppm): 70.2 (Ph$\underline{C}$H$_2$), 164.7 (COOAr), 163.0 (ArOBn), 159.7 (Ar'OBn), 145.3 (Ar'OCO), 134.0 (2C, o-ArH), 123.7 (2C, o-Ar'H), 122.0 (ArCOO), 118.6 (2C, m-Ar'H), 115.9 (m-Ar'H) ppm.

4-Hydroxyphenyl 4-hydroxybenzoate, **4**
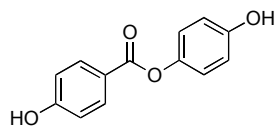
In a 500 mL two-necked, round-bottom flask, 7.50 g (18.3 mmol) of **3** were dissolved in 250 mL of dry THF and the solution flushed with argon. 100 mg of palladium in charcoal (10%) were slightly added and placed in a specially designed hydrogenation system. The mixture was stirred at room temperature until the starting product was consumed. The black suspension was filtered on Celite ® and the solvent evaporated in vaccuo to yield 4.2 g of a white solid (99 %). ^{1}H-NMR (300 MHz, (CD$_3$)$_2$CO): δ (ppm): 6.93 (2H, d, [HH]J=8.5 Hz, m-Ar), 7.07 (2H, d, [HH]J=8.9 Hz, m-Ar'), 7.23 (2H, d, [HH]J=8.9 Hz, o-Ar'), 7.95 (2H, s, OH), 8.03 (2H, d, [HH]J=8.5 Hz, o-Ar). ^{13}C-NMR (75 MHz, acetone-d_6): δ (ppm): 115.9 (2C, m-Ar'H), 118.6 (2C, m-Ar'H), 118.9 (ArCOO), 123.7 (2C, o-Ar'H), 134.0 (2C, o-ArH), 145.3 (Ar'OCO), 155.8 (Ar'OH), 164.1 (ArOH), 165.0 (COOAr).

4-(4-(Vinyloxy)butoxy)phenyl 4-(4-(vinyloxy)butoxy)benzoate, monomer **N2**
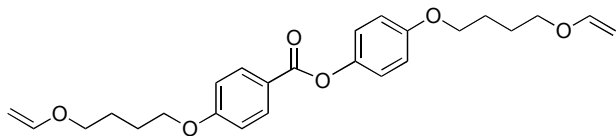
In a three-necked, round-bottom flask, 4.00 g (17.4 mmol) of di-4-hydroxyphenyl 4-hydroxybenzoate **(4)** and 10.94 g (41.7 mmol) of PPh$_3$ were added. An argon flush was performed and the solids were dissolved in 150 mL of anhydrous THF. The mixture was stirred and cooled down to 0ºC. Then 5.16 mL (41.7 mmol) of 4-vinyloxybutanol were added, immediately followed by 7.61 mL (36.5 mmol) of DIAD added dropwise. The reaction mixture was kept to 0ºC for 1 h and left to warm up to room temperature for 8 h. The resulting solution was concentrated to dryness and redissolved in a minimum quantity of a mixture of dichloromethane-cyclohexane (1:3) and purified by chromatography (triethylamine-neutralized SiO$_2$, dichloromethane-cyclohexane (1:3)). The fractions were collected and the solid obtained was finally crystallized from anhydrous methanol to give white crystals, 5.88 g (79 %). Elemental analysis for C$_{25}$H$_{30}$O$_6$ (MW = 426.5 g.mol^{-1}): Calcd: C% 70.40, H% 7.09; Found: C% 70.42, H% 6.91. ^{1}H-RMN (300 MHz, CDCl$_3$), δ (ppm): 1.88 (8H, m, C$\underline{H}_2$-CH$_2$O), 3.77 (4H, t, ^3J=5.9 Hz, CH$_2$O), 4.02 (2H, dd, ^{2gem}J=2.0 Hz; ^{3cis}J=6.0 Hz, C$\underline{H}_2$=CH-O), 4.10 (4H, t, ^3J=6.1 Hz, CH$_2$OAr), 4.20 (2H, dd, ^{2gem}J=1.3 Hz; $^{3trans}J$=14.5 Hz, C$\underline{H}_2$=CH-O), 6.50 (2H, dd, ^{3cis}J=6.8 Hz; $^{3trans}J$=14.3 Hz, CH$_2$=C$\underline{H}$-O), 6.92 (2H, d, ^{HH}J=6.8 Hz, m-Ar), 6.99 (2H, d, ^{HH}J=6.8 Hz, o-Ar), 8.14 (2H, d, ^{HH}J=7.8 Hz, m-Ar'), 8.17 (2H, d, ^{HH}J=7.9 Hz, o-Ar'). ^{13}C-NMR (75 MHz, CDCl$_3$) δ (ppm): 25.6 (CH$_2$), 25.7 (CH$_2$), 25.8 (CH$_2$), 25.9 (CH$_2$), 67.4 ($\underline{C}$H$_2$OCH=CH$_2$), 67.5 ($\underline{C}$H$_2$OCH=CH$_2$), 67.7 (CH$_2$OAr'), 67.8 (CH$_2$OAr), 86.4 (CH=$\underline{C}$H$_2$), 86.5 (CH=$\underline{C}$H$_2$), 114.2 (m-ArH), 115.0 (m-Ar'H), 121.8 (ArCOO), 122.5 (o-Ar'H), 132.2 (o-ArH), 144.4 (Ar'OCO), 151.8 ($\underline{C}$H=CH$_2$), 156.6 (Ar'OCH$_2$), 163.2 (ArOCH$_2$), 165.2 (COOAr).

2.2. Polymer Synthesis

2.2.1. General procedure

In a 5 mL vial, equimolar quantities of monomer(s) and chain extender (**HMTS** or **TMDS**) were dissolved in the appropriate solvent quantity of dry toluene to obtain a 1 M solution in almost all the cases (the corresponding quantities are listed in **Tables S1** and **S2**). The vial was heated at

60ºC and stirred until a colorless solution was obtained. Catalyst solution was immediately added (15 µL) and the reaction was kept at 60ºC for 24 h. The synthesized polymers were purified by precipitation and GPC.

Precipitation: The resulting viscous solution was dissolved in 3 mL of THF, and then added into a 100 mL beaker with methanol, to precipitate at the bottom of the beaker. The solid and the solution are recovered and centrifuged at 15000 rpm for 20 min. The washings were discarded and the polymer, laid on the bottom of the centrifuge tubes, was recovered. This procedure was repeated three times. The remaining polymer was put into a hermetic vial, cooled on liquid nitrogen and dried in vacuum for 24h.

Preparative gel permeation column: The solvent was evaporated and the polymer was purified into a GPC column containing Biorad SX1 biobeads using THF or dichloromethane as solvent.

Table S1 Table of composition of the **HMTS** polymers and copolymers

Polymers	Monomer **N1**		Monomer **N2**		**HMTS**		Yield
	m (mg)	η (mmol)	m (mg)	η (mmol)	m (mg)	η (mmol)	(%)
[N1+HMTS]$_p$	184	0.325	-	-	68	0.325	80
[N1$_{0.75}$+N2$_{0.25}$+HMTS]$_p$	210	0.375	53	0.175	104	0.500	99
[N1$_{0.50}$+N2$_{0.50}$+HMTS]$_p$	140	0.250	106	0.250	104	0.500	90
[N1$_{0.25}$+N2$_{0.75}$+HMTS]$_p$	70	0.175	159	0.375	104	0.500	98
[N2+HMTS]$_p$	-	-	213	0.500	104	0.500	78

Table S2 Table of composition of the **TMDS** polymers and copolymers

Polymers	Monomer **N1**		Monomer **N2**		**TMDS**		Yield
	m (mg)	η (mmol)	m (mg)	η (mmol)	m (mg)	η (mmol)	(%)
[N1$_{0.75}$+N2$_{0.25}$+TMDS]$_p$	210	0.375	53	0.175	35	0.500	50
[N1$_{0.50}$+N2$_{0.50}$+TMDS]$_p$	140	0.250	106	0.250	35	0.500	44
[N1$_{0.25}$+N2$_{0.75}$+TMDS]$_p$	70	0.175	159	0.375	35	0.500	80

2.2.1. Characterization

Analytical gel permeation chromatography (GPC) was performed to estimate the polymerization degrees. The eluent was THF and the calibration was performed using polystyrene as standard. The degree of polymerization (DP) was estimated using the next formula:

$$DPa = \frac{Ma}{\left[xM_{N1} + (1-x)M_{N2} \right] + M_{omos}} \qquad \text{for } a = n \text{ or } w$$

in which DPa (= p) is the Polymerization degree, M is the average molecular weight in number (Mn) or in weight (Mw); x is the theoretical molar fraction of the monomer **N1** added; M_{N1} and M_{N2} are the molar masses of the monomers **N1** and **N2**, respectively and M_{omos} is the molar mass of the oligosiloxane. Polydispersity (P) is calculated as the quotient between Mn and Mw. The results are shown in the **Tables S3** and **S4**, respectively.

Table S3 GPC results of the **HMTS** polymers and copolymers

Polymers	Mn	Mw	P	DPn	DPw
[N2+HMTS]$_p$	39100	112000	2.9	62	176
[N1$_{0.25}$+N2$_{0.75}$+HMTS]$_p$	164000	549000	3.3	246	821
[N1$_{0.50}$+N2$_{0.50}$+HMTS]$_p$	28500	106000	3.7	41	150
[N1$_{0.75}$+N2$_{0.25}$+HMTS]$_p$	30900	131000	4.2	42	177
[N1+HMTS]$_p$	30800	186000	6	40	242

Mn: molecular mass in number; Mw: molecular mass in weight; P: polydispersity index; DPn: degree of polymerization in number; DPw: degree of polymerization in weight.

Table S4 GPC results of the **TMDS** polymers and copolymers

Polymers	Mn	Mw	P	DPn	DPw
[N1$_{0.25}$+N2$_{0.75}$+TMDS]$_p$	25800	183000	7	43.5	310
[N1$_{0.50}$+N2$_{0.50}$+TMDS]$_p$	80400	280000	3.5	128	446
[N1$_{0.75}$+N2$_{0.25}$+TMDS]$_p$	74000	160000	2.1	110	241

Mn: molecular mass in number; Mw: molecular mass in weight; P: polydispersity index; DPn: degree of polymerization in number; DPw: degree of polymerization in weight.

To confirm that the monomer ratio within the polymers was preserved after polymerization, ^{1}H-NMR was employed. Indeed, the comparison of the integrations of the Si-CH$_2$ bond signal and the methyl singlet from **N1** moiety allowed us to give a fairly good approximation to the blends monomer ratio (**Figure S1**, **Table S5**). To estimate the molar proportion of the monomer **N1**, we used the equation, given for the **HTMS** polymers:

$$\frac{I^{CoP}_{O(CH_3)_2 SiO} + I^{CoP}_{O(CH_3)_2 SiCH_2}}{I^{CoP}_{CH_3 Ar}} = x_{N1} \left(\frac{I^{PN1T}_{O(CH_3)_2 SiO} + I^{PN1T}_{O(CH_3)_2 SiCH_2}}{I^{PN1T}_{CH_3 Ar}} \right)$$

in which the rate between **HMTS** moiety and the aromatic ring methyl integrations of a given copolymer (**CoP**) (left part of the equation) is equal to the product of monomer proportion (**xN1**)

and the rate in the homopolymer [**N1+HMTS**]$_p$ **(PN1T)** (right parenthesis of the equation). Assuming this rule, rearrangement of the above equation gives:

$$x_{N1} = \left(\frac{I^{CoP}_{O(CH_3)_2SiO} + I^{CoP}_{O(CH_3)_2SiCH_2}}{I^{CoP}_{CH_3Ar}} \right) \div \left(\frac{I^{PN1T}_{O(CH_3)_2SiO} + I^{PN1T}_{O(CH_3)_2SiCH_2}}{I^{PN1T}_{CH_3Ar}} \right)$$

The rate ensures that, even if we do not have the exact molar concentration in each NMR sample, the integral proportions will be kept constant without considering polymer chains interaction. The ^{1}H-NMR results presented above confirmed that the monomer proportion was maintained along polymerization as predicted, at least statistically. Similar results were obtained for the polymers of the **TMDS** series.

Table S5 Molar percent for the **HMTS** polymers calculated and found by ^{1}H-NMR

Polymers	Molar % ratio (N1/N2)	%molar found (N1)
[**N2+HMTS**]$_p$	0/100	0.0
[**N1$_{0.25}$+N2$_{0.75}$+HMTS**]$_p$	25/75	25.3
[**N1$_{0.50}$+N2$_{0.50}$+HMTS**]$_p$	50/50	52.4
[**N1$_{0.75}$+N2$_{0.25}$+HMTS**]$_p$	75/25	83.3
[**N1+HMTS**]$_p$	100/0	100.0
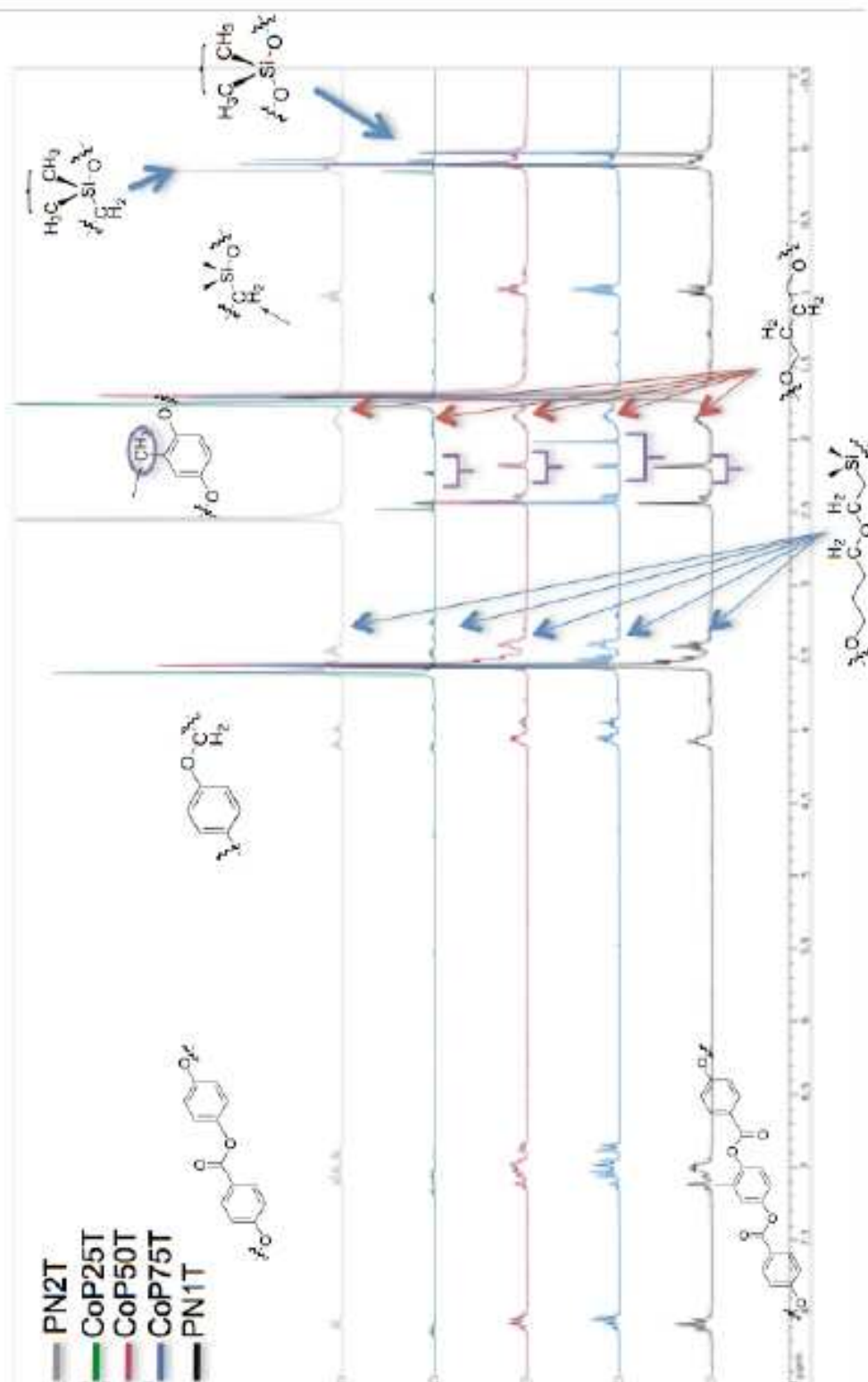
Figure S1 ¹H-NMR of the various co-polymers and polymers of the **HMTS** series, $[\mathbf{N1}_x+\mathbf{N2}_{1-x}+\mathbf{HMTS}]_p$ (the **N1**-content increases from top to bottom).

2.3. Elastomers synthesis

2.3.1. General Procedure

Liquid Crystalline Elastomer (LCE) films were prepared according to the spin casting procedure. In a 5 mL vial, were introduced the corresponding quantities of the monomers, cross-linker and chain extender, **always in this order**, and then dissolved in toluene (0.9 mL) and heated until a homogeneous solution was obtained (the quantities used of the three series are gathered in the **Tables S6** and **S7**). 10 µL of the catalyst solution was then added and the reaction mixture left to react at 60ºC for 5-10 minutes. The reaction mixture was then immediately poured into a specially designed cell with a Teflon® film, sealed and centrifuged at 3000 rpm at 60ºC until the formation of a gel film, generally after 1.5 h. After this time period, centrifugation was stopped, the cell was cooled down to room temperature and the film removed from the centrifuge's cell. The elastomeric film was then peeled off the Teflon® support, and cut into 3 pieces. Each piece was suspended and hung at one extremity to add weight and to perform the orientation process (**Figure S2**). Once being stretched, the opaque samples turned transparent. These were kept at 60ºC in a vacuum oven for 72 h, to complete the cross-linking reaction and fixed the alignment.

Table S6 Table of composition of the **HMTS** liquid crystalline elastomers and co-elastomers

Elastomers	Monomer N1		Monomer N2		HMTS		HD5	
	m (mg)	η (mmol)	m (mg)	η (mmol)	m (mg)	η (mmol)	m (mg)	η (mmol)
[N2+HMTS+HD5]	-	-	426	1.00	187	0.9	12	0.04
[N1$_{0.25}$+N2$_{0.75}$+HMTS+HD5]	140	0.25	319	0.75	187	0.9	12	0.04
[N1$_{0.50}$+N2$_{0.50}$+HTMS+HD5]	280	0.50	213	0.50	187	0.9	12	0.04
[N1$_{0.75}$+N2$_{0.25}$+HTMS+HD5]	420	0.75	106	0.25	187	0.9	12	0.04
[N1+HMTS+HD5]	560	1.00	-	-	187	0.9	12	0.04

Table S7 Table of composition of the **TMDS** liquid crystalline elastomers and co-elastomers

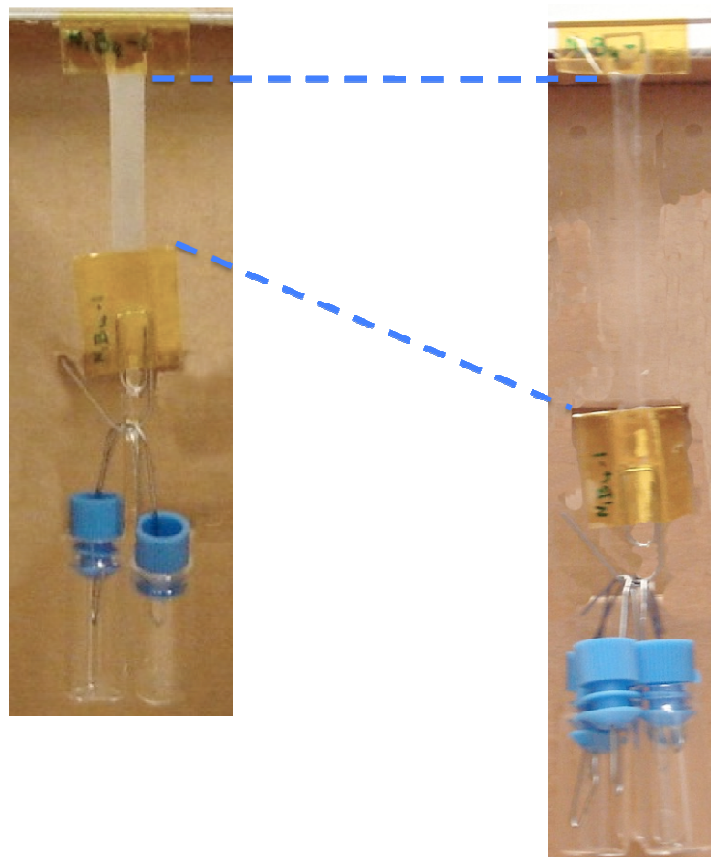| Elastomers	Monomer N1		Monomer N2		TMDS		HD5	
	m (mg)	η (mmol)	m (mg)	η (mmol)	m (mg)	η (mmol)	m (mg)	η (mmol)
[N1$_{0.25}$+N2$_{0.75}$+TMDS+HD5]	140	0.25	319	0.75	125	0.9	12	0.04
[N1$_{0.50}$+N2$_{0.50}$+TMDS+HD5]	280	0.50	213	0.50	125	0.9	12	0.04
[N1$_{0.75}$+N2$_{0.25}$+TMDS+HD5]	420	0.75	106	0.25	125	0.9	12	0.04

Figure S2 Orientation process of the LCEs by weight loading, starting from opaque "polydomain" to transparent "monodomain" (the same procedure was applied to all elastomers).

2.3.2. Swelling experiments

Swelling experiments were carried in toluene at 25°C. The dimensions of the sample were recorded after and before the swelling process. The quotient of the volume change is then calculated with the next formula:

$$q = \frac{(\bar{x} \cdot \bar{y} \cdot \bar{z})}{(x \cdot y \cdot z)}$$

in which x, y and z are the dimensions of the elastomer film before and $\bar{x}$, $\bar{y}$ and $\bar{z}$ the dimensions of the swollen film. In the case of this systems we can consider the align direction as the z dimension. Hence, the two others can be considered as equivalent (x = y). This equation can be simplified as:

$$q = \frac{\left(\overline{x}^2 \cdot \overline{z} \right)}{\left(x^2 \cdot z \right)}$$

Table S8 Swelling results for trisiloxane co-elastomers

HMTS elastomers	q_z	α_∞	$\alpha_\parallel$	q
[N1+HMTS+HD5]	1.1	3.0	2.8	24.9
[N1$_{0.75}$+N2$_{0.25}$+HMTS+HD5]	5.9	4.3	0.7	13.3
[N1$_{0.50}$+N2$_{0.50}$+HMTS+HD5]	4.9	4.3	0.9	16.1
[N1$_{0.25}$+N2$_{0.75}$+HMTS+HD5]	3.1	3.4	1.1	12.9
[N2+HMTS+HD5]	1.4	3.0	2.2	20.0

q_z: swelling anisotropy; **α_∞**: perpendicular to the director swelling; **$\alpha_\parallel$**:parallel to the director swelling **q**: Swelling factor. (**$q=\alpha_\infty^2\alpha_\parallel$**)

Table S9 Swelling results for disiloxane co-elastomers

TMDS elastomers	q_z	α_∞	$\alpha_\parallel$	q
[N1$_{0.25}$+N2$_{0.75}$+TMDS +HD5]	3.87	3.05	0.79	7.31
[N1$_{0.50}$+N2$_{0.50}$+TMDS+HD5]	3.67	3.33	0.91	10.10
[N1$_{0.75}$+N2$_{0.25}$+TMDS+HD5]	4.67	3.33	0.71	7.94

q_z: swelling anisotropy; **α_∞**: perpendicular to the director swelling; **$\alpha_\parallel$**:parallel to the director swelling **q**: Swelling factor.
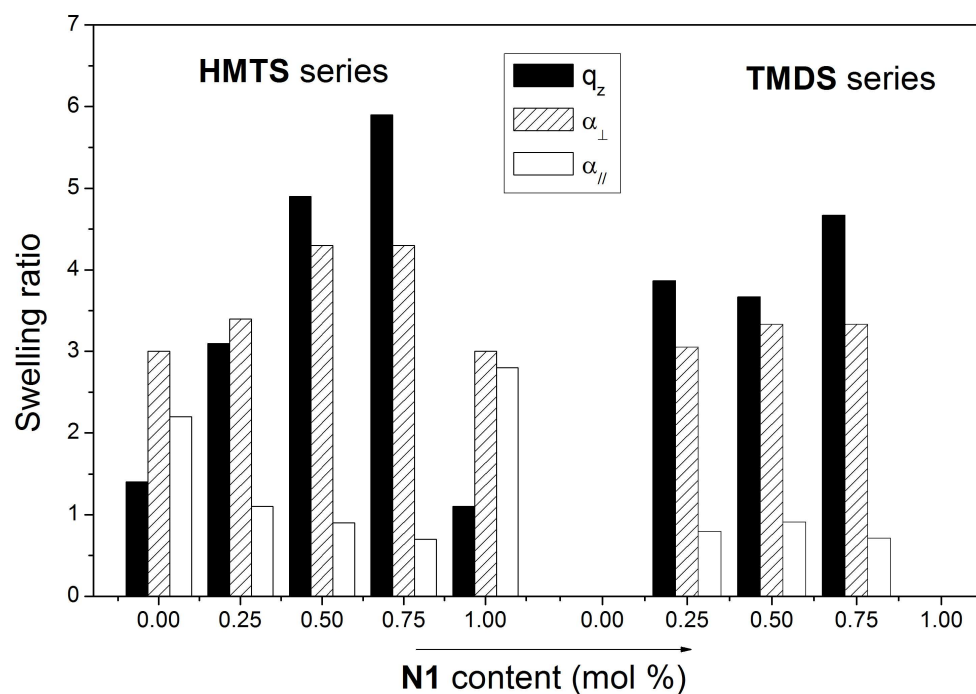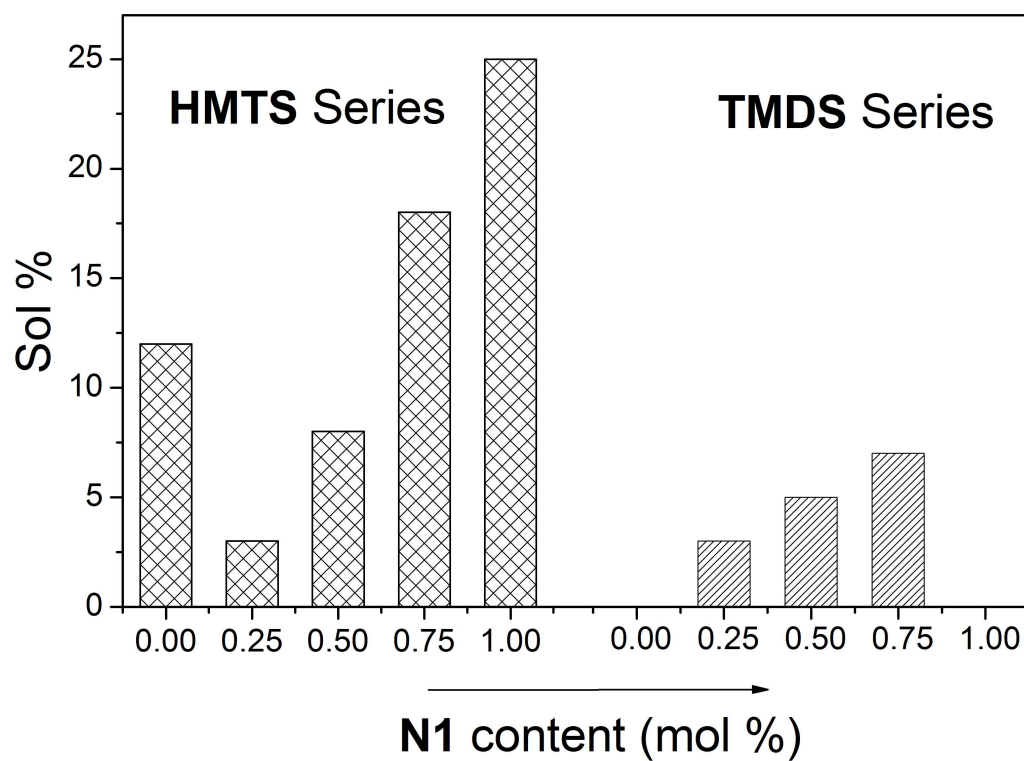
Figure S3 Soluble fractions (top) and swelling anisotropy values (bottom) as a function of the **N1** monomer content in **HMTS** and **TMDS** systems ([**N1$_x$+N2$_{1-x}$+HMTS+HD5**] and [**N1$_x$+N2$_{1-x}$+TMDS+HD5**]). $\alpha_\perp$ and $\alpha_{//}$ are the swelling ratios perpendicular and parallel to the direction of elongation, and $q_z = \alpha_\perp/\alpha_{//}$, is the swelling anisotropy.

3. Optical microscopy (POM)

3.1. Optical textures of the monomeric mixtures
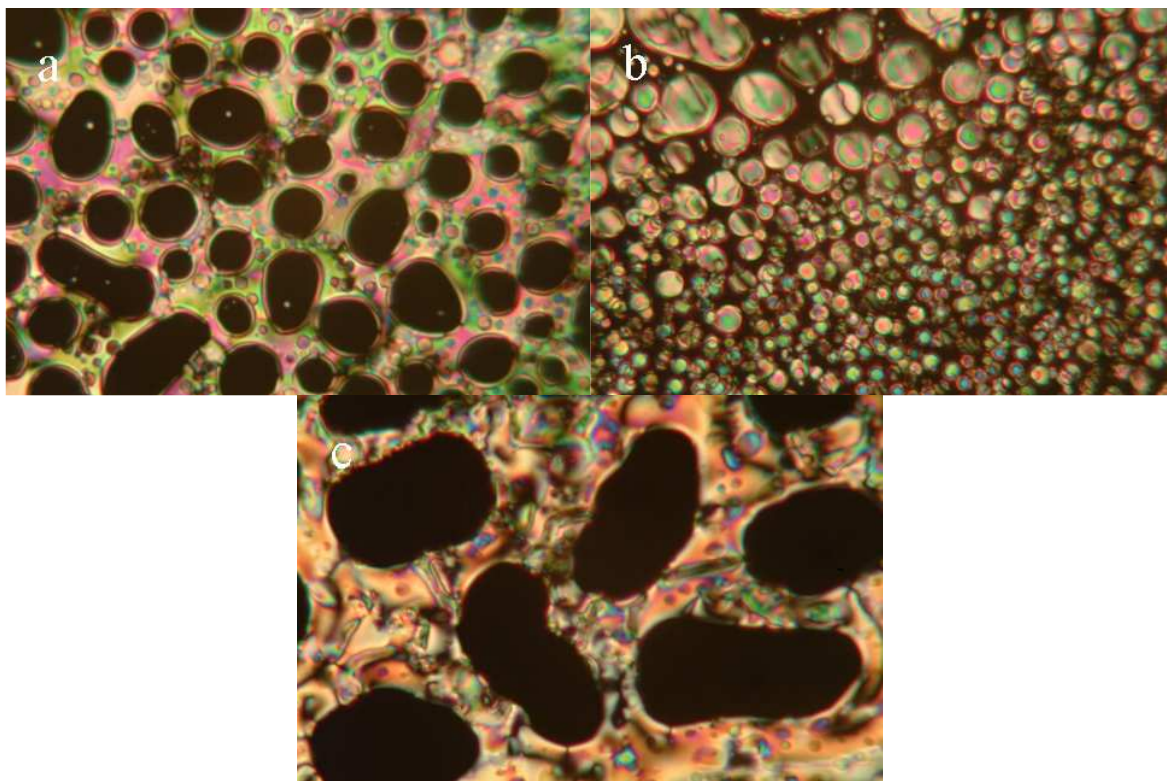
Figure S4 Optical microscopic textures exhibited by the binary mixtures of monomers a) **N1**:**N2** 0.25:0.75; b) **N1**:**N2** 0.50:0.50; c) **N1**:**N2** 0.75:0.25, observed on cooling from the isotropic liquid.

3.2. Optical textures of the polymers
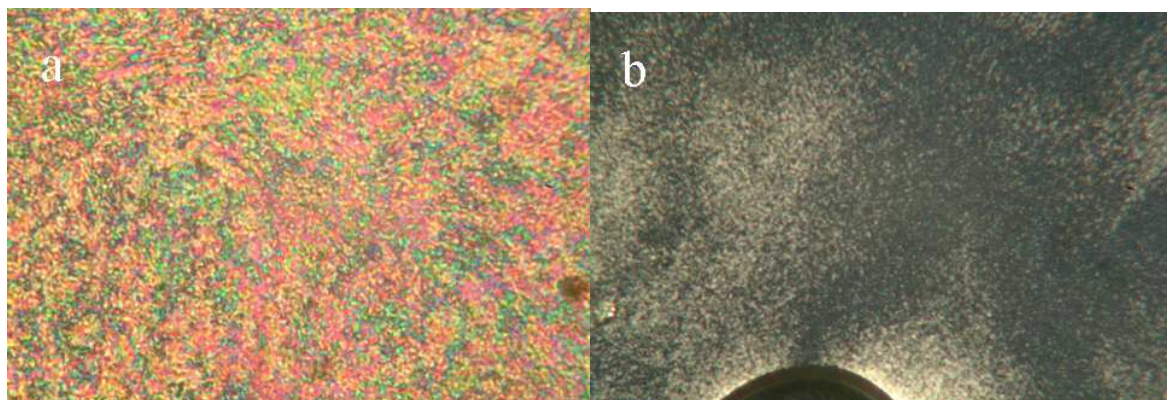
Figure S5 Representative optical textures exhibited by the polymer [$N1_{0.75}$+$N2_{0.25}$+$HMTS$]$_p$ a) at room temperature; b) cooling down to 70 °C (slightly below isotropic-Smectic transition temperature)
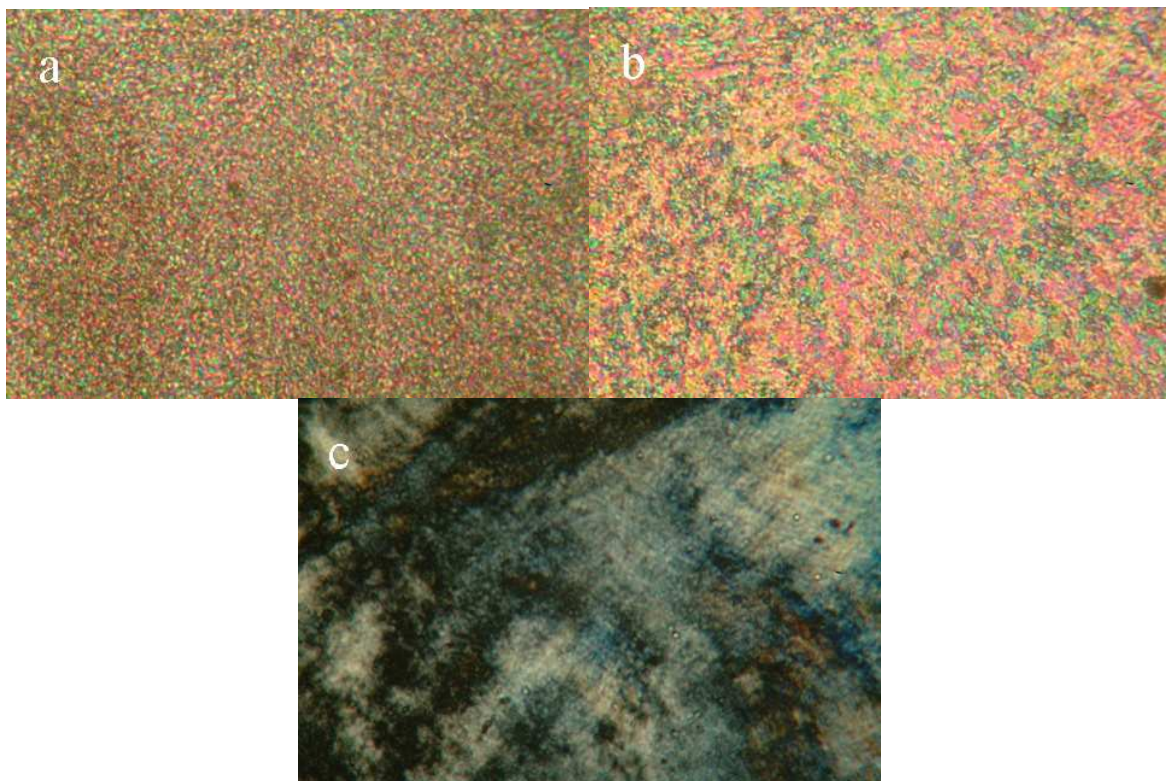
Figure S6 Representative optical textures exhibited by the polymer [$N1_{0.75}$+$N2_{0.25}$+$TMDS$]$_p$ a) at 60; b) At 80° degrees (Nematic mesophase); c) at 82 °C (at the transition isotropic liquid-to-nematic mesophase)

3.4. Optical textures of the elastomers
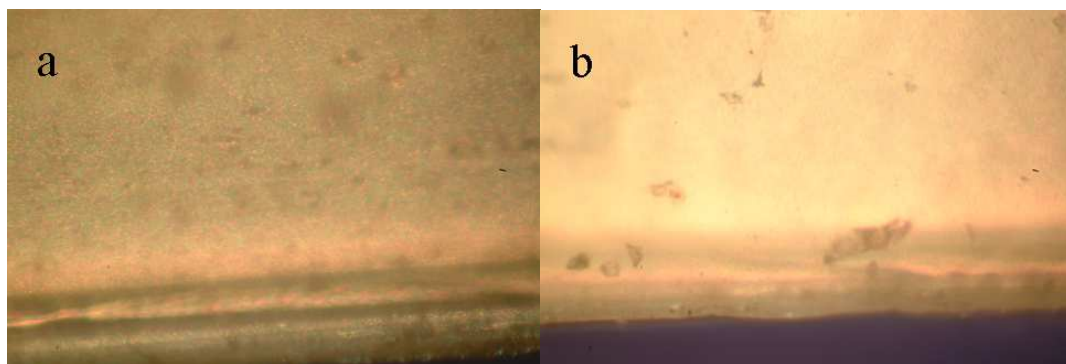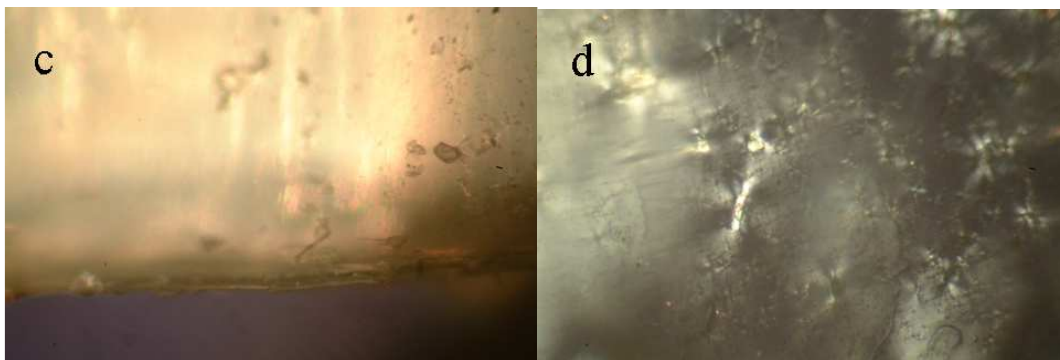
Figure S7 Representative optical textures of the co-elastomer [**N1**$_{0.75}$+**N2**$_{0.25}$+**TMDS**+**HD5**] a) at room temperature (Smectic C mesophase); b) at 76° degrees (Nematic mesophase); c) at 105 °C (in the nematic phase, close to the transition to the paranematic-like state); d) at 110°C (in the paranematic-like state).

4. Thermal behavior (DSC)

4.1. Monomers and mixtures
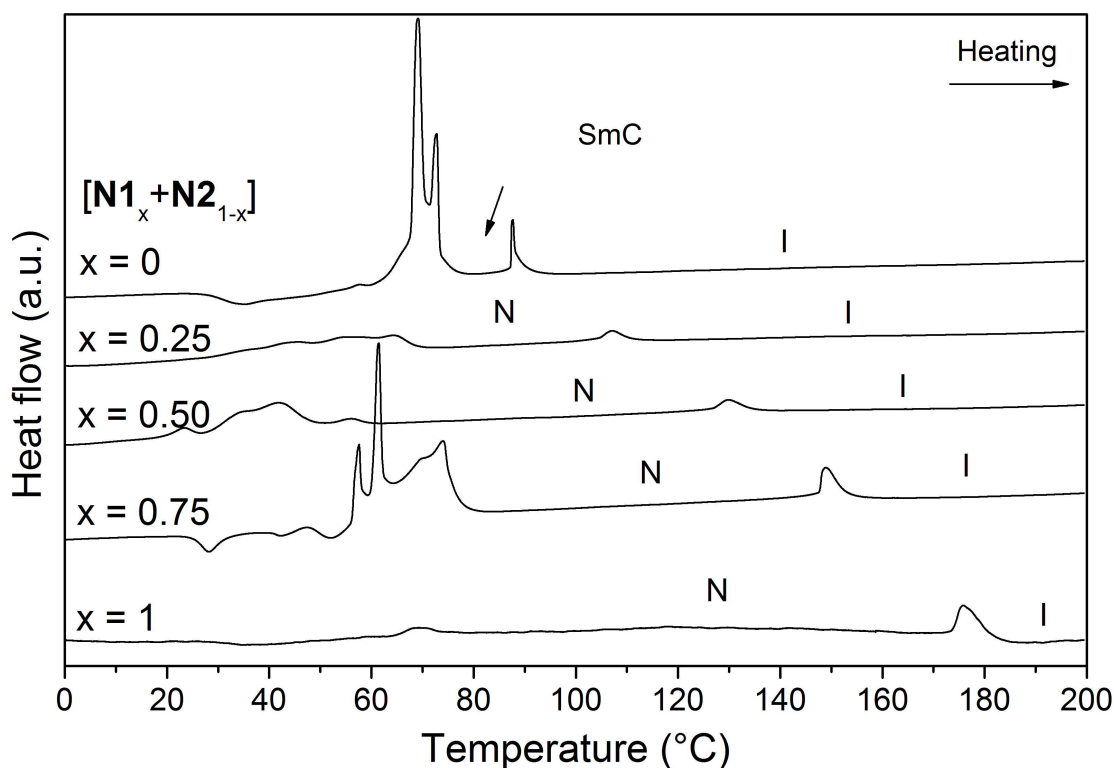
Figure S8 DSC traces of the monomers and mixtures, recorded during the third heating cycle at 2°C/min.

Table S10 Transition temperatures and phase sequences of the monomers and their mixtures

Ratio **N1**:**N2** (mol %)	Thermal Behavior	ΔT (N)[a]
0:100	Cr 72 [90.0] SmC 87 [3.0] I	0
25:75	Cr 37 Cr' 65 [21.0][b] N 107 [4.8] I	42
50:50	Cr 22 Cr' 34 Cr'' 42 [20.0][b] N 129 [4.2] I	87
75:25	Cr 42 Cr' 69 [35.2][b] N 148 [6.0] I	79
100:0	Cr 72 [45.5] N 168 [3.9] I	96

Transition temperatures (°C) and enthalpies [J.g^{-1}] of the monomers **N1** and **N2** and their mixtures determined from DSC heating runs at 2°C/min heating rate during the third heating. Abbreviations: SmC, smectic C phase; N, nematic phase; I, isotropic liquid; Cr, Cr', Cr'', crystalline phases. [a]ΔT (N) is the N phase temperature range (°C). [b]Cumulated enthalpies.
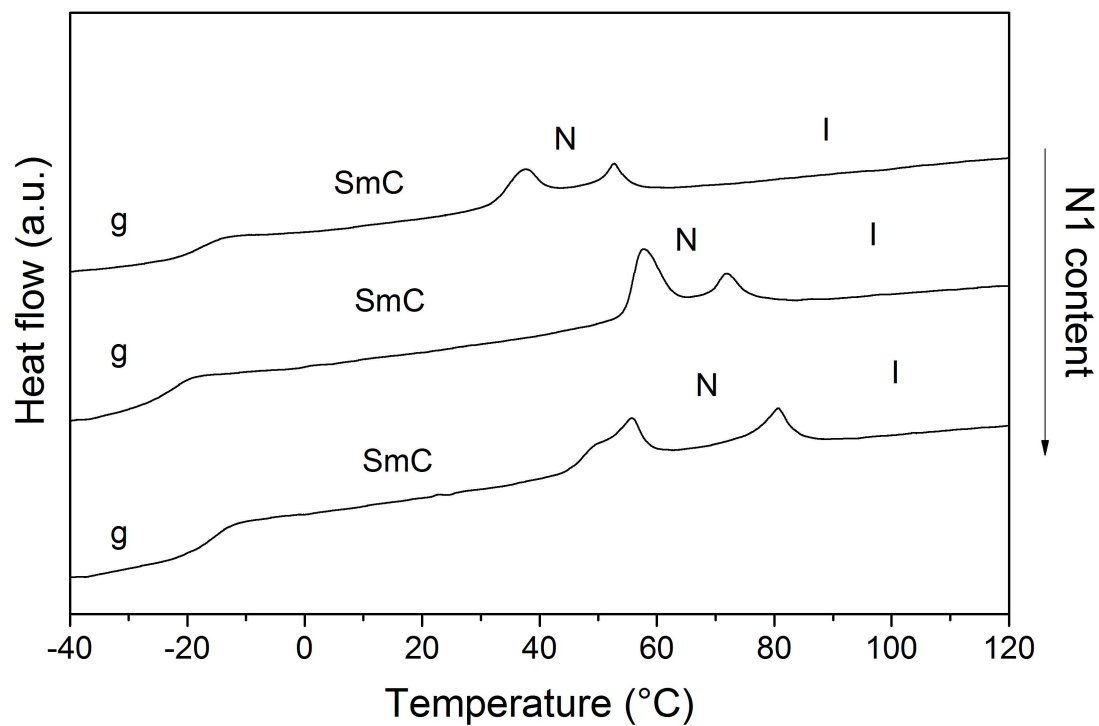
4.2. Polymers

Figure S9 DSC traces (heating, 2°C.min^{-1}, exotherm down) of the **TMDS** polymers [**N1**$_x$+**N2**$_{1-x}$+**TMDS**]$_p$ (from top to bottom, the ratio **N1**:**N2** varies as 0.25:0.75, 0.50:0.50, and 0.75:0.25). I, isotropic liquid; N, nematic phase; SmC, smectic phase; g, glassy state.
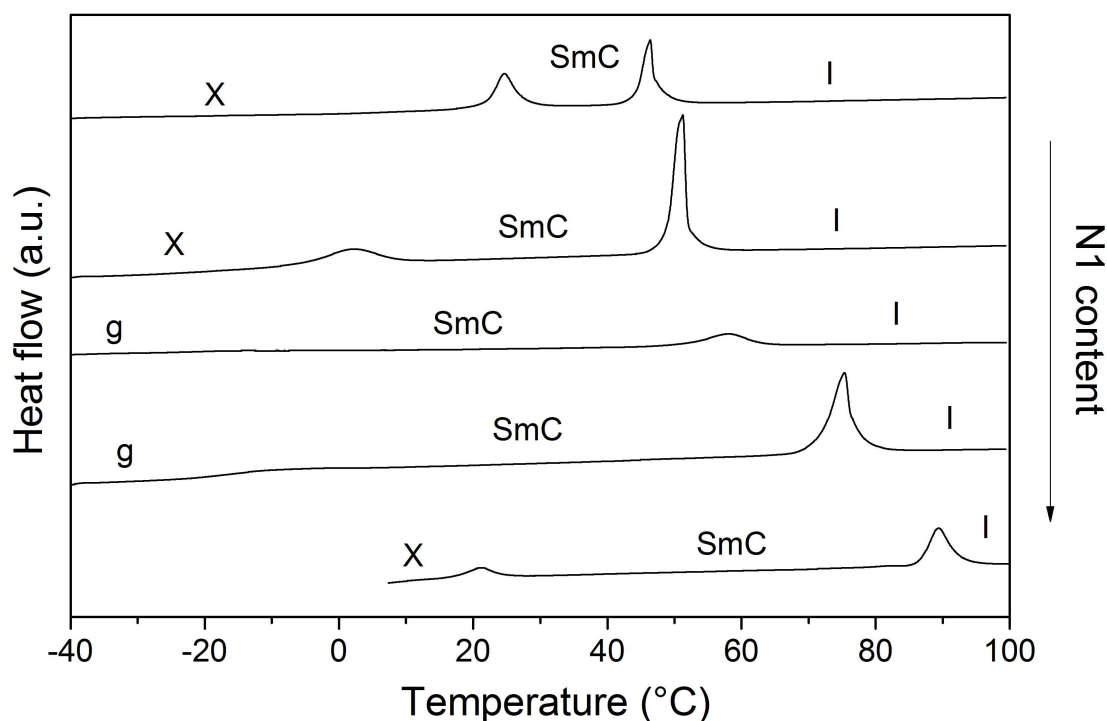
Figure S10 DSC traces (heating, 2°C.min^{-1}, exotherm down) of the **HMTS** polymers [**N1**$_x$+**N2**$_{1-x}$+**HMTS**]$_p$ (from top to bottom, the ratio **N1**:**N2** varies as 0:1, 0.25:0.75, 0.50:0.50, 0.75:0.25 and 1:0).

Table S11 Thermal behavior of the disiloxane and trisiloxane polymers and co-polymers, [**N1**$_x$+**N2**$_{1-x}$+**TMDS**]$_p$ and [**N1**$_x$+**N2**$_{1-x}$+**HMTS**]$_p$

Polymers	Phase sequence and entahlpy	$\Delta T_{SmC/N}$
[**N1**$_{0.25}$+**N2**$_{0.75}$+**TMDS**]$_p$	g -17.0 [0.2] SmC 35.4 [1.2] N 52.6 [1.1] I	52.4/17.2
[**N1**$_{0.50}$+**N2**$_{0.50}$+**TMDS**]$_p$	g -23.0 [0.3] SmC 57.7 [3.9] N 71.8 [0.9] I	48.7/14.1
[**N1**$_{0.75}$+**N2**$_{0.25}$+**TMDS**]$_p$	g -17.0 [0.3] SmC 53.3 [2.4] N 79.5 [1.5] I	70.3/26.2
[**N2**+**HMTS**]$_p$	X 22.5 [8.8] SmC 42.2 [14.3] I	19.7
[**N1**$_{0.25}$+**N2**$_{0.75}$+**HMTS**]$_p$	X -3.3 [2.9] SmC 47.2 [12.1] I	50.5
[**N1**$_{0.50}$+**N2**$_{0.50}$+**HMTS**]$_p$	g -20.0 [0.0] SmC 53.8 [9.9] I	53.8
[**N1**$_{0.75}$+**N2**$_{0.25}$+**HMTS**]$_p$	g -13.0 [0.2] SmC 71.1 [9.4] I	84.1
[**N1**+**HMTS**]$_p$	X 14.5 [2.0] SmC 87.0 [9.2] I	72.5

Transition temperatures in °C, from DSC heating runs at 2°C.min^{-1}; in brackets: heat capacities ΔCp [J.g^{-1}K^{-1}] and latent heats ΔH [J.g^{-1}]. Abbreviations: g, glassy state; SmC, Smectic C mesophase; N, nematic phase; I, isotropic liquid. $\Delta T_{SmC/N}$: temperature range in °C of the SmC (above the glassy state) and N phase.
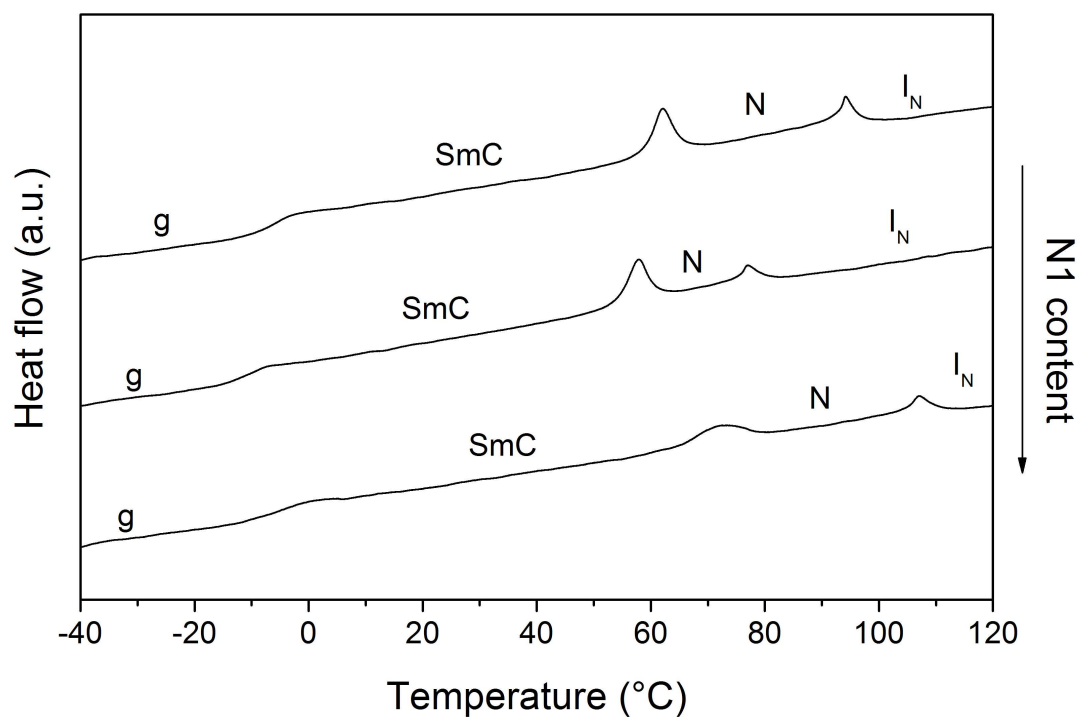
4.3. Elastomers

22

Figure S11 DSC traces of **TMDS** co-elastomers (heating, 2°C.min^{-1}, exotherm down), [**N1$_x$+N2$_{1-x}$+TMDS+HD5**], performed at a heating/cooling rate of 2ºC/min (from top to bottom, the ratio **N1**:**N2** varies as 0.25:0.75, 0.50:0.50, and 0.75:0.25). N, nematic phase; SmC, smectic C phase; g, glassy state; I$_N$, paranematic-like state.
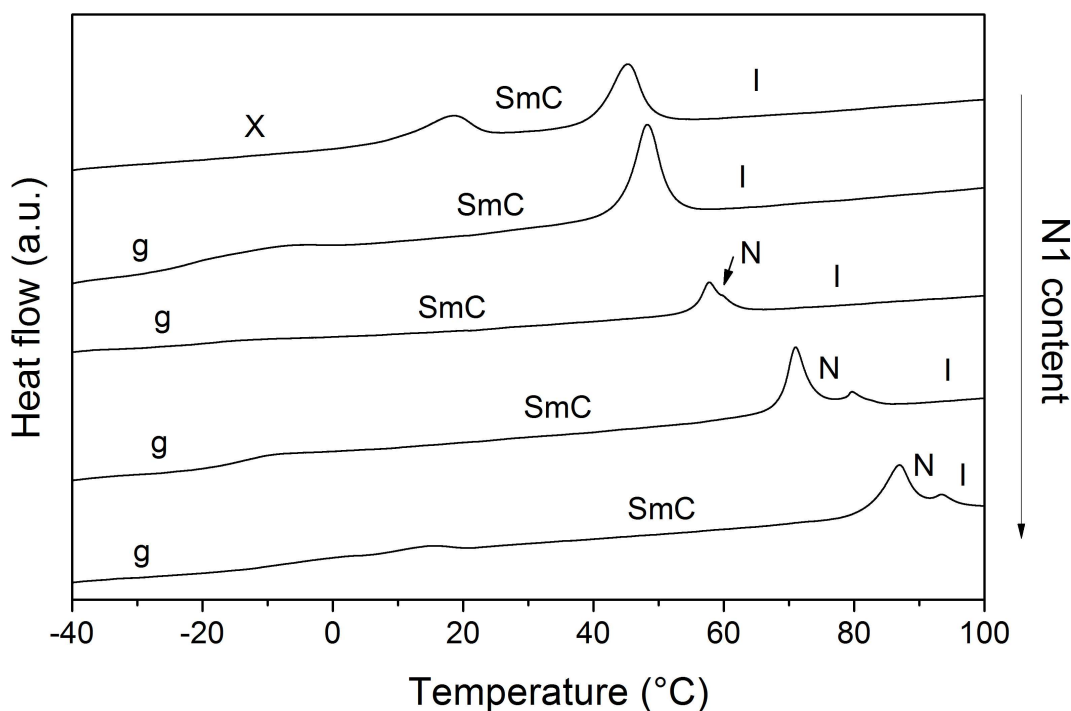
Figure S12 DSC traces (heating, 2°C.min^{-1}, exotherm down) of the **HMTS** co-elastomers, [**N1**$_x$+**N2**$_{1-x}$+**HMTS**+**HD5**], recorded during the third heating cycle at 2°C/min (from bottom to top, the ratio **N1**:**N2** varies as 0:1, 0.25:0.75, 0.50:0.50, 0.75:0.25 and 1:0). N, nematic phase; SmC, smectic C phase; g, glassy state; X, unidentified phase; I, isotropic state.

Table S12 Thermal behavior of the disiloxane and trisiloxane elastomers and co-elastomers, [**N1**$_x$+**N2**$_{1-x}$+**TMDS**+**HD5**] and [**N1**$_x$+**N2**$_{1-x}$+**HMTS**+**HD5**] (4 mol% **HD5**).

Elastomers	Thermal behavior	$\Delta T_{SmC/N}$
[**N1**$_{0.25}$+**N2**$_{0.75}$+**TMDS**+**HD5**]	g -4.3 [0.2] SmC 61.4 [2.61] N 93.5 [1.43] I$_N$	65.7/32.1
[**N1**$_{0.50}$+**N2**$_{0.50}$+**TMDS**+**HD5**]	g -7.7 [0.1] SmC 56.1 [3.94] N 76.3 [1.05] I$_N$	63.8/20.2
[**N1**$_{0.75}$+**N2**$_{0.25}$+**TMDS**+**HD5**]	g -1.4 [0.2] SmC 71.5 [2.12] N 106.7 [1.31] I$_N$	72.9/35.2
[**N2**+**HMTS**+**HD5**]	X 16.4 [4.6] SmC 41.8 [10.3] I	25.4
[**N1**$_{0.25}$+**N2**$_{0.75}$+**HMTS**+**HD5**]	g -19.1 [0.3] SmC 45.6 [8.5] I	64.7
[**N1**$_{0.50}$+**N2**$_{0.50}$+**HMTS**+**HD5**]	g -22.0 [0.0] SmC 55.9 N[a] 57.1 [8.5][b] I	77.9/1.2
[**N1**$_{0.75}$+**N2**$_{0.25}$+**HMTS**+**HD5**]	g -11.5 [0.2] SmC 69.9 N[a] 72.2 [3.5][b] I	81.4/2.3
[**N1**+**HMTS**+**HD5**]	g -6 [0.2] SmC 84.7 N[a] 86.6 [3.1][b] I	90.7/1.9

Transition temperatures in °C, from DSC runs at 2°C/min.; in brackets: heat capacities ΔCp [J.g^{-1}K[-1]] and latent heats ΔH [J.g^{-1}]. Abbreviations: g: glassy state; SmC, Smectic C mesophase; X, unidentified phase; N, nematic phase; I, isotropic state; I$_N$, paranematic-like state (see text). $\Delta T_{smC/N}$: temperature range of the SmC (above glassy state) and N phase. [a]cumulated enthalpy of unresolved peak.
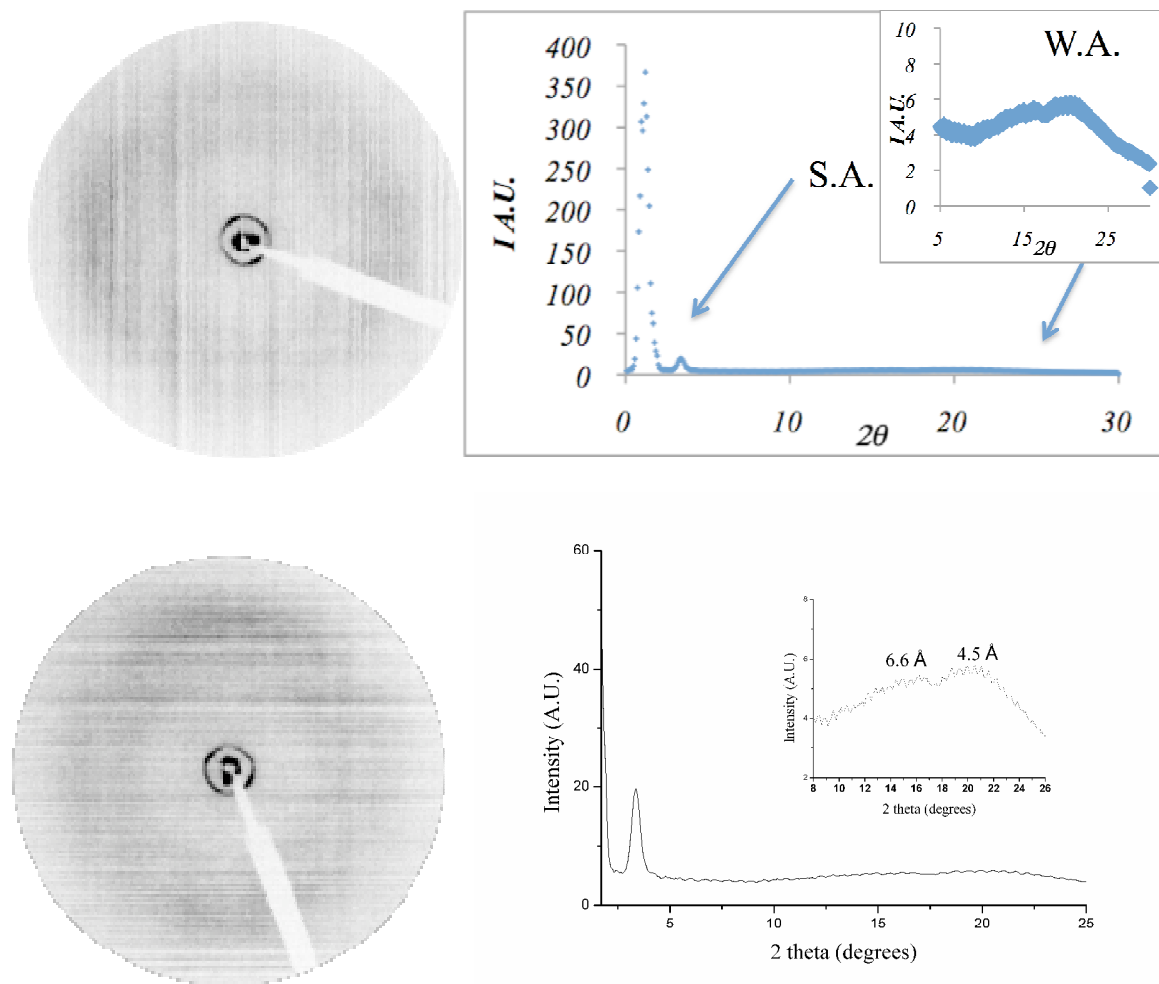
5. SAXS

5.1. Patterns of polymers

Figure S13 Representative diffraction patterns and radial profiles over 360° of the corresponding mesophases recorded in the SmC phase (T = 25°C) of the co-polymers [**N1**$_{0.75}$+**N2**$_{0.25}$+**HMTS**]$_p$ (top) and [**N1**$_{0.25}$+**N2**$_{0.75}$ +**HMTS**]$_P$ (bottom). All the other SAXS patterns recorded for the other polymers are similar.
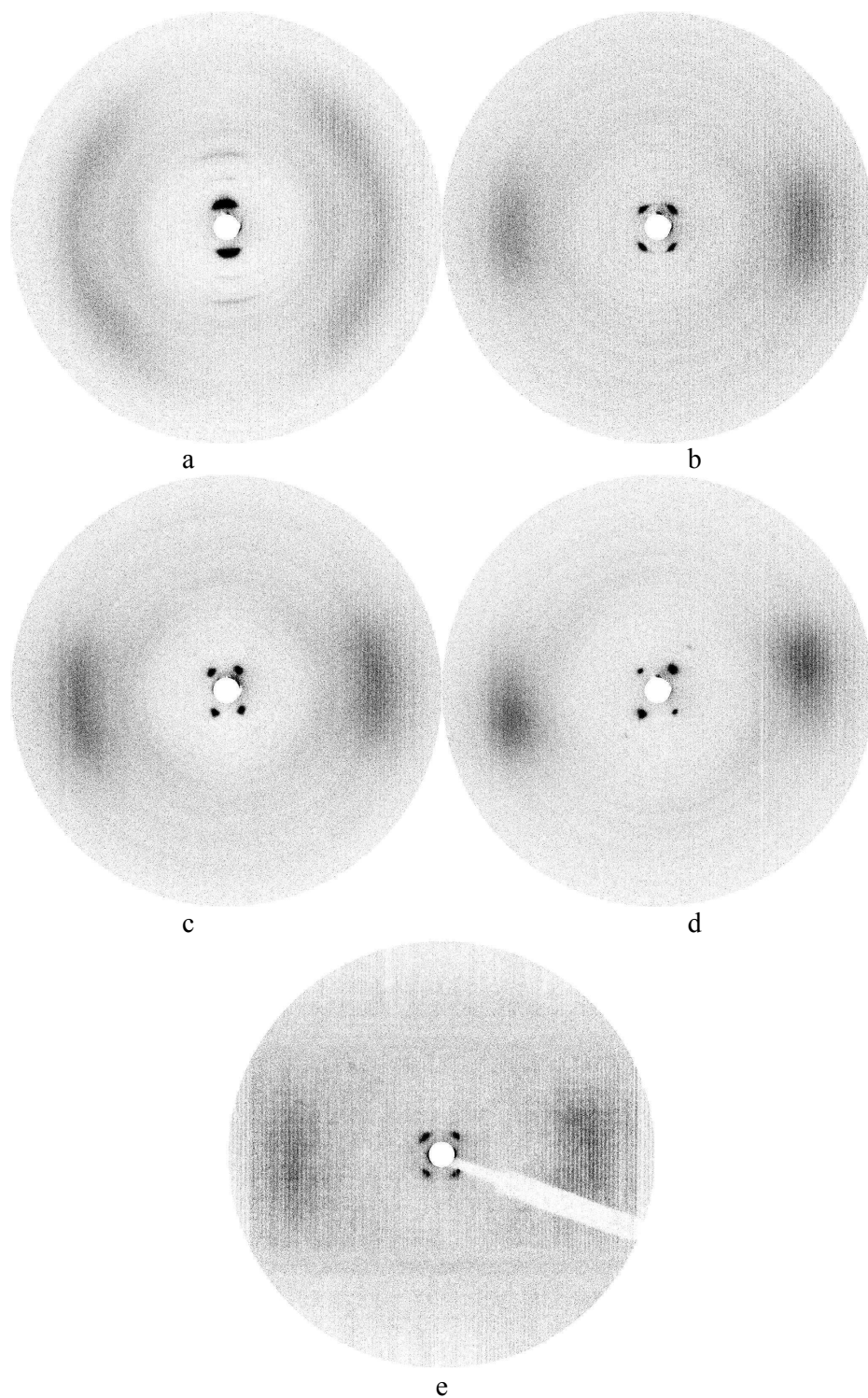
5.2. Oriented patterns of elastomers

Figure S14 Oriented SAXS patterns recorded in the SmC phase (T = 25°C) of the co-elastomers of the series [**N1**$_x$+**N2**$_{1-x}$+**HMTS**+**HD5**] (a-e: x = 0, 0.25, 0.50, 0.75, 1)
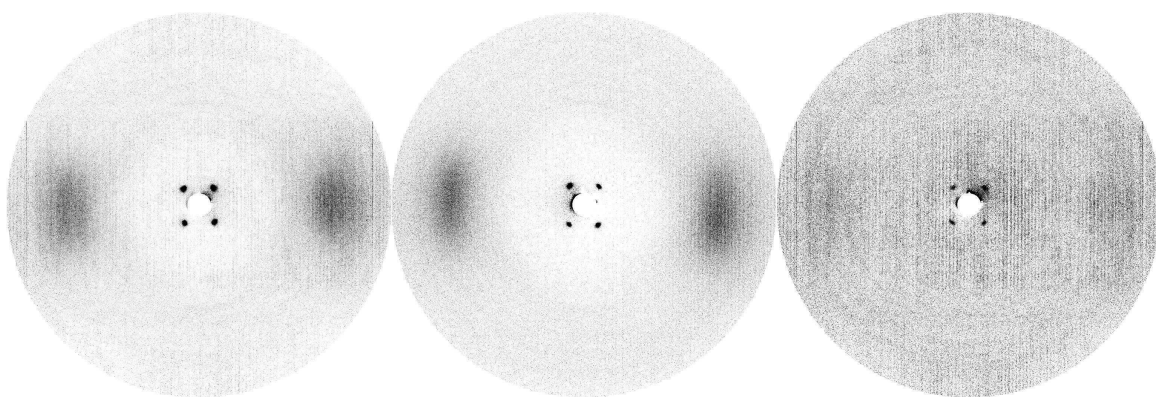
Figure S15 Oriented SAXS patterns recorded in the SmC phase (T = 25°C) of the co-elastomers of the series [**N1$_x$+N2$_{1-x}$+TMDS+HD5**] (with x = 0.25, 0.50 and 0.75 from left to right)

6. Thermo-elastic measurements
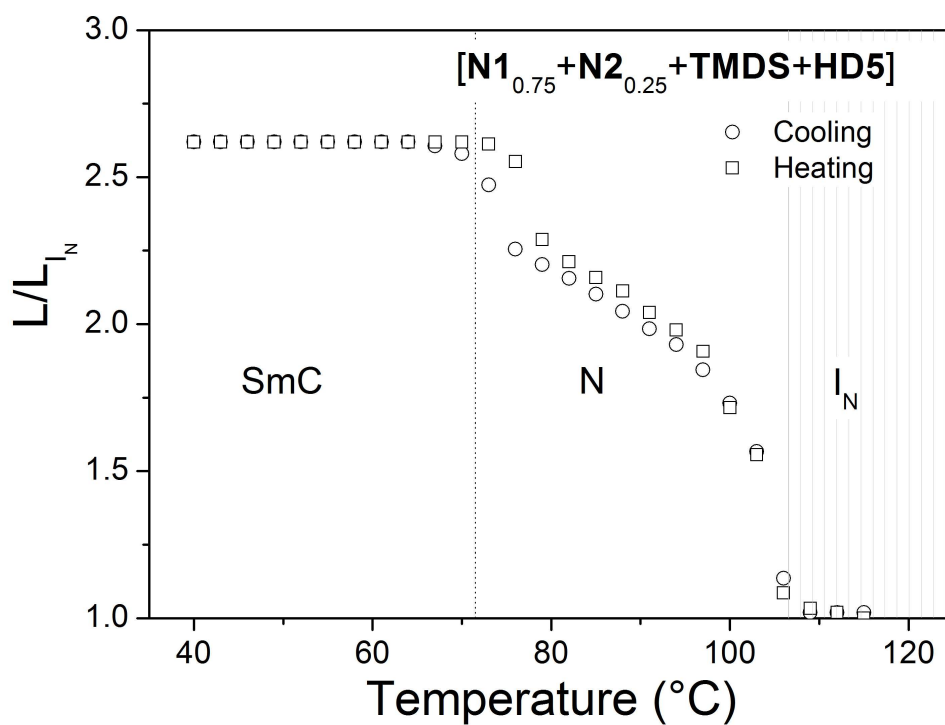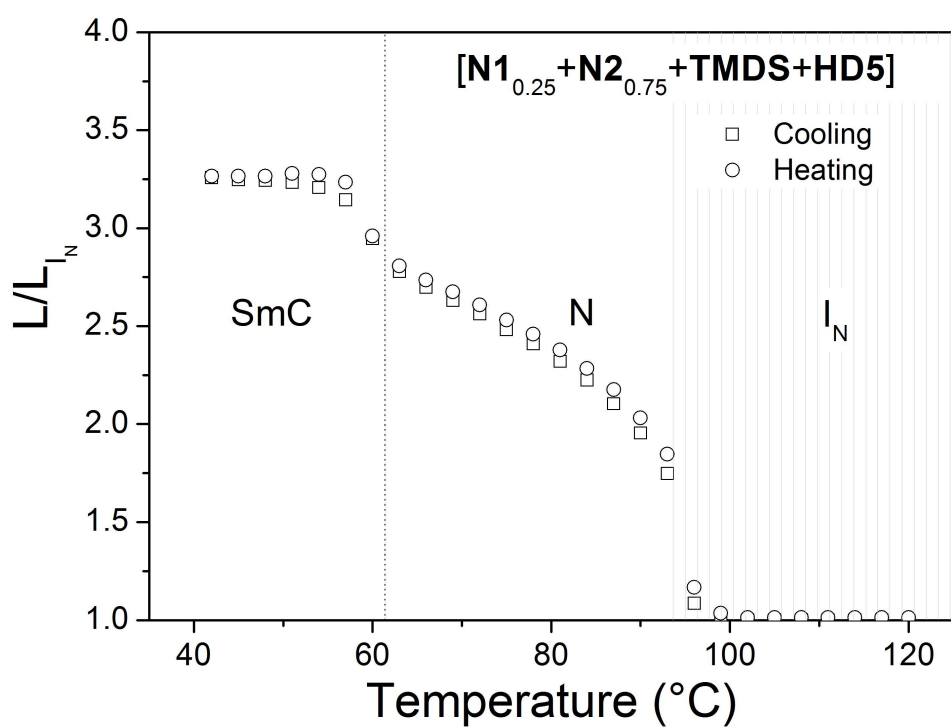
Figure S16 Thermo-elastic behaviors of [**N1**$_{0.75}$+**N2**$_{0.25}$+**TMDS**+**HD5**] (top) and [**N1**$_{0.25}$+**N2**$_{0.75}$+**TMDS**+**HD5**] (bottom), measured on heating/cooling cycle.
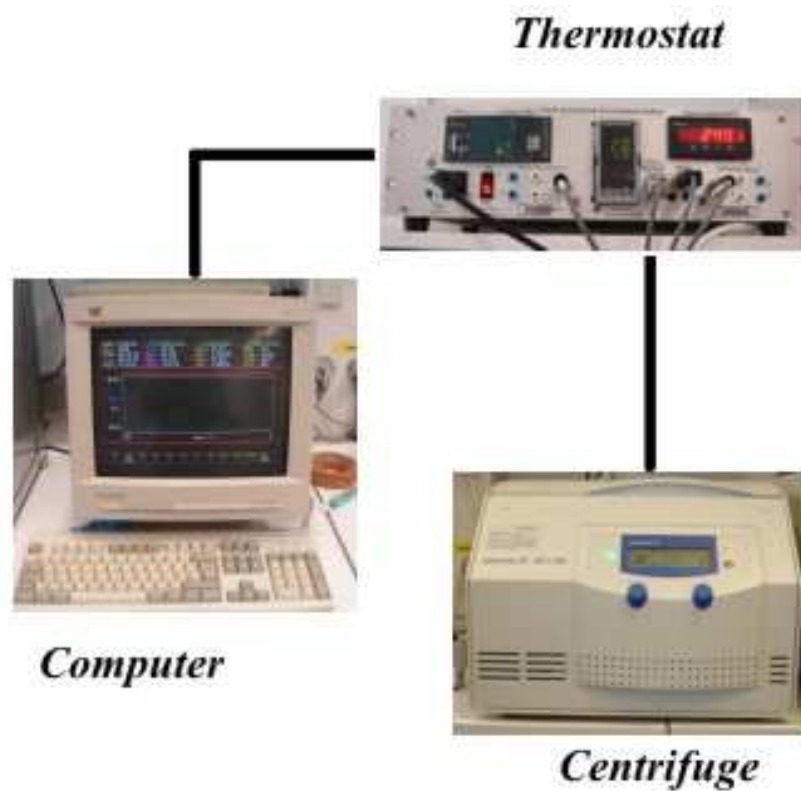
7. Centrifuge images
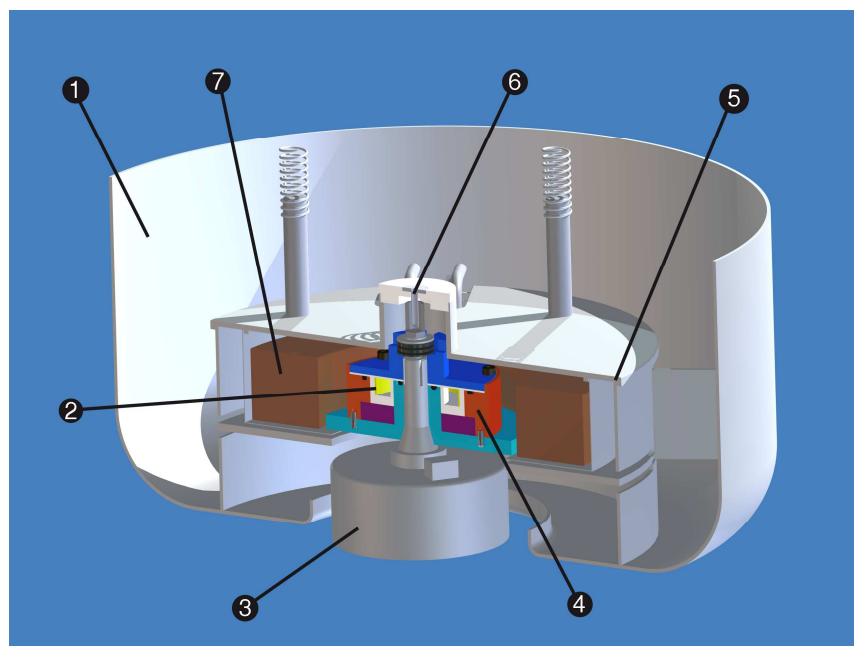

Figure S17 General set-up

Figure S18 General view of the centrifuge. Legend: 1, centrifuge tank; 2, elastomer film; 3, centrifuge motor; 4, rotor/polymerization cell; 5, thermal armor-form; 6, temperature inlet; 7, heating matrix
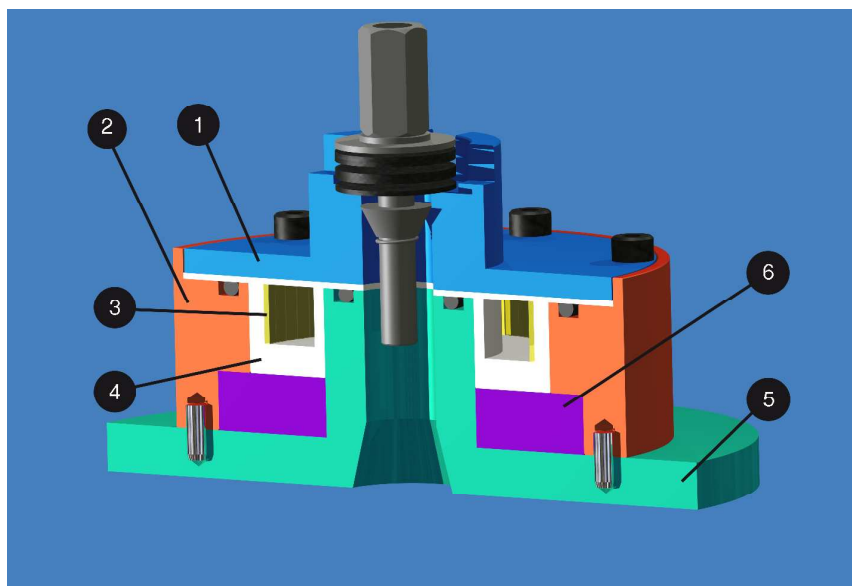
Figure S19 Sketch of the polymerization cell. Legend: 1, upper lid; 2, body; 3, elastomer film; 4, PTFE tank; 5, lower lid; 6, wedge