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Supporting Information

Proton Conductive Ionic Liquid Crystalline Poly(ethyleneimine) Polymers Functionalized with Oxadiazole

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1. Experimental Section

1.1. Materials and Methods.

b-PEI-$(NH_2)_x$ and *l*-PEI-$(NH_2)_x$ were purchased from Aldrich and were used as received. Anhydrous THF used for polymer preparation was purchased from Scharlab and dried using a solvent purification system.

The infrared spectra of all the compounds were obtained with a Nicolet Avatar 360 FTIR spectrophotometer in the 400-4000 cm^{-1} spectral range using KBr pellets and NaCl cells. ^{1}H-NMR was performed on a Bruker AVANCE 400 spectrometer and on a Bruker AVANCE 300 spectrometer. ^{13}C-NMR was performed on a Bruker AVANCE 400 spectrometer operating at 100 MHz and on a Bruker AVANCE 300 spectrometer operating at 75 MHz.

Mesogenic behavior and transition temperatures were determined using an Olympus DP12 polarizing optical microscope equipped with a Linkam TMS91 hot stage and a CS196 central processor. Differential scanning calorimetry (DSC) experiments were performed in DSC TA Instruments Q-20 and Q-2000 equipments. Samples were sealed in aluminum pans and a scanning rate of 10 $°C{\cdot}min^{-1}$ under a nitrogen atmosphere was used. The apparatus was calibrated with indium (156.6°C; 28.4 $J{\cdot}g^{-1}$) as the standard. Three thermal cycles were carried out. The mesophase transition temperatures were read at the maximum of the corresponding peaks. Thermogravimetric analysis (TGA) was performed using a TA instrument TGA Q5000 at a rate of $10ºC{\cdot}min^{-1}$ under argon atmosphere. The XRD experiments were performed in a pinhole camera (Anton-Paar) operating with a point-focused Ni-filtered Cu-Kα beam. Lindemann glass capillaries with 0.9 mm diameter were used to contain the sample. A variable-temperature oven was used to heat the sample. The capillary axis was placed perpendicular to the X-ray beam and the pattern was collected on flat photographic film perpendicular to the X-ray beam. Bragg's law was used to obtain the spacing.

Electrochemical impedance spectroscopy was recorded on an Autolab potentiostat equipped with a temperature controller in the frequency range from 1 Hz to 1 MHz (applied voltage: 10 mV). The conductivities were studied as a function of temperature between 30°C and 225°C at 5°C intervals. For the preparation of the cells for ionic conductivities, the appropriate amount of the ionic dendrimer was placed onto an ITO electrode that was sandwiched with another ITO electrode controlling the thickness by using glass spacers (20 μm). The cell was heated up to a few degrees above the melting point of the liquid crystal and the cell was pressed to obtain the thin film.

The impedance spectrum can be modeled as an equivalent circuit and divided into imaginary (Z'') and real (Z') components. The resistance (R_b) was estimated from the intersection of the real axis (Z') and the semicircle of the impedance spectrum. The proton conductivities σ ($S \cdot cm^{-1}$) were calculated with the formula:

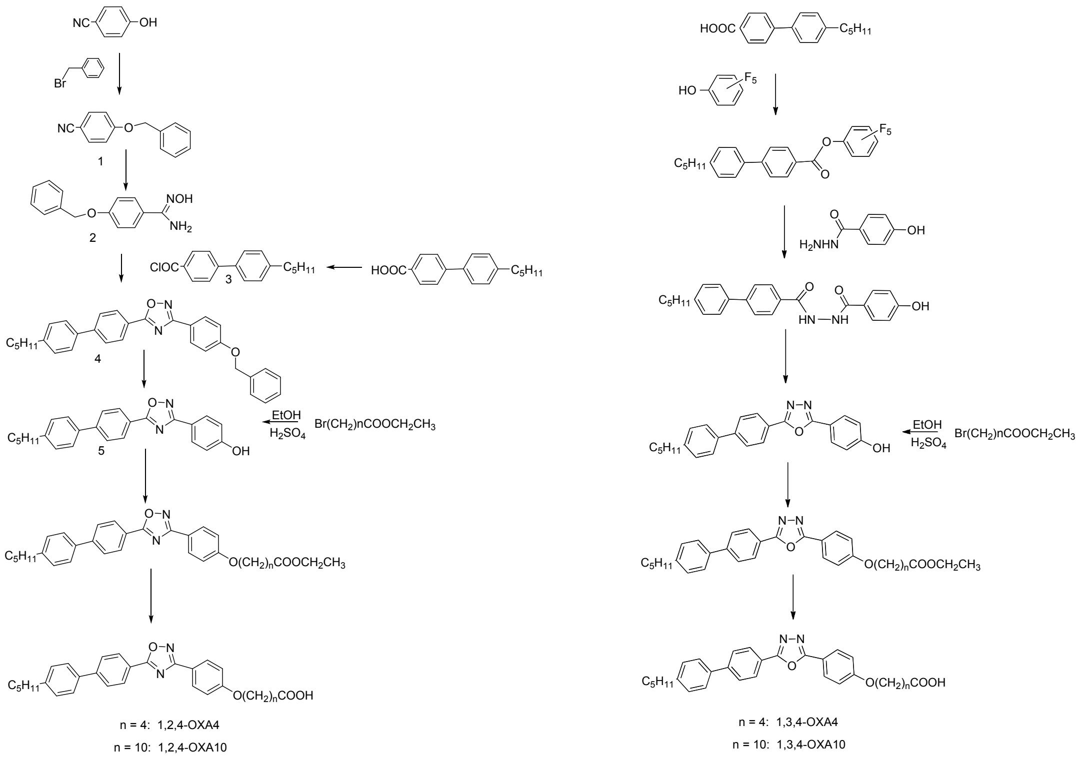
$$\sigma = d/(R_b \cdot A))$$

where d (cm) is the thickness of the film, A (cm^2) is the area of the film and R_b (Ω) is the resistance of the sample.

1.2. Synthetic procedures and chemical compound information

1.2.1. Synthesis scheme of the oxadiazol acids *(described in Macromolecules* ***2012,*** *45, 1006-1015).*

The synthesis of 1,2,4-OXA$_m$ and 1,3,4-OXA$_m$ acids was performed as shown in Scheme S1



(a) **(b)**

Scheme S1. Synthetic Route and Nomenclature of Intermediates for a) 1,2,4-OXA$_m$ acids; b) 1,3,4-OXA$_m$ acids

1.2.2. Synthesis and characterization data of the ionic polymers

General synthetic procedure

The synthesis of ionic polymers was performed following a previously described method. X equiv. of the appropriate oxadiazole acid were dissolved in anhydrous THF.

The mixture was added to a solution of 1 equiv. of corresponding PEI polymer in anhydrous tetrahydrofuran and sonicated for 15 minutes. The mixture was then slowly evaporated at room temperature and dried in vacuum until the weight remains constant for ca. 12 h at 40ºC.

Characterization data of the ionic polymers

_b_-PEI-(1,2,4-OXA$_4$)$_n$

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.29 – 8.21 (m, 2H), 8.14 – 8.05 (m, 2H), 7.81 – 7.72 (m, 2H), 7.63 – 7.54 (m, 2H), 7.34 – 7.15 (m, 2H), 7.06 – 6.97 (m, 2H), 4.08 (t, *J* = 6.0 Hz, 2H), 3.96-2.8 (m, 12H), 2.67 (t, *J* = 7.7 Hz, 2H), 2.42 (t, *J* = 7.0 Hz, 2H), 1.96 – 1.80 (m, 4H), 1.73 – 1.64 (m, 2H), 1.42 – 1.33 (m, 4H), 0.95 – 0.84 (m, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 177.7, 175.1, 168.4, 161.1, 145.1, 143.2, 136.8, 128.91, 128.87, 128.9, 128.4, 127.2, 126.8, 122.6, 119.1, 114.5, 67.5, 35.4, 34.4, 31.3, 30.9, 28.5, 22.3, 21.7, 13.8.

_l_-PEI-(1,2,4-OXA$_4$)$_n$

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.23 –7.93 (m, 4H), 7.74 – 7.58 (m, 2H), 7.58 – 7.39 (m, 2H), 7.28 – 7.15 (m, 2H), 7.08 – 6.76 (m, 2H), 4.8-4.1 (s_{br}, 4H), 4.10 – 3.83 (m, 2H), 3.18 – 2.79 (m, 2H), 2.74 – 2.49 (m, 2H), 2.49 – 2.10 (m, 2H), 1.97 – 1.72 (m, 4H), 1.72 – 1.54 (m, 2H), 1.45 – 1.29 (m, 4H), 1.00 – 0.79 (m, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 178.1, 175.3, 168.6, 161.4, 145.2, 143.3, 137.0, 129.0, 128.6, 127.3, 127.0, 122.8, 119.5, 114.7, 77.3, 77.2, 77.0, 76.7, 67.7, 46.1, 35.6, 35.1, 31.6, 31.0, 28.9, 22.5, 22.1, 14.0.

b-PEI-(1,2,4-OXA$_{10}$)$_n$

^{13}C-CPMAS (None, 101 MHz): δ 183-176, 173.9, 166.8, 159.8, 158.1, 140.4, 135.8, 133.4, 127.4, 126.2, 124.9, 121.8, 120.7, 66.6, 65-44, 34.3, 31.1, 29.7, 25.9, 22.3, 13.6.

b-PEI-(1,3,4-OXA$_4$)$_n$

^{13}C-CPMAS (None, 101 MHz): δ 183-172, 174.7, 162.5, 160.7, 139.6, 135.2, 133.7, 127.1, 125.2, 122.8, 115.0, 109.6, 66.7, 66-38, 34.3, 31.7, 29.3, 23.2, 21.8, 13.3.

l-PEI-(1,3,4-OXA$_4$)$_n$

^{1}H NMR (DMSO, 500 MHz): δ 8.22 – 8.14 (m, 2H), 8.11 – 8.04 (m, 2H), 7.93 – 7.88 (m, 2H), 7.72 – 7.66 (m, 2H), 7.36 – 7.30 (m, 2H), 7.20 – 7.13 (m, 2H), 4.09 (t, *J* = 6.3 Hz, 2H), 2.97 (s_{br}, 4H), 2.63 (t, *J* = 7.6 Hz, 2H), 2.31 (t, *J* = 7.3 Hz, 2H), 1.83 – 1.73 (m, 2H), 1.72 – 1.56 (m, 4H), 1.39 – 1.24 (m, 4H), 0.87 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (DMSO, 126 MHz): δ 174.4, 164.0, 163.5, 161.6, 143.2, 142.8, 136.2, 129.1, 128.6, 127.3, 127.2, 126.7, 122.0, 115.6, 115.3, 67.6, 34.8, 33.3, 30.9, 30.6, 28.0, 22.0, 21.2, 13.9.

b-PEI(1,3,4-OXA$_{10}$)$_n$

^{13}C-CPMAS (None, 101 MHz): δ 182-175, 162.1, 159.8, 137.6, 135.4, 133.4, 128.2, 126.4, 124.3, 123.6, 122.3, 118.4, 114.6, 109.2, 67.8, 65.5,63.1, 58.7, 38.1, 35.4, 34.2, 31.4, 28.9, 27.0, 24.7, 23.4, 14.4.

2. Supplementary Tables

Table S1. FTIR data for the Acids, Dendritic Polymers and their Complexes: PEI-acid

Compound	COOH	NH_3^+	C=O acido	as (COO^-)	sym (COO^-)	NH_2
***b*-PEI-NH_2**						3426
***l*-PEI-NH_2**						3355
1,2,4-OXA_4	3438	-	1707	-	-	
***b*-PEI-(1,2,4-OXA_4)$_n$**	-	3431	-.	1559	1403	
***l*-PEI-(1,2,4-OXA_4)$_n$**	-	3026	-	1589	1493	
1,2,4-OXA_{10}	3500	-	1705	-	-	
***b*-PEI-(1,2,4-OXA_{10})$_n$**	-	3428	-	1556	1498	
1,3,4-OXA_4	3500	-	1699	-	-	
***b*-PEI-(1,3,4-OXA_4)$_n$**	-	3428	-	1556	1498	
***l*-PEI-(1,3,4-OXA_4)$_n$**		3032		1563	1495	
1,3,4-OXA_{10}	3500	-	1707	-	-	
***b*-PEI-(1,3,4-OXA_{10})$_n$**	-	3344	-	1565	1463	

Table S2. 1H NMR Data of Oxadiazole Acid, Dendritic Polymers and Their Complexes in $CDCl_3$. Data in parenthesis corresponding to a DMSO-d_6 solution.

Compound	COOH	$-CH_2-COO-$	$-NH_2/-NH-$	$-NH_3^+/-NH_2^+$	$-CH_2NH_2$	$-CH_2N^+$
1,2,4-OXA_4	9.25	2.48				
1,3,4-OXA_4	10.76 / (12.08)	2.48 / (2.30)				
***l*-PEI**			1.62		2.73 /(2.56)	
***b*-PEI**			1.05		2.38-1.60	
***b*-PEI(1,2,4-OXA_4)$_n$**		2.39		3.7-3.9		3.97-3.2
***l*-PEI(1,2,4-OXA_4)$_n$**		2.36		4.8-4.1		3.18-2.79
***l*-PEI(1,3,4-OXA_4)$_n$**		(2.31)		Not obs.		(2.97) (br)

Table S3. ^{13}C NMR Data of Oxadiazole Acid, Dendritic Polymers and Their Complexes in $CDCl_3$. Data in parenthesis corresponding to a DMSO-d_6 solution

Compound	COOH	$-CH_2-COO-$	$-CH_2NH-$	$-CH_2NH_2^+-$	$-CH_2NH_2$	$-CH_2NH$ / $-CH_2N-$	$-CH_2NH_3^+$	$-CH_2NH_2^+$ / $-CH_2NH^+$
1,2,4-OXA$_4$	178.9	33.6						
1,3,4-OXA$_4$	178.1 / (174.4)	33.8 / (33.2)						
***l*-PEI-NH$_2$**			49.1 / (48.8)					
***b*-PEI-NH$_2$**					40.7, 38.9	57.6-45.5		
***l*-PEI(1,2,4-OXA$_4$)$_n$**	178.1	35.1		46.1				
***b*-PEI(1,2,4-OXA$_4$)$_n$**	177.7	34.6		Not obs.			Not obs.	59-62(HSQC)
***l*-PEI(1,3,4-OXA$_4$)$_n$**	(174.4)	(33.3)		(46-44, HSQC)				

Table S4. Thermal stability of the ionic polymers

Compound	$T_{5\%}$ [a]	T_{onset} [b]
***b*-PEI-(1,2,4-OXA$_4$)$_n$**	230	256
***l*-PEI-(1,2,4-OXA$_4$)$_n$**	245	270
***b*-PEI-(1,2,4-OXA$_{10}$)$_n$**	200	261
***b*-PEI-(1,3,4-OXA$_4$)$_n$**	200	333
***l*-PEI-(1,3,4-OXA$_4$)$_n$**	297	326
***b*-PEI-(1,3,4-OXA$_{10}$)$_n$**	222	298

a Temperature (°C) at which 5% of the initial mass is lost.

b Onset temperature of the decomposition of the main process

3. Supplementary figures

3.1. NMR Spectra

Two-dimensional correlated ^1H ^{13}C HSQC and NOESY experiments

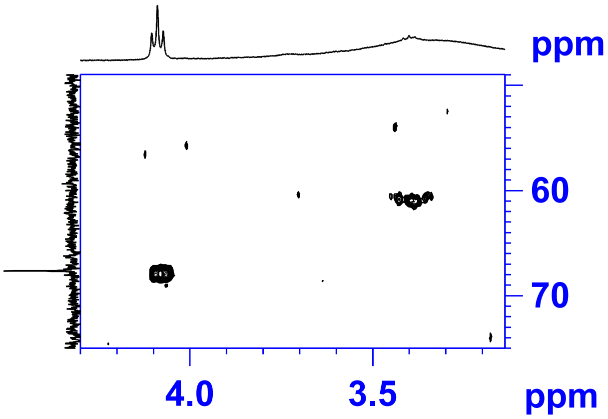


Figure S1. Partial HSQC spectrum of ***b*-PEI(1,2,4-OXA$_4$)$_n$** complex in DMSO-d$_6$. (400MHz, 333K)

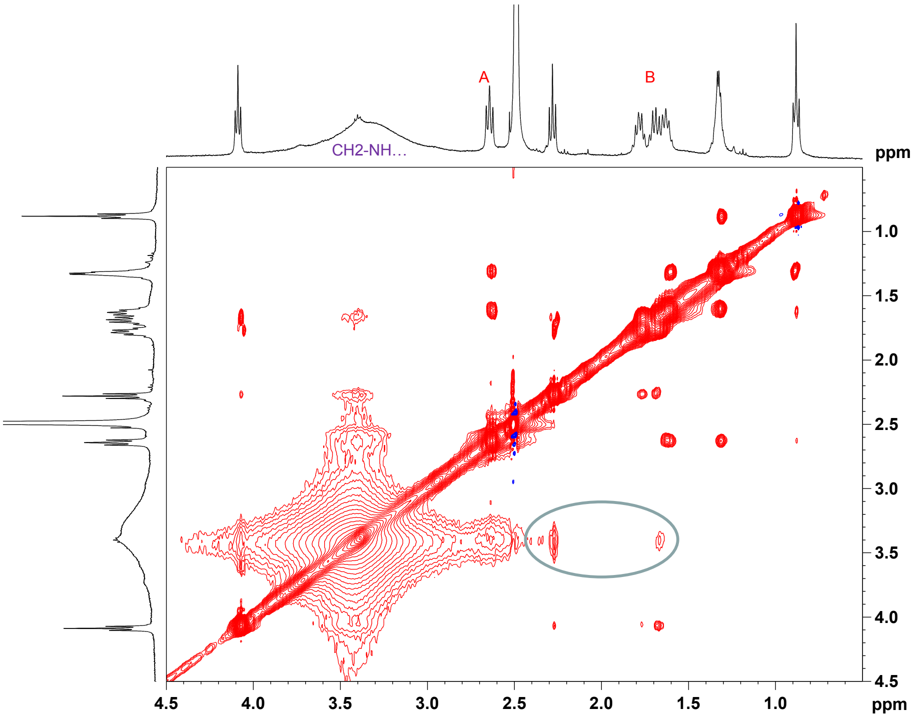
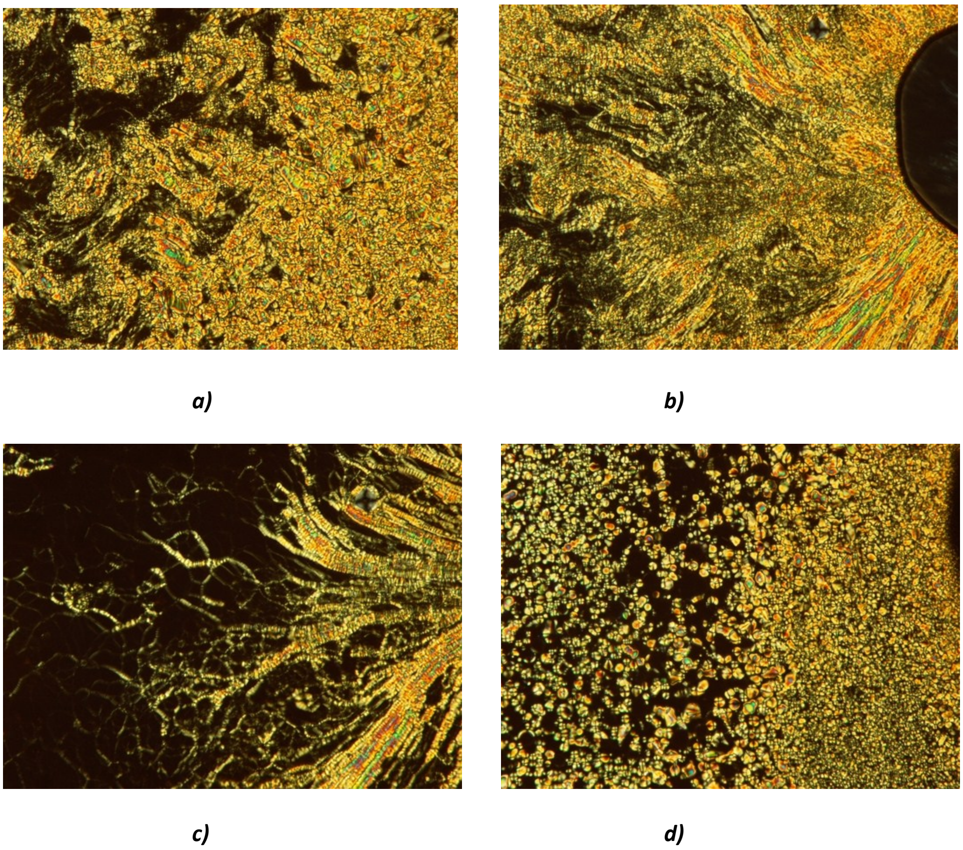


Figure S2. Partial NOESY spectrum of ***b*-PEI(1,2,4-OXA$_4$)$_n$** complex in DMSO-d$_6$ (400MHz, RT, t_{mix}=300ms)

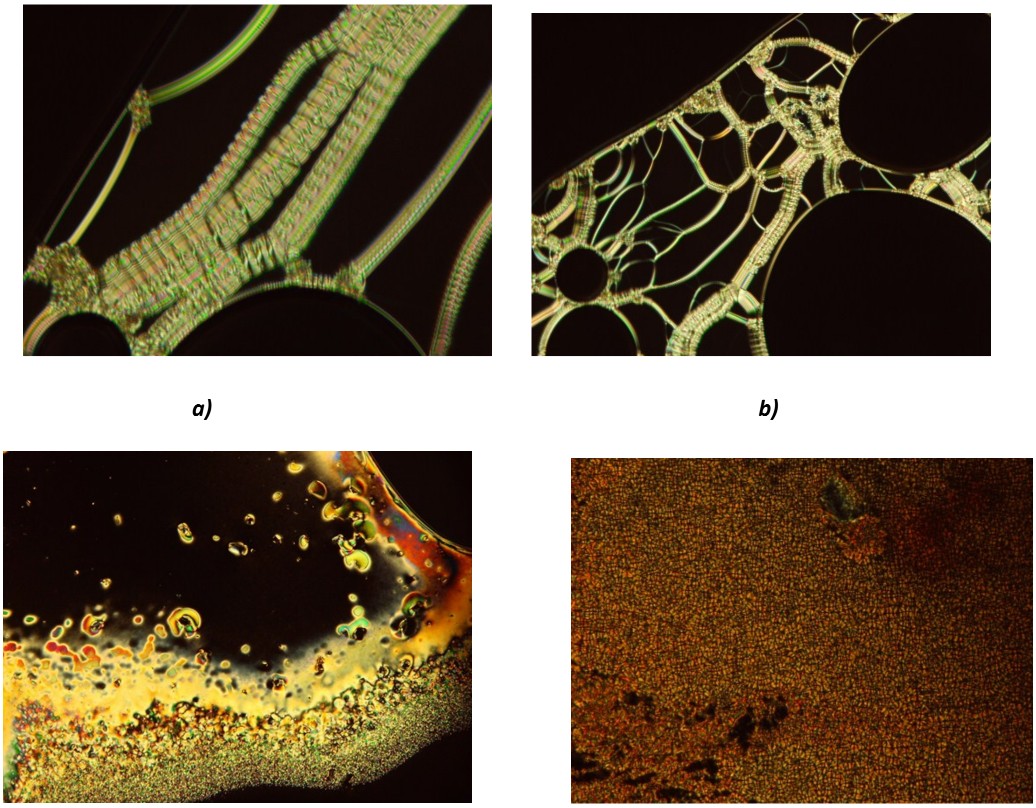
3.2. POM textures.



a) *b)*

c) *d)*

Figure S3. Textures observed by POM of ***b*-PEI-(1,2,4-OXA$_4$)$_n$**. *a)* taken at 27 °C in the second heating process; *b)* taken at 140 °C in the second heating process; *c)* taken at 185 °C in the second heating process; *d)* taken at 179 °C in the second cooling process.



a) *b)*

c) *d)*

Figure S4. Textures observed by POM of ***l*-PEI-(1,2,4-OXA$_4$)$_n$.** *a)* taken at 185 ^{o}C in the first heating process; *b)* taken at 186 ^{o}C in the first heating process; *c)* taken at 223 ^{o}C in the in the first cooling process; *d)* taken at 111 ^{o}C in the first cooling process.

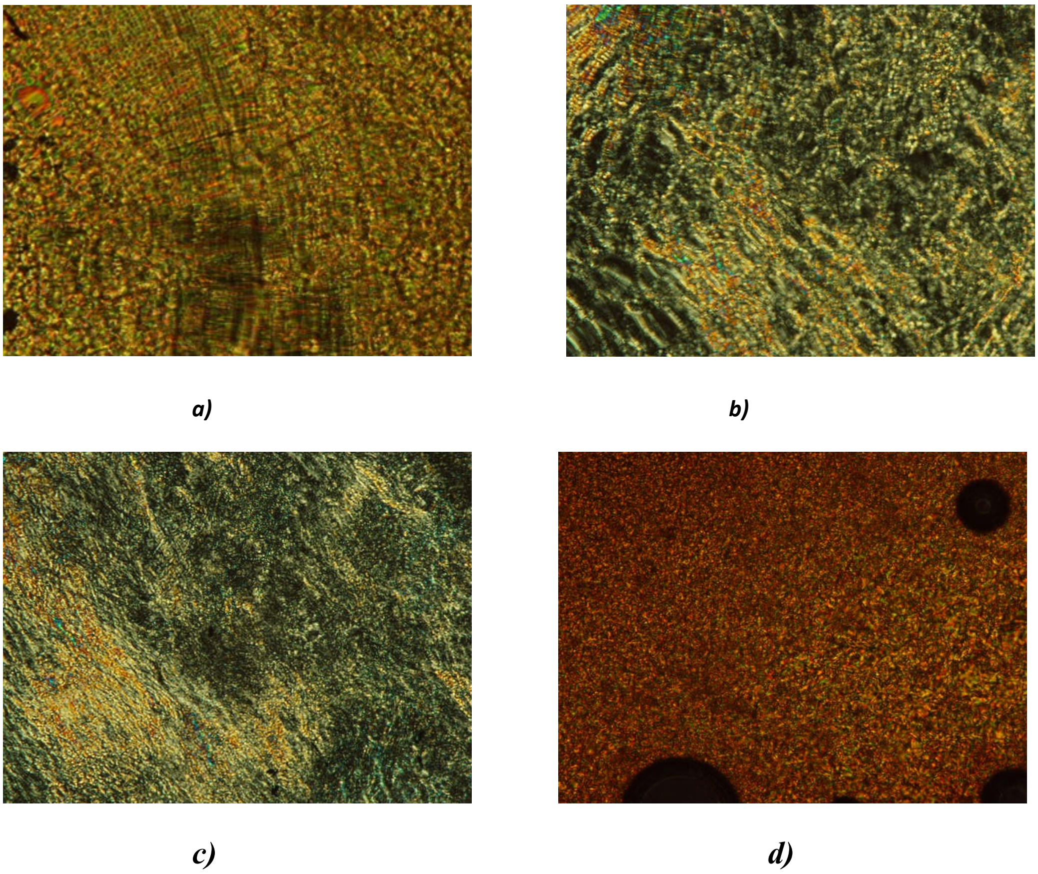
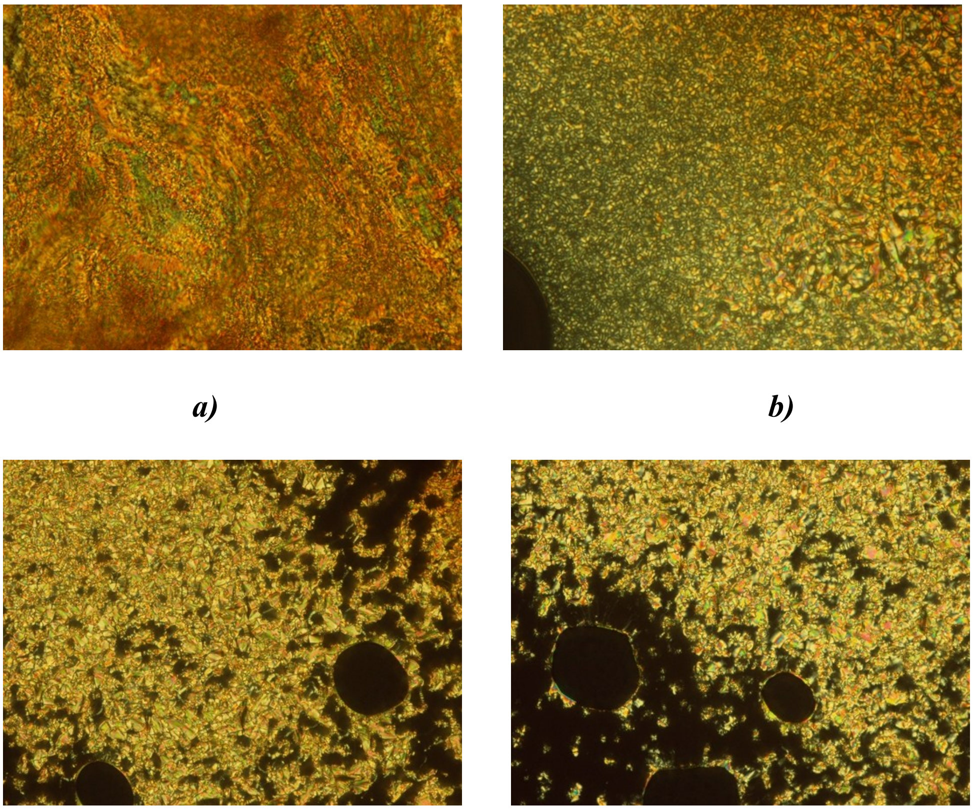


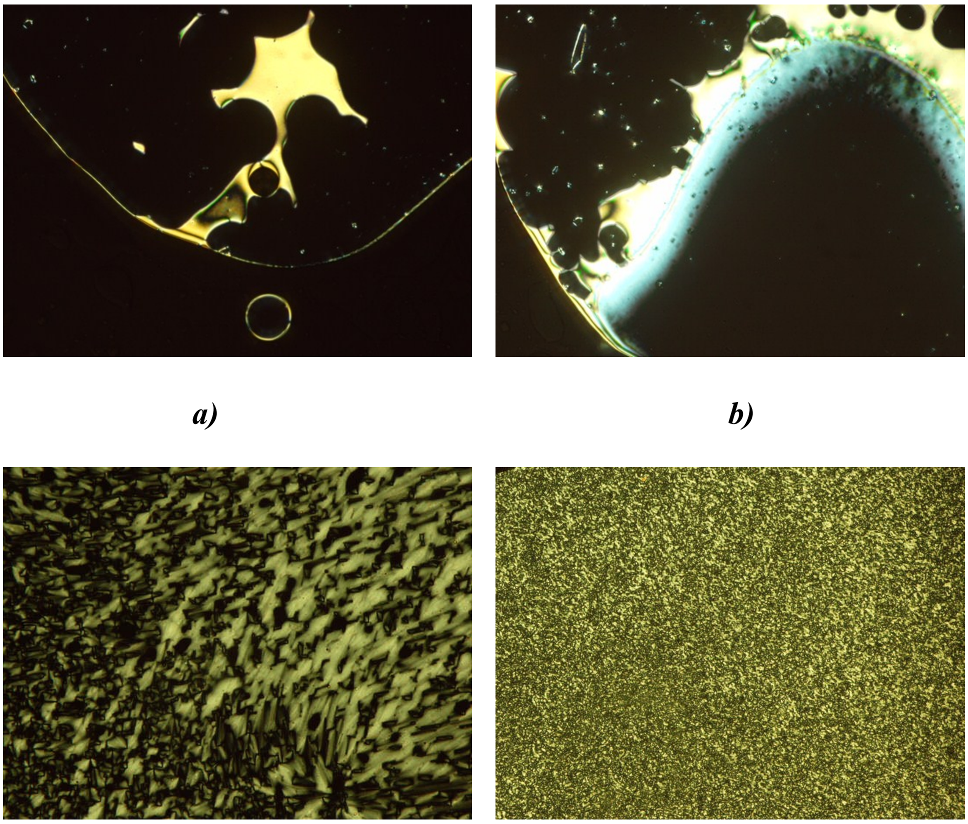
Figure S5. Textures observed by POM of ***b*-PEI-(1,2,4-OXA$_{10}$)$_n$.** *a)* taken at 229 °C in the first heating process; *b)* taken at 171 °C in the first heating process; *c)* taken at 148 °C in the first cooling process; *d)* taken at 127 °C in the second cooling process.



a) *b)*

c) *d)*

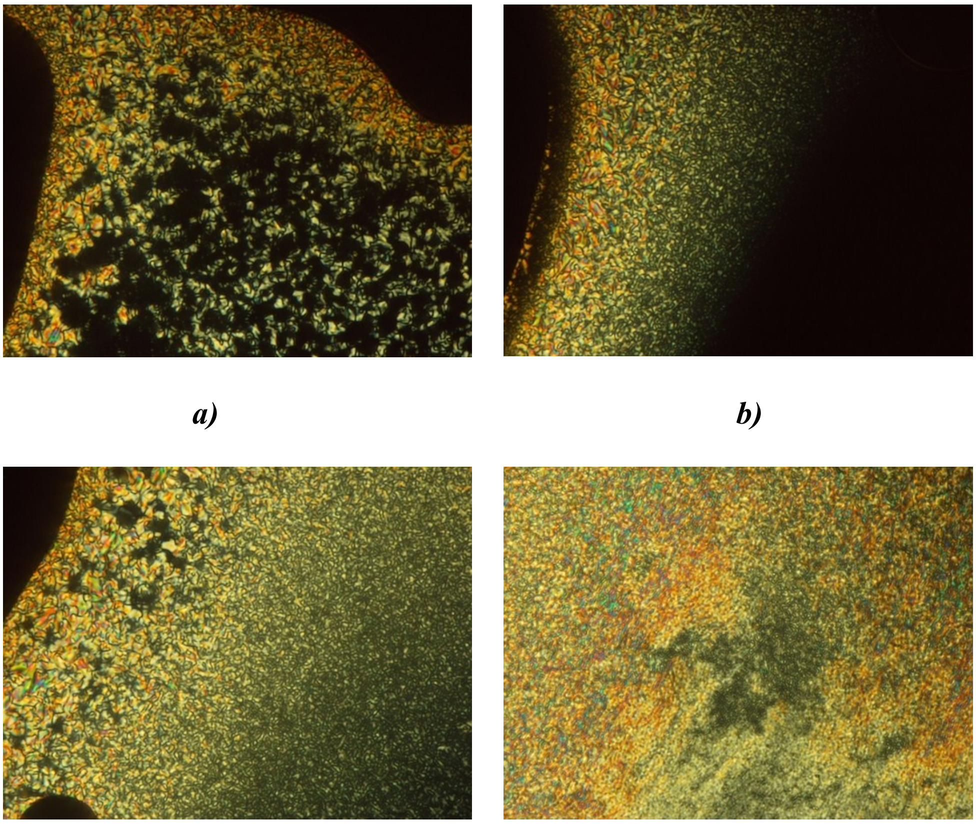
Figure S6. Textures observed by POM of ***b*-PEI-(1,3,4-OXA$_4$)$_n$** *a)* taken at 138^{o}C in the first heating process; *b)* taken at 170 ^{o}C in the second cooling process; *c)* taken at 127 ^{o}C in the in second cooling process; *d)* taken at 45 ^{o}C in the second cooling process.



a) *b)*

c) *d)*

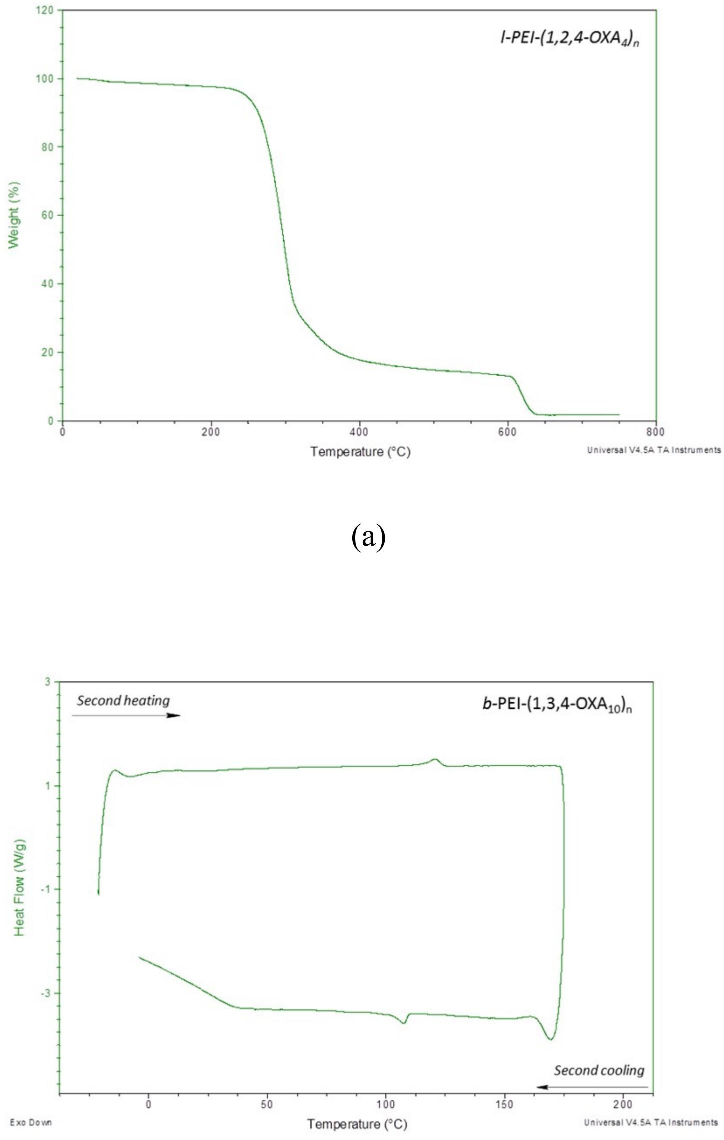
Figure S7. Textures observed by POM of ***l*-PEI-(1,3,4-OXA$_4$)$_n$**. *a)* taken at 163°C in the first heating process; *b)* taken at 163 °C in the second cooling process; *c)* taken at 105 °C in the in second heating process; *d)* taken at 45 °C in the third cooling process.



a) *b)* *c)* *d)*

Figure S8. Textures observed by POM of ***b*-PEI-(1,3,4-OXA$_{10}$)$_n$.** *a)* taken at 165^{o}C in the first heating process; *b)* taken at 160 ^{o}C in the second cooling process; *c)* taken at 155 ^{o}C in the in second cooling process; *d)* taken at 115 ^{o}C in the second cooling process.

3.3. TGA and DSC thermograms

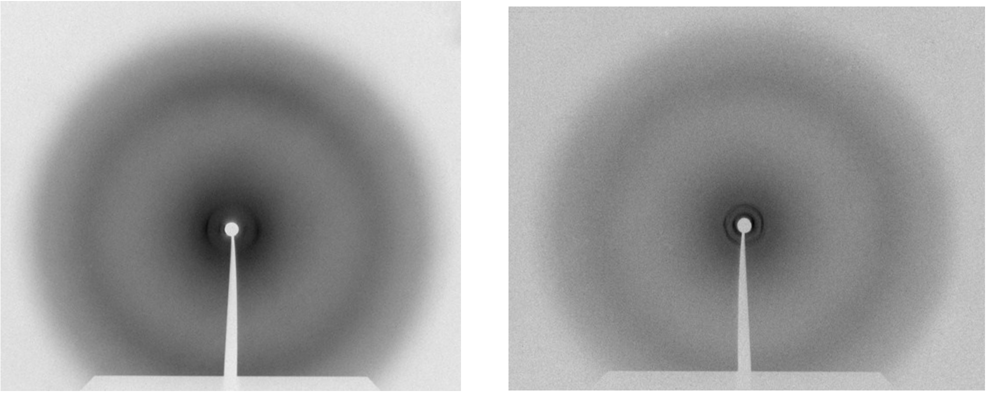


(a)

(b)

Fig. S9. (a) The TGA thermographs of compound ***l*-PEI-(1,2,4)-OXA$_{10}$)$_n$** under nitrogen gas at a heating rate of 10.0 °C /min. (b) DSC trace of compound ***b*-PEI-(1,3,4)-OXA$_{10}$)$_n$** registered during the second heating-cooling cycle (scan rate 10 °C/min).

3.4. XRD patterns



(a) **(b)**

Figure S10 (a) X-ray pattern of ***b*-PEI-(1,2,4)-OXA$_4$)$_n$** taken at 150 ºC in its smectic A mesophase. (b) X-ray pattern of ***l*-PEI-(1,2,4)-OXA$_4$)$_n$** taken at 150 ºC in its smectic A mesophase.