

SUPPORTING INFORMATION

Self-assembled bent-core side-chain liquid crystalline polymers

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Synthesis of the compounds. All of the compounds were prepared according to the synthetic routes and following methods similar to those reported in the literature. The synthesis of stilbazoles **1** (m.p. 108.2 °C) and **2** (m.p. 168.9 °C) is reported in ref. 3. The synthesis of monomer **M11** (m.p. 108 °C) appears in ref. 10 and a similar method was followed to prepare **M6** (K 81 °C N 94 °C I). Polymers **P6** (m.p. 171 °C) and **P11** (m.p. 154 °C) were prepared by radical polymerization of the corresponding monomers in DMF (10% w/v) with azobis(isobutyronitrile) (AIBN) (1% weight ratio) as reported elsewhere [see R. Gimenez et al. *Polymer*, (2005), 46, 9230–9242].

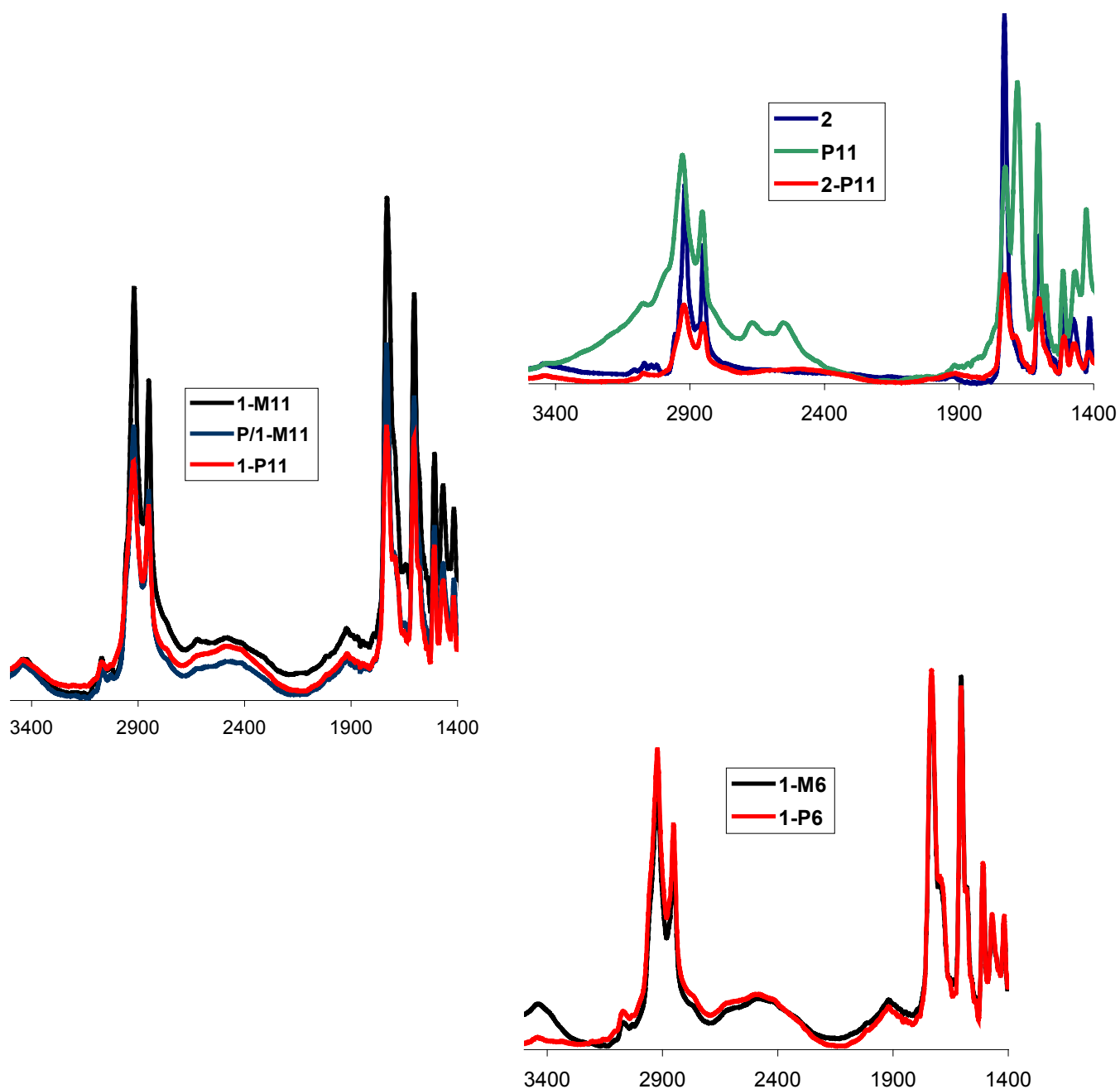
In situ photopolymerization. The photopolymerizable samples were prepared by dissolving the appropriate proportions of the reactive monomers, 1% (weight) of the photoinitiator IRGACURE 369 (CIBA Geigy) and 200 ppm of 2,6-di-*tert*-butyl-4-methylphenol (thermal inhibitor) in freshly distilled dichloromethane. The solvent was evaporated at room temperature and the residual solvent was removed by heating the sample at 30 °C under vacuum overnight.

In situ photopolymerization was studied by DSC using a Perkin-Elmer DSC-7 suitably modified for the study of photopolymerization processes. 2–6 mg of photopolymerizable sample (**1-M11**) was placed in an open aluminum DSC pan. Experiments were carried out under a nitrogen atmosphere in order to avoid oxygen inhibition. A UV lamp (Philips PL-S 9W/10), at a distance of 15 cm from the sample and reference holders, was used to irradiate the samples. The sample was heated to a temperature slightly above the isotropization point and then to the selected polymerization temperature (90 °C). The sample was maintained at this temperature for 5 min before irradiation under isothermal conditions. Irradiation was maintained for 15 min and the photopolymerization was detected as an exotherm in the DSC trace. The degree of conversion was calculated from the enthalpy content of this polymerization peak, taking 57 kJ/mol as the polymerization enthalpy of one mole of methacrylate.

Samples to be photopolymerized between uncoated glass cells or in ITO covered cells (Linkam) to produce polymeric films were introduced between the two glass plates by capillary action at a temperature 10 °C above the clearing point before cooling to the SmCP mesophase. After standing for several min to achieve stabilization, the mixtures were irradiated with a UV-A Philips PL-S 9W/10 ($\lambda = 365$ nm) lamp placed 15 cm from the cell and irradiation was maintained for 15 min.

Techniques. Infrared spectra for all the complexes were obtained using a Perkin-Elmer 1600 (FTIR) spectrophotometer in the 400–4000 cm^{-1} spectral range. Mesomorphic properties were studied by optical microscopy using an Olympus BH2 microscope with crossed polarizers. The microscope was connected to a Linkam THMS 600 hot stage. Transition temperatures were determined by differential scanning calorimetry (DSC) using either a TA2910 differential calorimeter or Perkin-Elmer DSC-7 calorimeter. Each apparatus was calibrated with indium (156.6 °C, 28.44 J/g) and tin (232.1 °C, 60.5 J/g) using a scanning rate of 10 °C/min in most cases. X-ray diffraction patterns were obtained with an evacuated Pinhole Camera (Anton-Paar) operating with a point-focused Ni-filtered Cu-K α beam. The samples were held in Lindemann glass capillaries (1 mm diameter) and heated, where necessary, with a variable-temperature attachment. The diffraction patterns were collected on flat photographic film.

Figure S1. Comparative IR spectra of different materials at room temperature.



The formation of the H-bonds is detected through the modification of the O-H stretching band of the acid. The complexes exhibit two absorptions at ca. 2500 cm⁻¹ and 1950 cm⁻¹, corresponding to the OH---N(Py), while carboxylic acid dimers show the O-H band at ca. 2650 cm⁻¹. On the other hand, an absorption at ca. 1683 cm⁻¹, corresponding to the acid dimers is not detected for the bent complexes.

Figure S2. Comparative IR spectra of different polymers at variable temperature.

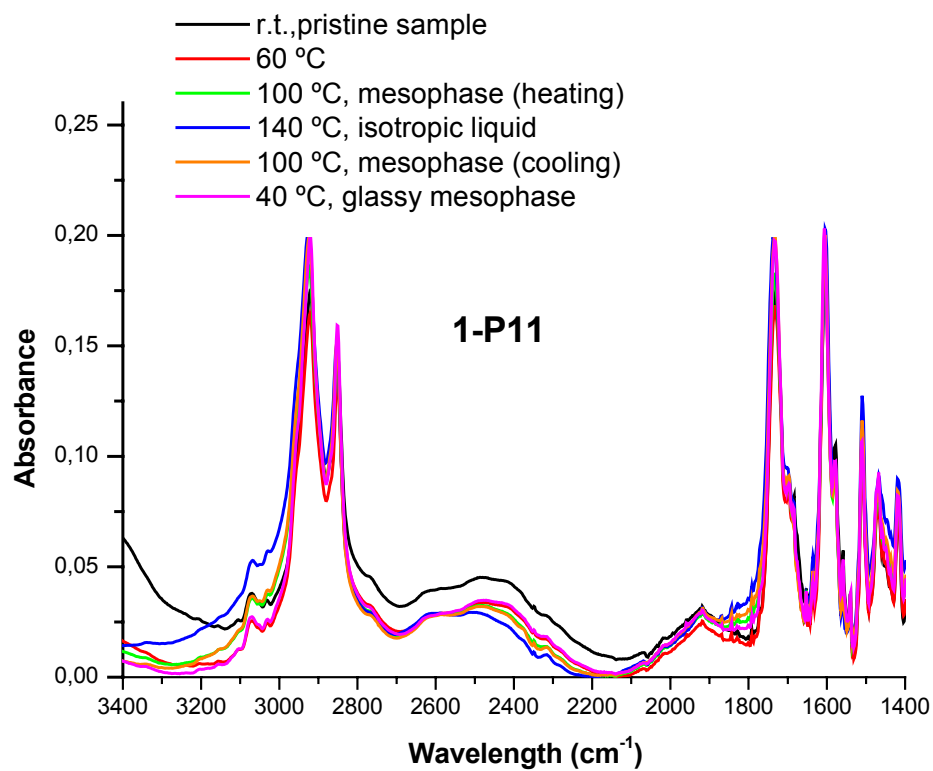
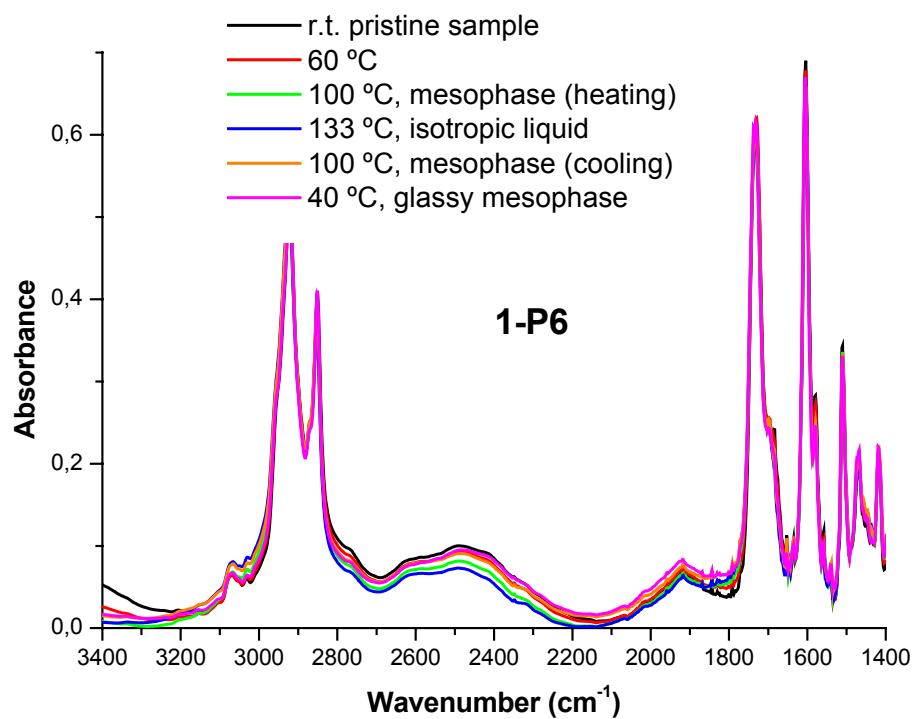


Figure S2 (cont.). Comparative IR spectra of different polymers at variable temperature.

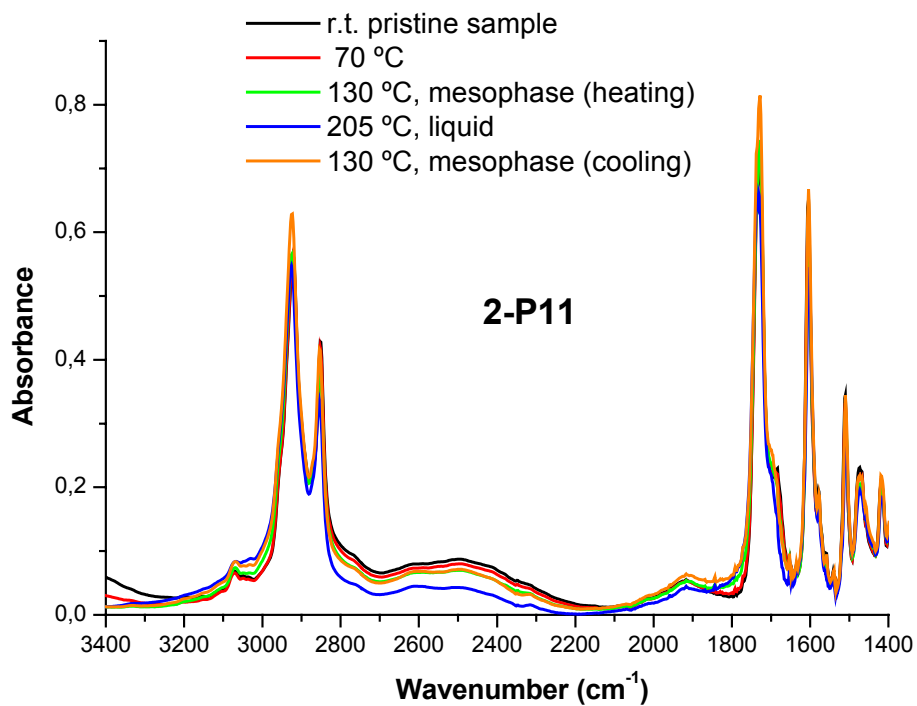
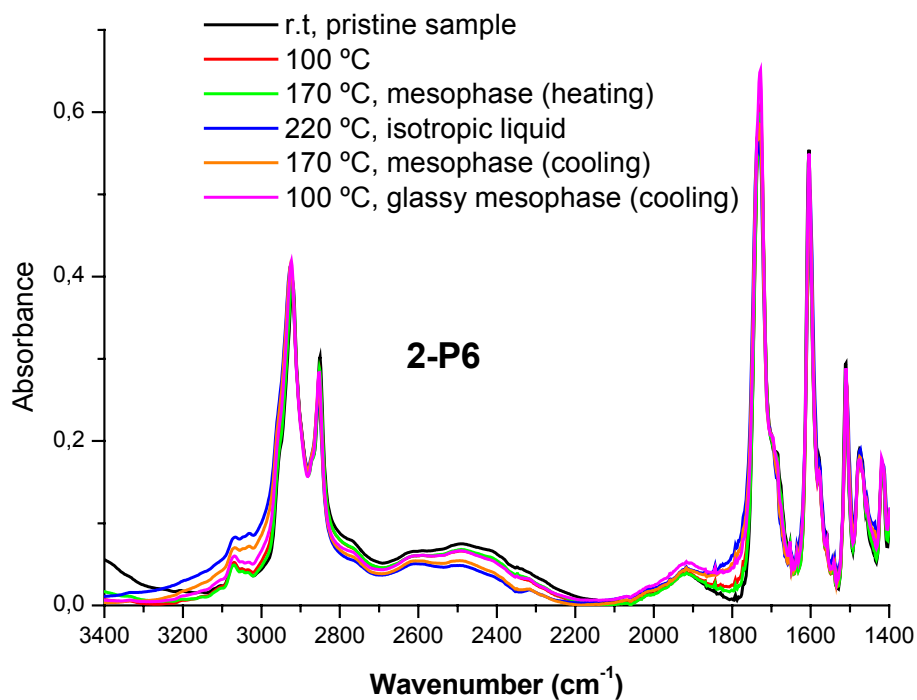


Figure S3. X-ray diffraction patterns of (a) the polymer **2-P11** (Smectic order) and (b) the polymer **1-P6** (Col order) obtained in the liquid crystal phase and at room temperature (glassy phase).

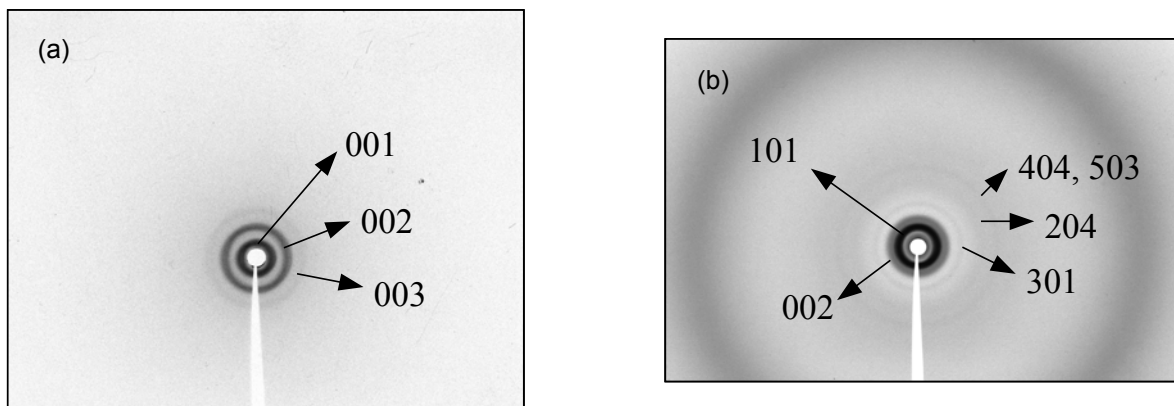


Figure S4. (a) Conversion vs. time and (b) polymerization rate vs. %conversion for **1-11M** at 90 °C (SmCP mesophase).

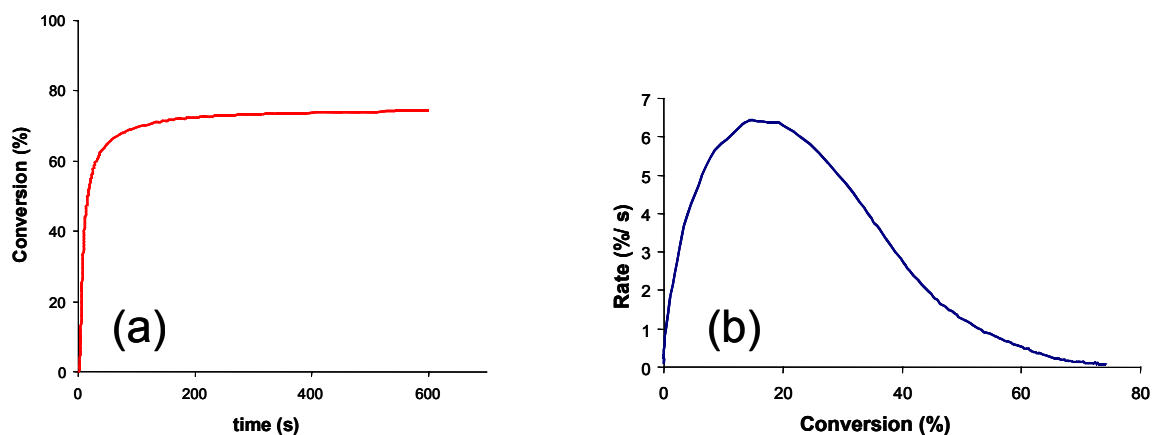


Figure S5. DSC thermograms of second scans at a rate of 10 °/min, corresponding to the polymers: (a) 1-P11 and (b) P/1-M11.

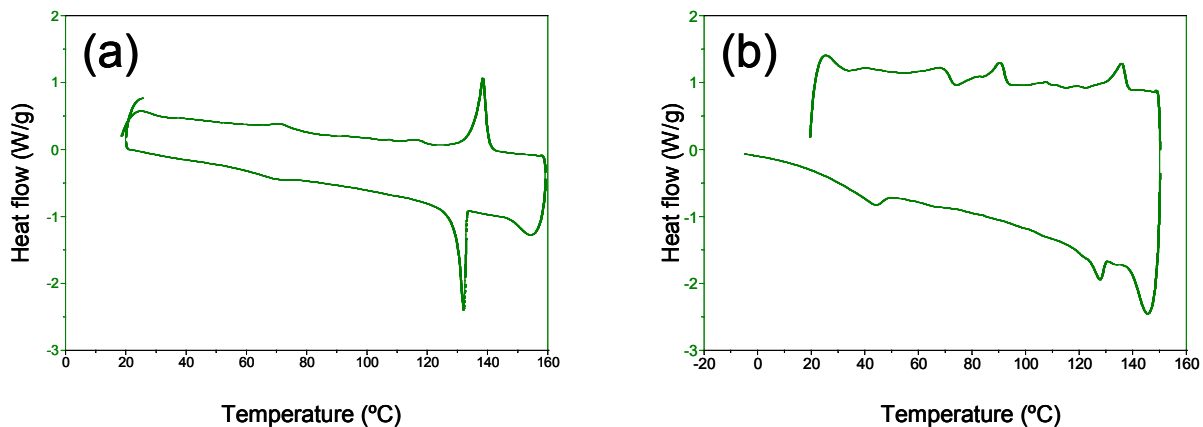


Figure S6. . Schematic representations used for bent-shaped molecules (upper part). Four types proposed for the SmCP phase packings which are distinguished by the relative tilt sense and the polar order in the smectic layers. S and A denote a synclinic or an anticlinic tilt. F and A refer to ferroelectric or antiferroelectric polar order.

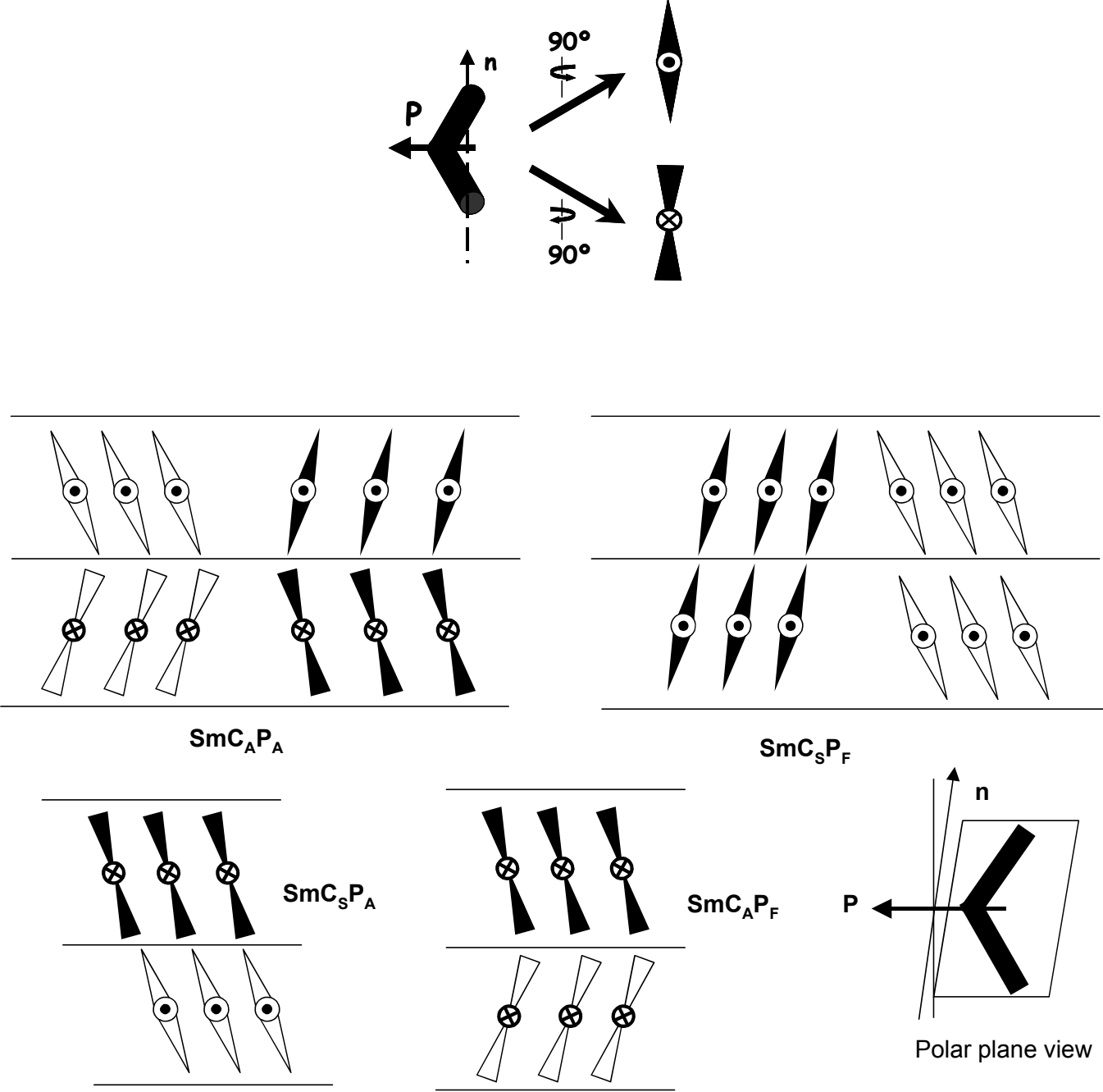


Figure S7. Models proposed for the arrangements of the polymers in the columnar rectangular mesophase and glass (Col_r) (upper part). And models proposed for the arrangements of the polymers in the smectic packings. If polar smectic C phases are assumed, a non centrosymmetric antiferroelectric arrangement is proposed for these materials based on the polymers do not show SHG activity.

