



Structure formation in photo-switchable liquid-crystalline comb-like polymers

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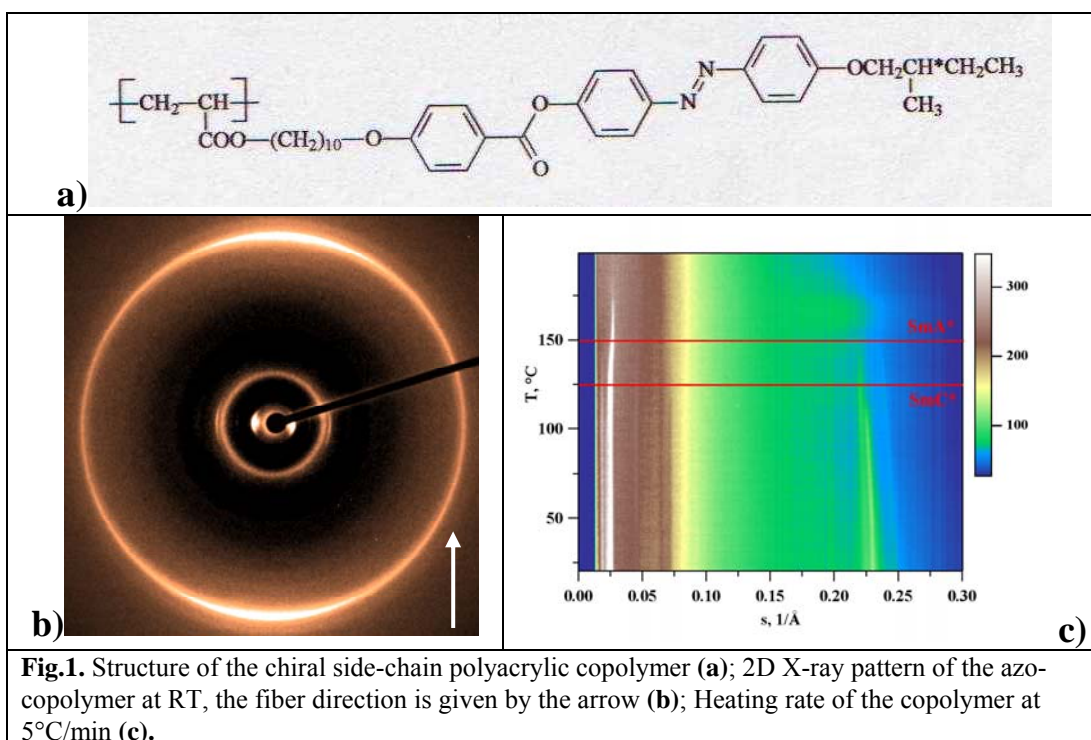
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Report:

Photo-controlled and photo-switchable materials based on liquid crystals (LC) hold promise for many practical applications' such as coloured information recording, photo-optical triggers and display units^{1,2}. It is well known that optical and electrical properties strongly depend on orientation and morphology of the polymers³. This is why optimization of the final device performance is



directly linked to understanding the supramolecular organisation of the material⁴.

In this project, we studied optically active chiral and non-chiral comb-like polymethacrylic copolymers with side-chain oxycyanoazobenzene fragments (Fig.1a). The 2D X-ray patterns were collected in transmission geometry with 2D Frelon[®] CCD camera for WAXD experiments using a 2x2 binning with pixel resolution of 100µm in both lateral directions. For the measurements, the uniaxially oriented material was placed with its fiber axis perpendicular to the incident X-ray beam with wavelength of 1.03Å.

A typical 2D GIWAXS pattern of polyacrylic based copolymer reveals multiple well-oriented reflexes of orthorhombic lattice with $a=77.6\text{\AA}$ (smectic direction), $b=61.8\text{\AA}$, $c=16.28\text{\AA}$ (Fig. 1b). The unit cell contains 36 molecules which are organized in columns each of which contains 6 side groups per layer. (Fig.2). Upon heating, the small-angle peak ($d=48.6\text{\AA}$) disappears at ca. 120°C , which corresponds to a crystal-smC* transition. The smectic structure has a period of 35\AA . Upon reaching 150°C the smC*-smA* transition occurs, and above 185°C the isotropisation takes place. It is worth to mention that the peak at 48.6\AA does not reappear immediately on cooling (cooling ramp is not shown here). It is likely that longer annealing time at RT is required.

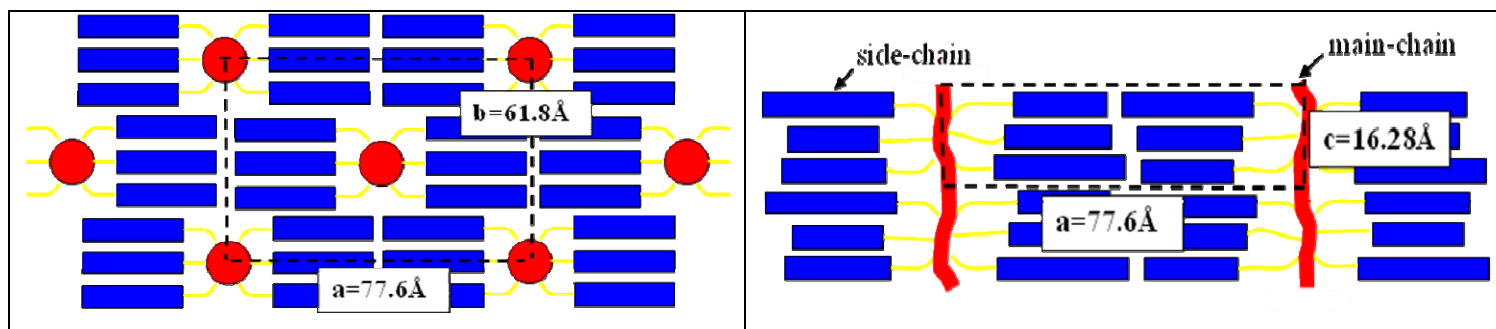


Fig.2. Schematic model of the photo-variable comblike polyacrylic copolymer (cf. Fig. 1a). The left and right panels depict the ab and ac planes of the lattice. .

To obtain highly oriented mesomorphic films PTFE-rubbed surfaces were used as substrates. The studied polymer was melted between two PTFE substrates at 130°C . After holding the film for 30min above the isotropisation T, it was slowly cooled down to RT. A free standing film was obtained by floating-off in 1% HF solution. The pattern acquired in normal direction shows two oriented equatorial peaks at 48.5\AA and 38.1\AA indexed as 110 and 200 peaks of the orthorhombic unit cell (Fig.3, right). These low-angle peaks correspond to ordering of the azobenzene-containing side groups. Moreover, due to the fact that rubbing direction is along the equator one could conclude that the columns are oriented perpendicular to the machine direction, MD (Fig.3). On the diffraction pattern recorded with the X-ray beam along the MD strong meridional peaks are observed confirming such orientation of the copolymer columns.

In summary, structural analysis of optically active comb-like copolymers was performed. The influence of the 2D-

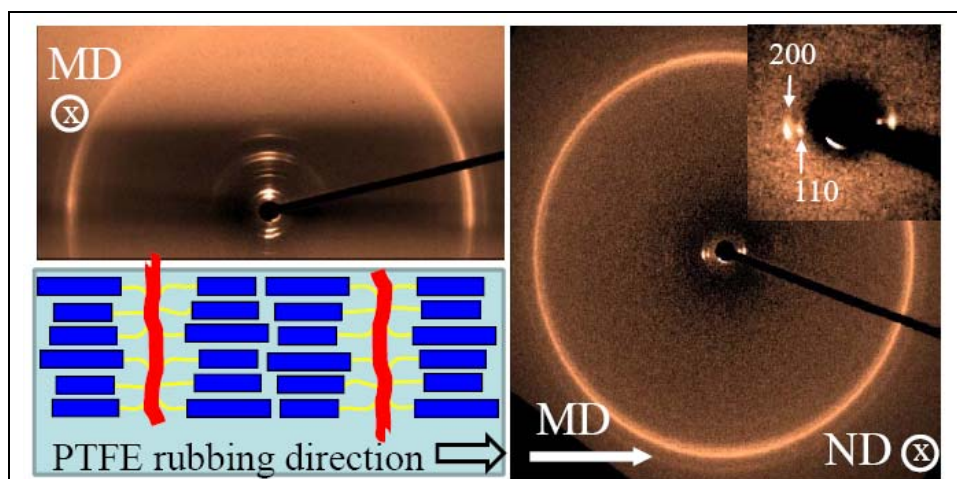


Fig.3. 2D X-ray patterns of the photo-active copolymer obtained with the beam along the normal direction (ND) to the film (right) and along the MD (left). Schematic representation of the microstructure of the LC film on the rubbed PTFE surface with the c-axis perpendicular to the rubbing direction (bottom left).

confined environment on the supramolecular organization of the polymers was examined. It was found that thin films of the mesomorphic comb-like polymer can be aligned on PTFE-rubbed substrates. The polyacrylic backbone chains are oriented perpendicular to the PTFE chain direction, which is unusual for epitaxial LC films. Subsequent crystallization of the polymer arrests the chain orientation giving rise to a macroscopically-oriented highly crystalline free-standing film. The

obtained results help to better understand the structure formation of the novel LC-polymers, which is of high importance for the development of mechanically-stable optically-active materials.

References

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