# Aligned Polyfluorene Thin Films

*M. Knaapila, B.P. Lyons, J.P. Foreman, A.P. Monkman, R. Stepanyan*[1], *K. Kisko*[2], *U. Vainio*[2], *M. Torkkeli*[2], *R. Serimaa*[2], *O. Seeck*[3]

*Department of Physics, University of Durham, South Road, Durham DH1 3LE, United Kingdom*
[1]*Physics of Complex Fluids Group, Department of Applied Physics, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands*
[2]*Division of X-ray Physics, Department of Physical Sciences, P.O. Box 64, FIN-00014, University of Helsinki, Finland*
[3] *Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, D-52452 Jülich, Germany*

Polyfluorenes (PFs) are a promising class of electroluminescent polymers for thin film applications, such as organic light emitting diodes (OLED), for use in displays of digital cameras or mobile phones. They can be recognized as hairy rod type polymers consisting of a rigid rod backbone and a dense set of flexible side chains [1]. Rod-coils with long enough segments self-organize to a thermotropic phase where the flexible and rigid parts microphase separate. Physical properties such as solubility and liquid crystallinity depend greatly on whether the side chains are linear or branched. The PF studied here, Poly(9,9-bis(ethylhexyl)-fluorene-2,7-diyl), PF2/6 *cf.* Fig 1A, is a branced chain, hole-transporting material with high photoluminescence and electroluminescence quantum yields emitting in the blue.
Due to liquid crystallinity, the rods may be easily aligned to films of high degree of order, where uniaxial alignment of the rigid backbones lead to strong optical anisotropy and excellent polarized electroluminescence [3, 4]. The alignment is carried out on a rubbed polyimide alignment layer deposited on an ITO glass substrate.
Thin films of low and high molar weight (LMW and HMW) PF2/6 have been investigated by grazing incidence X-ray diffraction (GIXD) and specular X-ray reflectivity (XR) at the beamline W1.1 (ROEWI). The samples were prepared by spin coating them on the rubbed substrates and annealing 175 $\circ$C, where the PF2/6 is nematic. Film thicknesses varied between 20-180 nm[3].

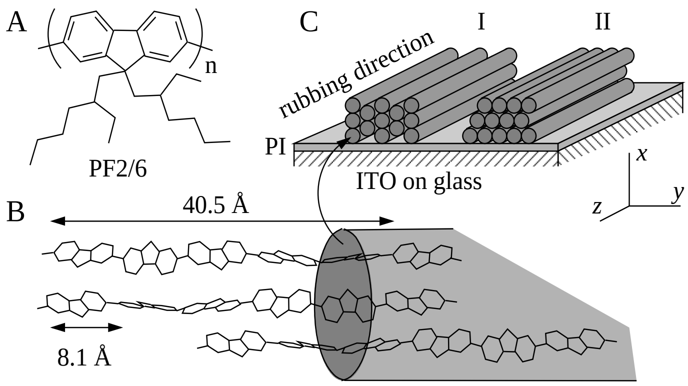


Figure 1: A) Chemical structure of PF2/6. HMW-PF2/6 has $M_w/M_n$ = 262/147 kg/mol, whereas LMW-PF2/6 has $M_w/M_n$ = 15/7.6 kg/mol (20 monomers). B) The backbone forms probably a 5/2 helix, which makes two turns per five monomers 40.5 Å. C) Organization of the polymer on the alignment substrate. The molecules pack three per hexagonal unit cell, $a = 16.7$ Å. The $c$-axis is along the rubbing direction. The hexagons have two orientational possibilities, I and II, which coexist in thin films.

HMW-PF2/6 has been found to form well ordered morphology in thin films same as in the bulk[2]. The material shows better crystallinity along $c$-axis, while lateral order is paracrystalline[1]. When prepared carefully under clean-room conditions, the films are holeless in optical resolution and

XR also indicates uniform film quality. The birefringence is less uniform which may be related to observed multiple orientation in GIXD, see Figure 2A.

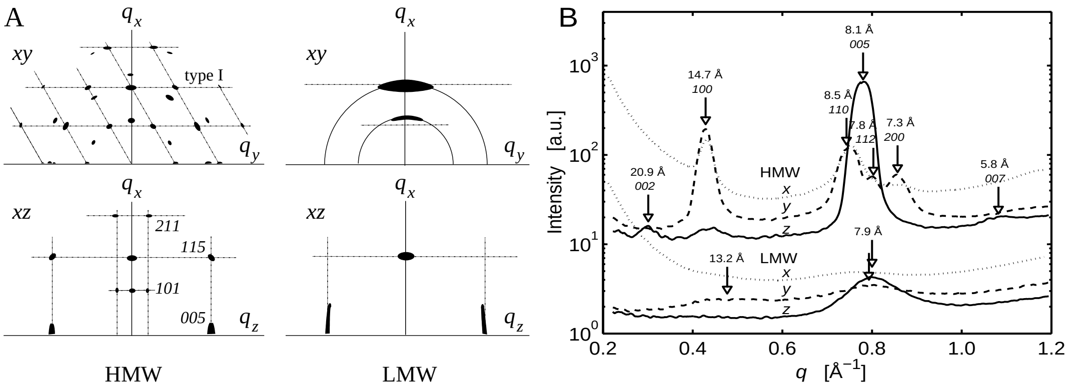


Figure 2: A) Representative Image plate patters of HMW and LMW PF2/6. Intensities were measured using energy 8.8 keV and incident angle 0.13°. The $xy$-plane of HMW shows reflection spots of both orientations, type I at the nodes of the grid lines, and type II in between. The $xz$-plane shows reflections related to the helical repeat 40.5 Å and monomer repeat 8.1 Å. The LMW polymer has much weaker, nematic order. B) Intensity curves taken along $x$-,$y$- and $z$-axes. The helical repeat of LMW polymer is ca. 1 Å shorter, while their lateral packing appears also significantly denser.

LMW-PF2/6 is also found to be a thermotropic liquid crystal consisting of rodlike helices. On rubbed substrates, considerably higher dichroic ratios in absorption than in similarly processed HMW-PF2 are found, indicating much better axial alignment. GIXD shows that LMW-PF2/6 is less ordered on the $xy$-plane than HMW-PF2/6 and nematic rather than hexagonal. The structure differs from the nematic state obtained above $T_c$ = 165 °C in that the hexagonal cell of three polymer chains still persists. The 8 Å reflection remains relatively sharp and since its position does not change very much, we do not expect a large change in the polymer conformation.

In conclusion, using low molar weight PF2/6 seems to produce more uniform films and higher dichroic ratios. The alignment is improved perhaps due to fewer chain entanglements and there are differences in lateral packing and order. Most importantly these do not affect optical properties; 20 monomer units is clearly more than the effective conjugation length.

# References


[1] M. Knaapila, R. Stepanyan, B. P. Lyons, M. Torkkeli, T. P. A. Hase, R. Serimaa, R. Güntner, O. H. Seeck, U. Scherf, and A. P. Monkman, Macromolecules, submitted.

[2] M. Knaapila, B.P. Lyons, K. Kisko, J.P. Foreman, U. Vainio, M. Mihaylova, O.H. Seeck, L.-O. Pålsson, R. Serimaa, M. Torkkeli and A.P. Monkman, J.Phys.Chem. B 107 12425 (2003)

[3] M. Knaapila, K. Kisko, B. P. Lyons, R. Stepanyan, J. P. Foreman, O. H. Seeck, U. Vainio, L-O. Pålsson, R. Serimaa, M. Torkkeli, and A. P. Monkman J.Phys.Chem. B, 108, 10711 (2004).

[4] M. Knaapila, B. P. Lyons, K. Kisko, O. H. Seeck, J. P. Foreman, U. Vainio, R. Serimaa, M. Torkkeli, and A. P. Monkman, Proceedings of SPIE: The International Society for Optical Engineering, (Organic Light Emitting Devices VIII), Ed. Z. H. Kafafi, Vol. 5519, 226 (2004)