



FIRST SYNTHESIS OF ISOTACTIC POLY(9-ALKYL₁-9-ALKYL₂FLUORENE) VIA DIRECTED ARYL-ARYL COUPLING OF CHIRAL AB-TYPE MONOMERS

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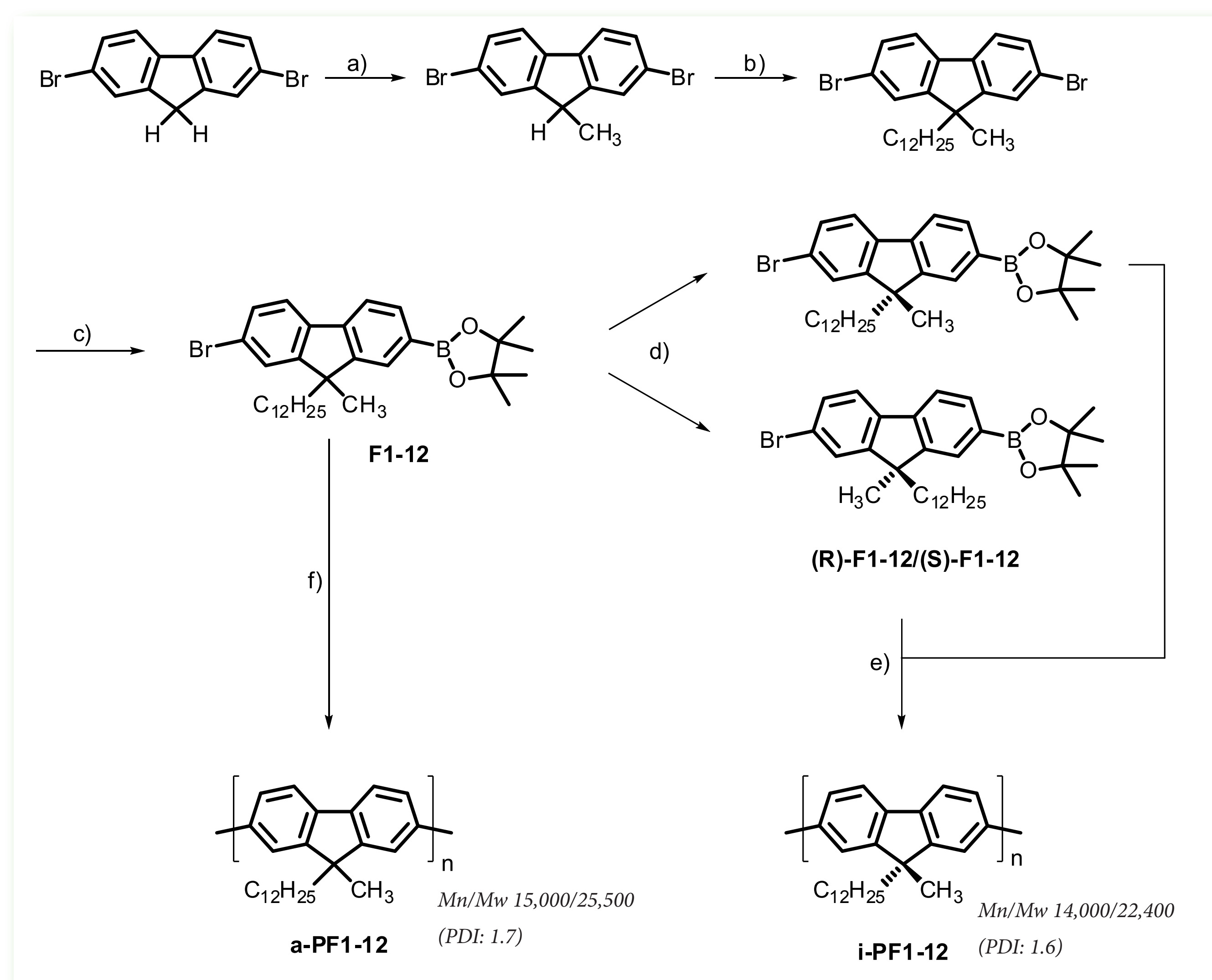
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ABSTRACT:

Non-symmetrically substituted chiral 9-alkyl₁-9-alkyl₂-fluorene monomers of the AB-type allow for their directed, stereoregular aryl-aryl cross coupling after Suzuki the synthesis of isotactic poly(9-alkyl₁-9-alkyl₂-fluorene). Therefore, we have studied an alternate synthetic route towards non-symmetrically substituted, isotactic poly(9-alkyl₁-9-alkyl₂-fluorene)s. *Scheme 3* illustrates the chemical structures of atactic, isotactic and syndiotactic poly(9-dodecyl-9-methylfluorene) **PF1-12**. Hereby, our primary target was poly(9-dodecyl-9-methylfluorene) **PF1-12** with its two alkyl substituents of rather different alkyl length. The main focus of our work was, therefore, the development of a synthetic scheme towards isotactic poly(9-dodecyl-9-methylfluorene) **i-PF1-12** (*Scheme 1*). Further on, we tried to collect first structure data on the resulting solid state properties in the comparison of atactic and isotactic poly(9-dodecyl-9-methylfluorene) (**a-PF1-12** and **i-PF1-12**) with similar average molecular weights and molecular weight distributions.

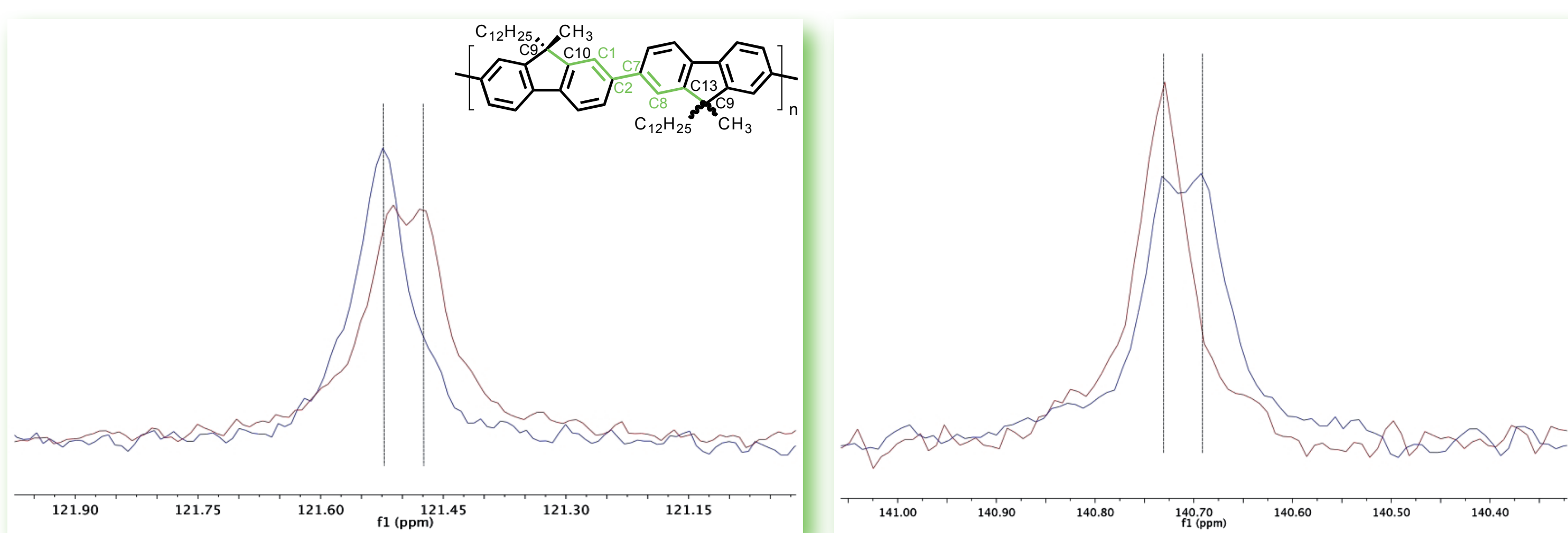
As expected, the isotactic poly(9-dodecyl-9-methylfluorene) **i-PF1-12** of this study shows an increased solid state ordering and distinctly different thermal properties when compared to its corresponding atactic, stereoirregular polyfluorene counterpart **a-PF1-12**.

SYNTHESIS:



• **SCHEME 1** - Synthesis of **i-PF1-12** and **a-PF1-12**; **a)** n-Butyl-Li/CH₃I; **b)** KOH/C₁₂H₂₅Br; **c)** n-Butyl-Li/[C(CH₃)₃]₂O₂ BOCH(CH₃)₂; **d)** preparative HPLC; column: Chiracel OD; eluent: 2-propanol/n-hexane (0.1 : 99.9; v/v); **e)** and **f)** 0.05 mol% PdCl₂[PPh₃]₂/KOH.

NMR STUDIES:

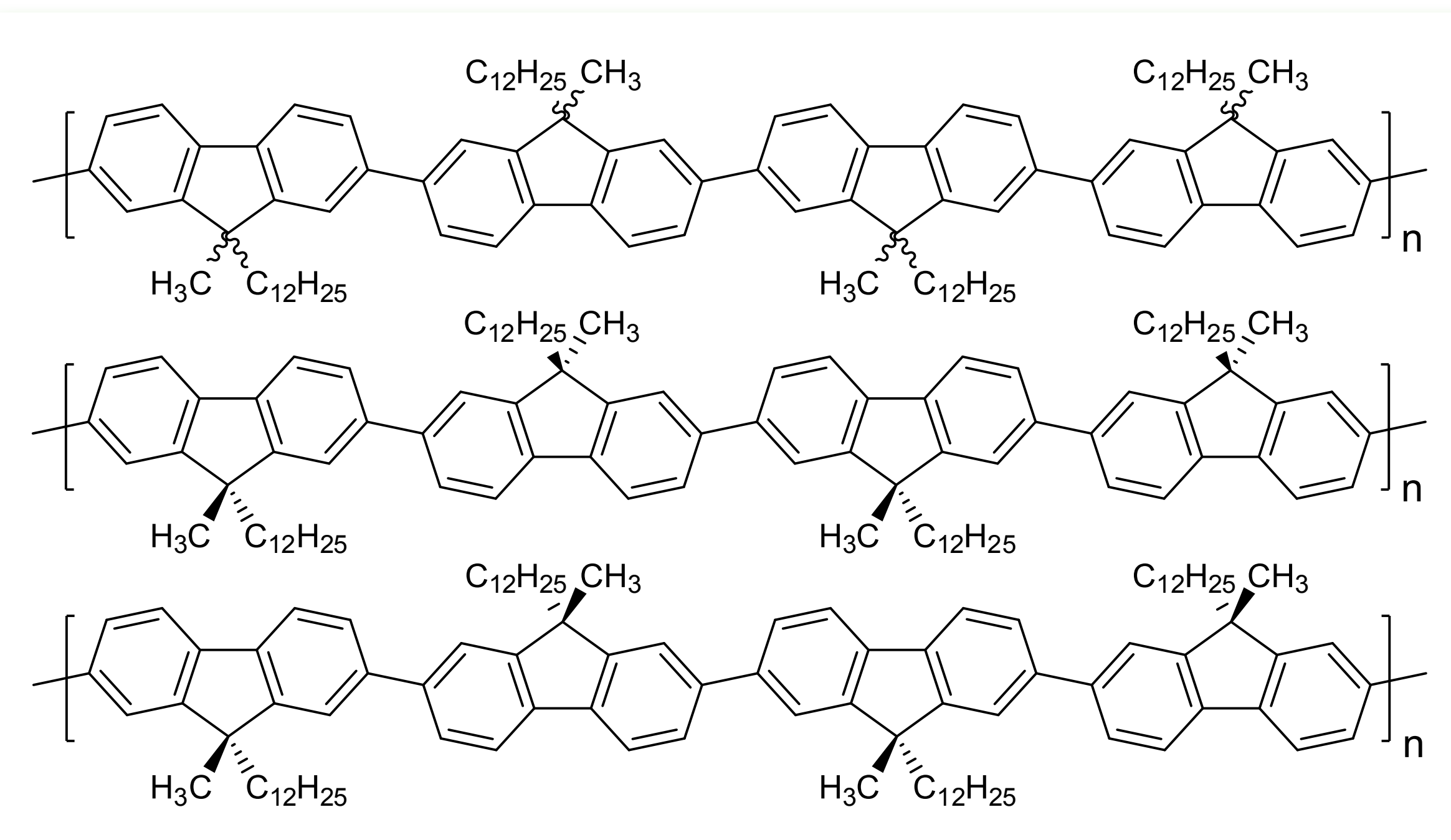


• **SCHEME 3** - Signal splitting for the ¹³C-NMR signals of **a-PF1-12** (left:C1/8; right: C2/7); in contrast **i-PF1-12** shows only single signals.

The ¹H- und ¹³C-NMR spectra of **i-PF1-12** and **a-PF1-12**, are nearly identical in a first inspection. However, two of the six non-equivalent aromatic carbons in the ¹³C-NMR spectrum of the atactic **a-PF1-12** form signal pairs with a δ of 0.03 and 0.05 ppm, due to the presence of the two different isomeric dyads (RR/SS and RS): one ternary C_{ar}-H with a chemical shift at 121.5 ppm (121.51/121.48) and one quaternary C_{ar} at 140.7 ppm (140.74/140.69). These two signal pairs have been assigned to the four central carbons of the shortest connection between two adjacent, dialkylated C9 stereo centres (see *Scheme 3*), in fully agreement with the known ¹³C-NMR data of related poly(9,9-dialkylfluorene)s. Hereby, the signal splitting is somewhat more pronounced for the carbons C2/C7 of the central aryl-aryl single bond.

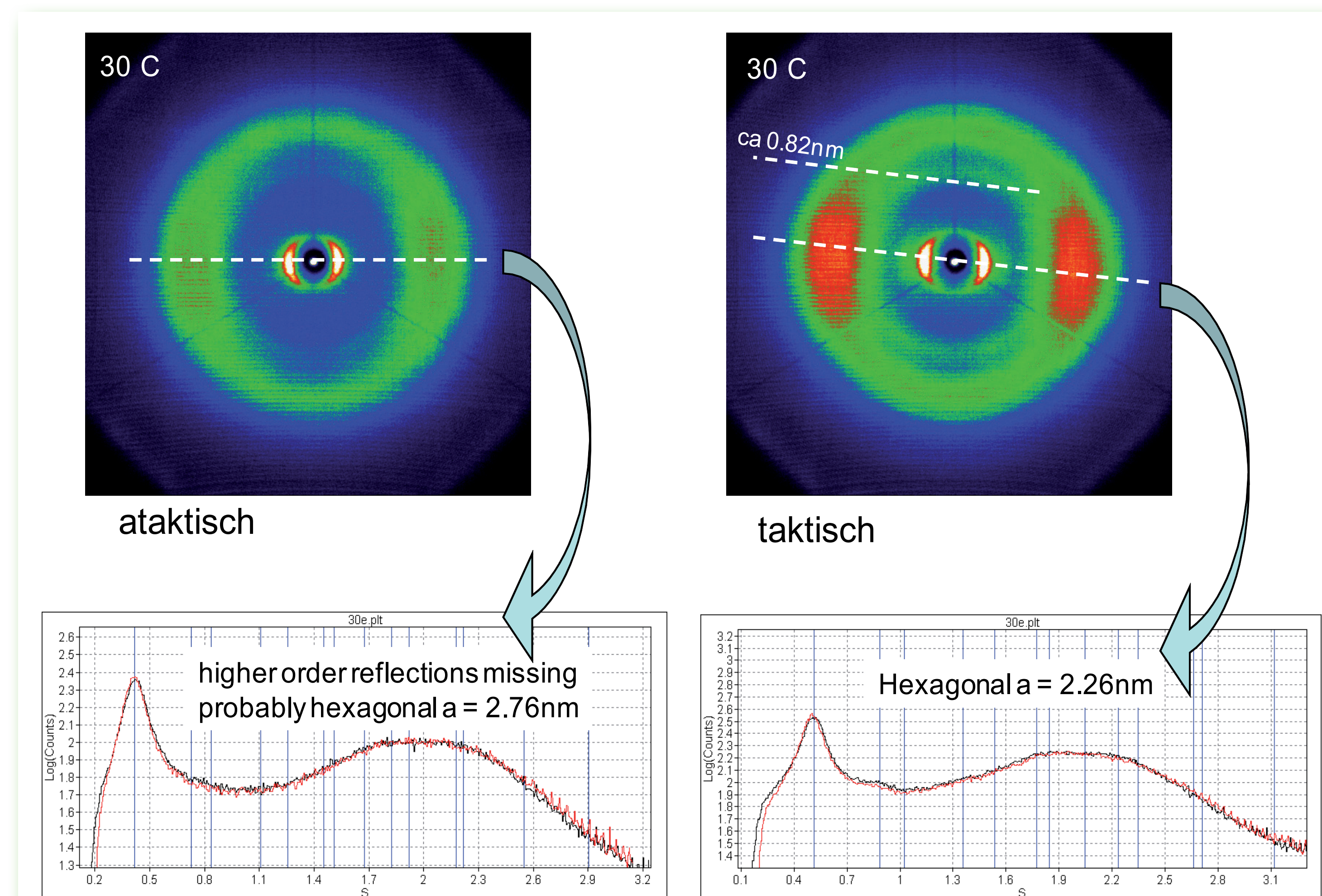
CONCLUSION & OUTLOOK:

- Confirmation of the expected packing difference between atactic and isotactic PF1-12
- Differences in thermal behavior of **a-PF1-12/i-PF1-12**
- Further experiments to the solid state structure are planned (X-ray diffraction experiments in the temperature range of 20-300°C)



• **SCHEME 3** - Chemical structures of atactic (top), isotactic (middle) and syndiotactic (bottom) poly(9-dodecyl-9-methylfluorene) **PF1-12**.

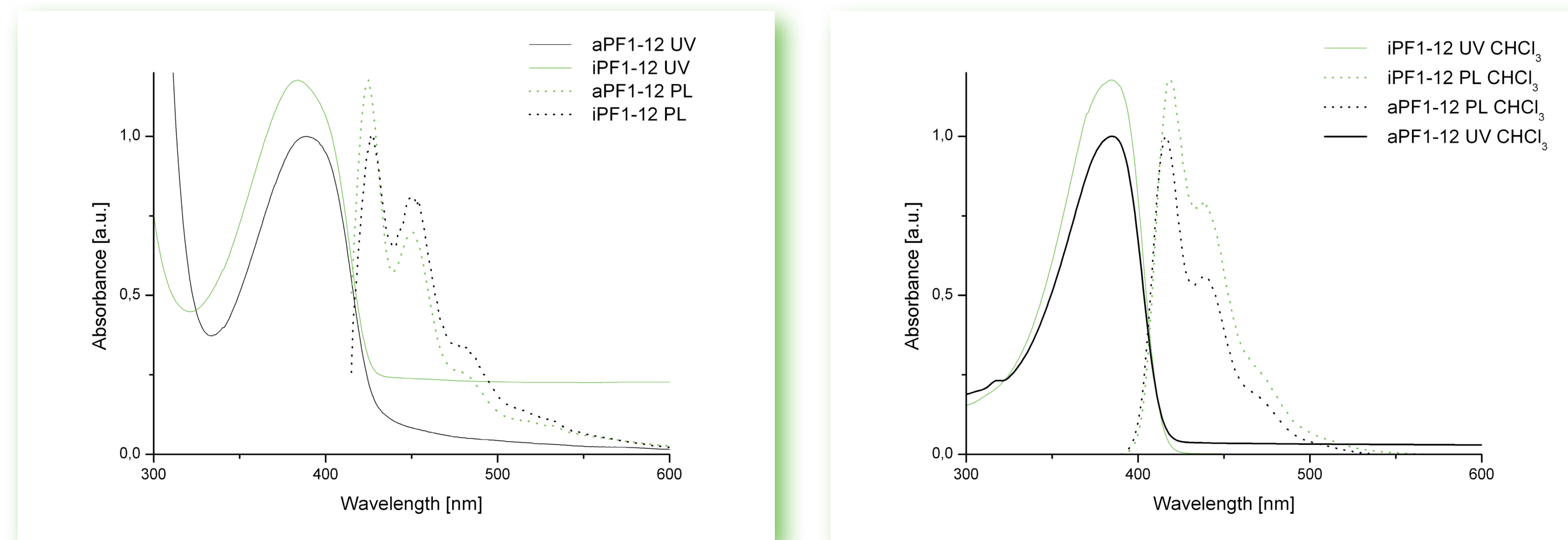
X-RAY (2D-WAXS) - STUDIES:



• **SCHEME 4** - 2D-WAXS images of atactic **a-PF1-12** and isotactic **i-PF1-12** (recorded at 30 °C).

The solid state organization of **a-PF1-12** and **i-PF1-12** was investigated by using twodimensional wide-angle scattering X-ray (2D-WAXS) on fibre extruded samples. *Scheme 4* shows the characteristic patterns with relatively broad reflections indicating for both polymers a relatively weak arrangement. Equatorial higher order reflections suggest a better packing for **i-PF1-12** in comparison to the atactic derivative and correlate to a hexagonal arrangement of the chains to each other with an interchain distance of 2.26 nm. The **a-PF1-12** polymer does not exhibit this kind of higher order reflections due to lower order. Assuming also a hexagonal lattice for **a-PF1-12**, the unit cell parameter of 2.76 nm is derived being significantly larger in comparison to **i-PF1-12**. This pronounced difference in packing parameters is due to the influence of the stereoregular, isotactic side chain arrangement allowing a much closer packing density and leading to a loss of the liquid crystalline properties in **i-PF1-12**. In comparison to these values, the well studied **PF2/6** with significantly shorter 2-ethylhexyl chains revealed a hexagonal packing parameter of 1.65 nm.

OPTICAL PROPERTIES:



• **SCHEME 5** - UV/Vis absorption and photoluminescence (PL) spectra of **a-PF1-12** and **i-PF1-12** in the solid state (left) and in dilute chloroform solution (right)

- Planning to do a variation of the alkyl chain length and incorporation of substituent couples of different polarity (non-polar/polar).
- Moreover, the availability of our isotactic polyfluorene derivatives of the **i-PF1-12** type provides access to chiral, all-conjugated block copolymers.