

## SUPPLEMENTARY MATERIALS

### Influence of backbone ladderization and side chain variation on the orientation of diketopyrrolopyrrole-based donor-acceptor copolymers

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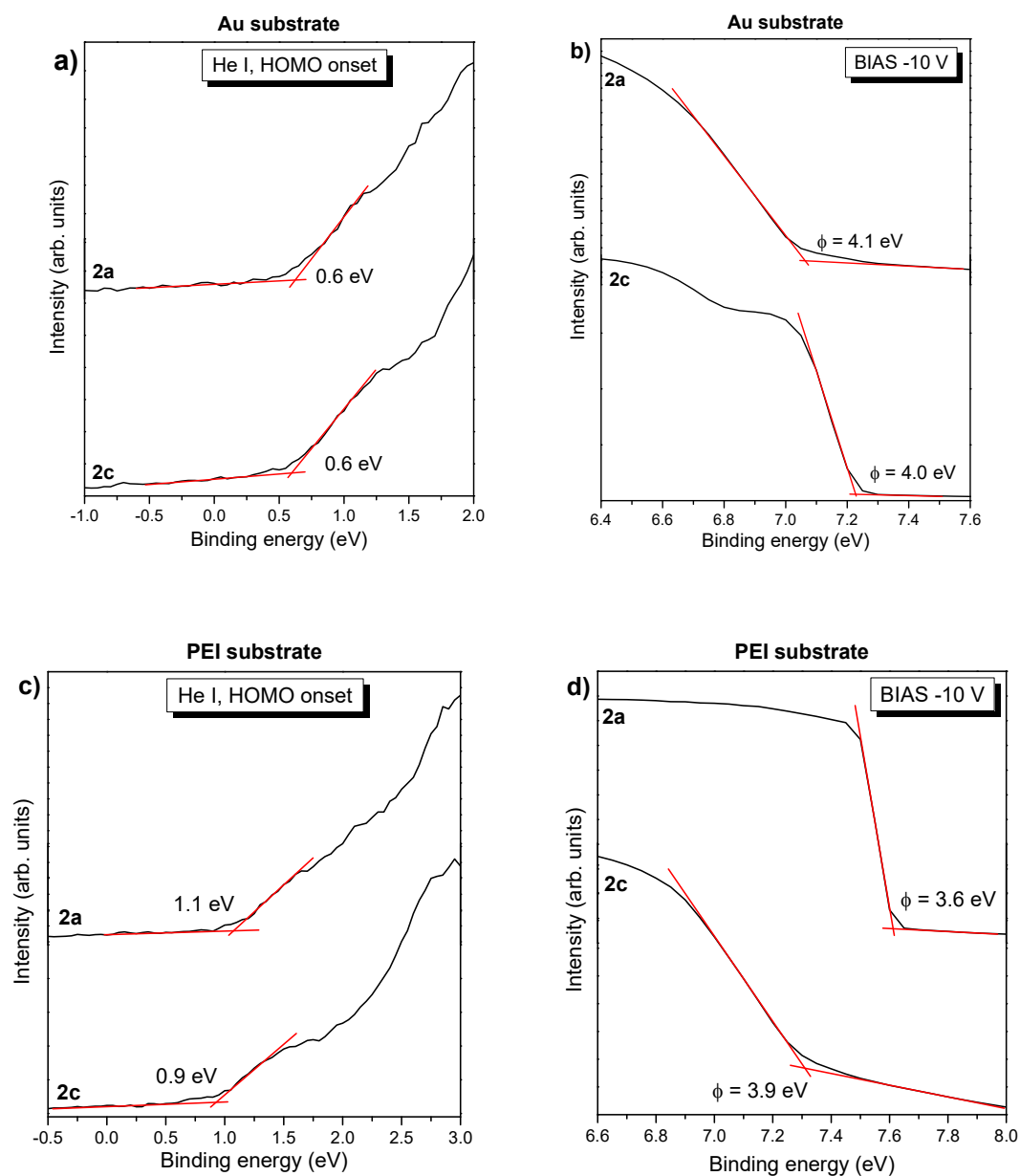
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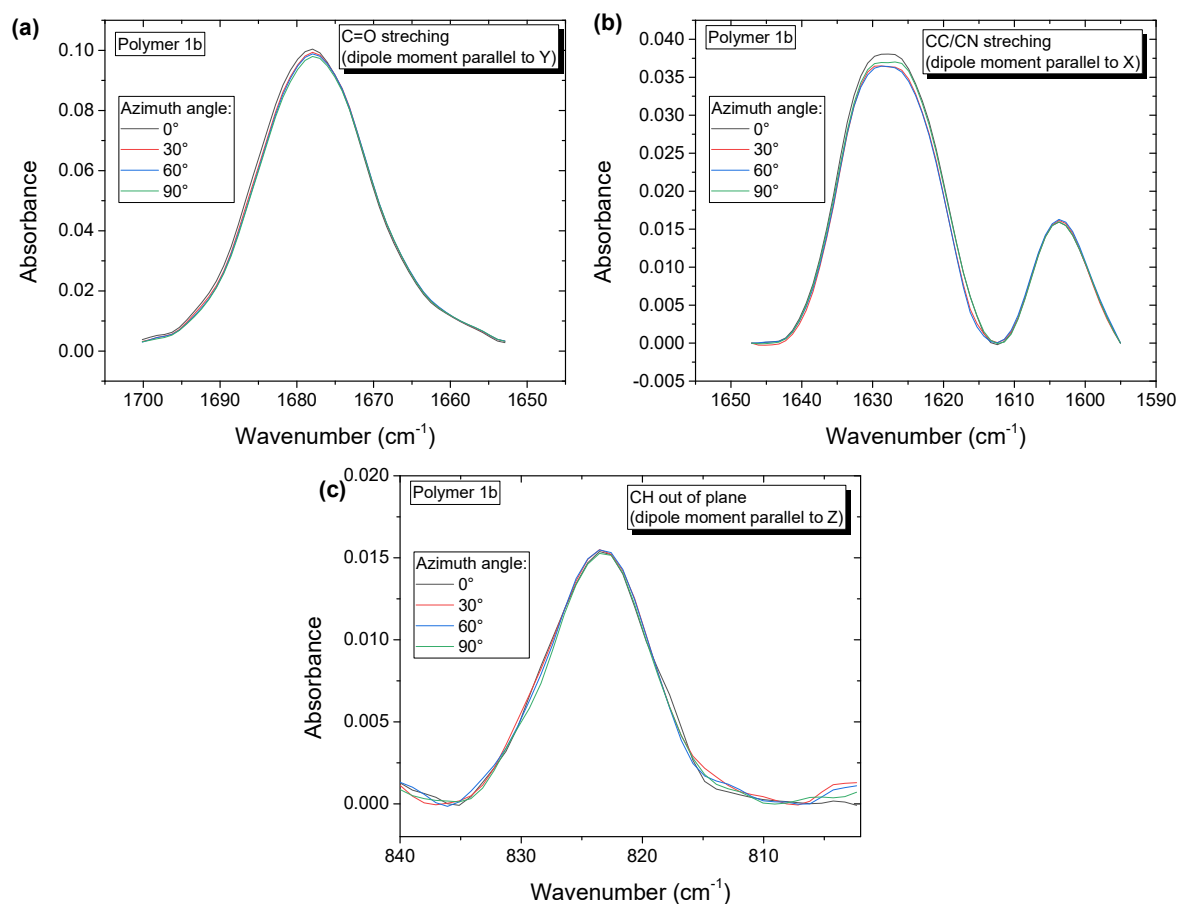
#### Content

- Ultraviolet photoelectron spectra for the determination of the ionization potential of polymers 2a and 2c
- IR spectra of thin films in transmission as a function of the azimuthal angle for polymers 1b, 2a, 2b and 2c
- IR spectra in transmission of film and pellet for polymers 1b, 2a, 2b and 2c

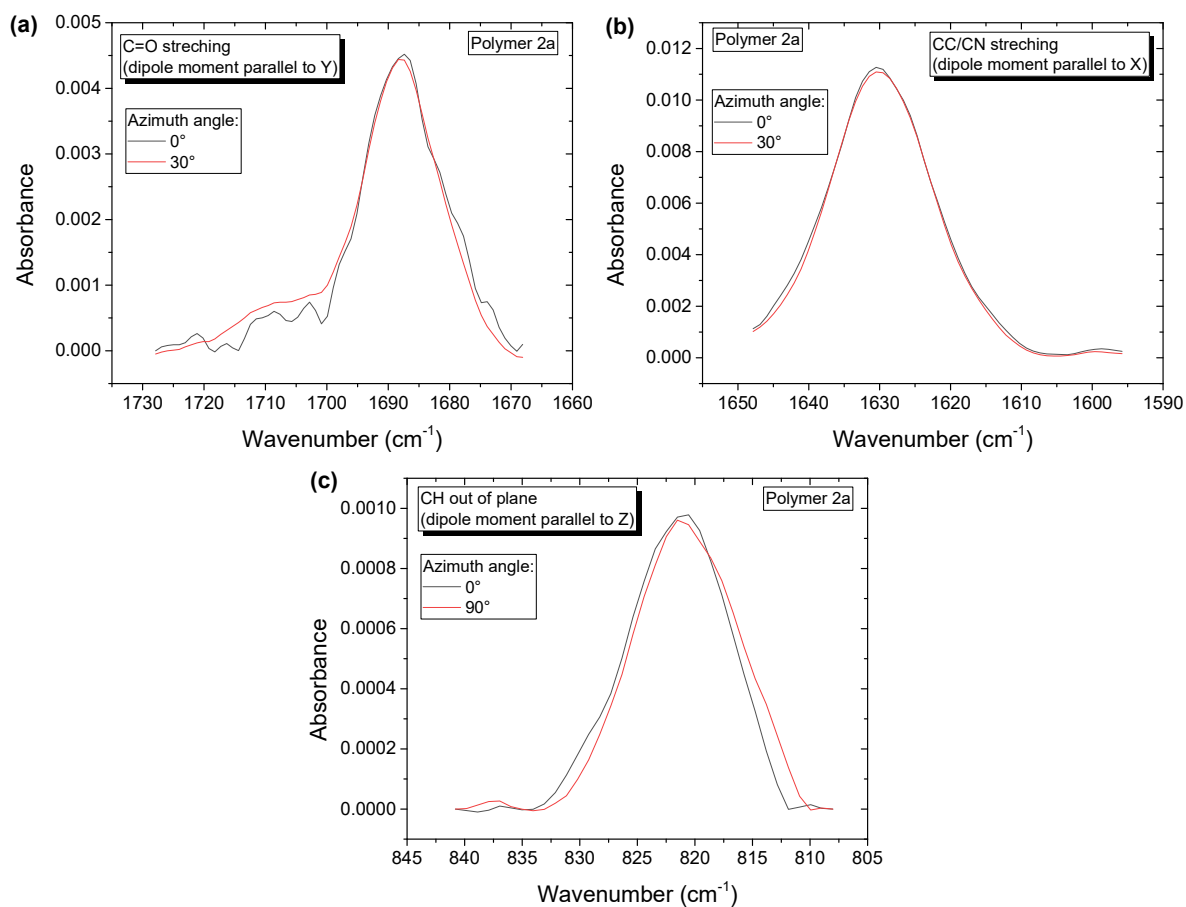


**Figure S1.** Zoom into the high and low binding energy region of ultraviolet photoelectron spectra (UPS) (excitation: He I radiation) of polymers 2a and 2c for the determination of the HOMO onset  $E_{HOMO}$  and the work function  $\Phi$ . a) and b) are on gold substrate with  $\Phi = 5.2$  eV and c) and d) on PEI with  $\Phi = 3.3$  eV. The sum of  $E_{HOMO}$  and  $\Phi$  represents the ionization potential IP of the polymers ( $4.7 \pm 0.1$  eV).

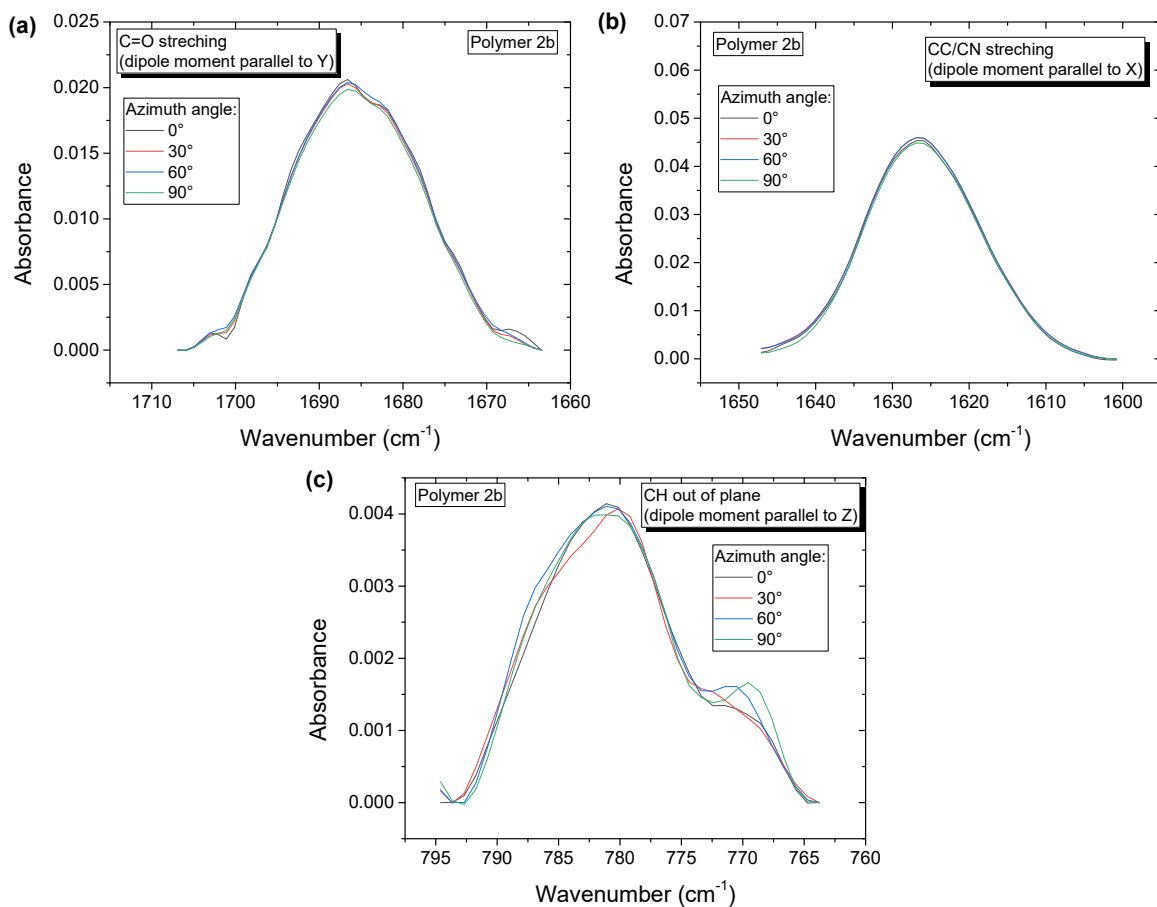
IR spectra of thin films in transmission as a function of the azimuthal angle for polymers 1b, 2a, 2b and 2c  
(Figure S2 – S5)



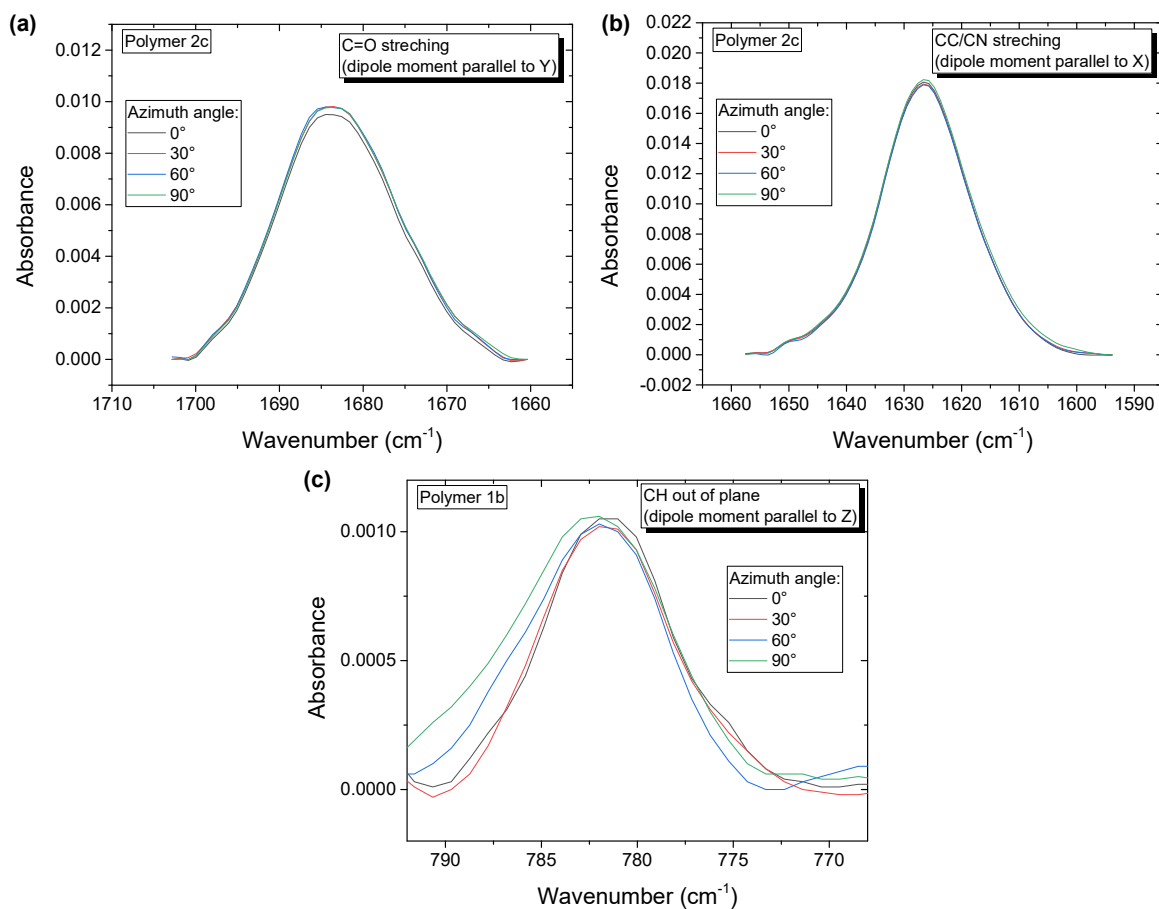
**Figure S2.** *Polymer 1b*: IR spectra in transmission (polar angle 0°) of an approx. 1200 nm thick film of polymer 1a. (a) C=O stretching vibration b) CN/CC stretching vibration c) CH out-of-plane vibration.



**Figure S3.** *Polymer 2a*: IR spectra in transmission (polar angle 0°) of an approx. 1200 nm thick film of polymer 1a. (a) C=O stretching vibration b) CN/CC stretching vibration c) CH out-of-plan vibration.

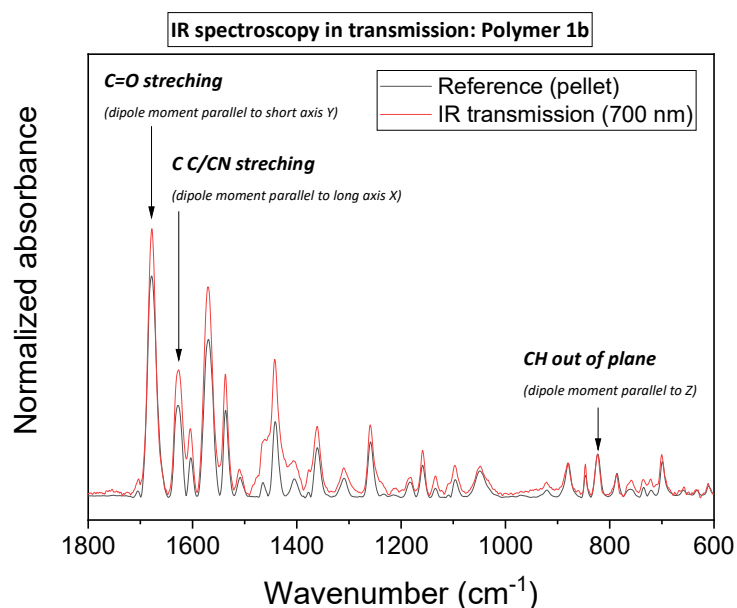


**Figure S4.** *Polymer 2b*: IR spectra in transmission (polar angle  $0^\circ$ ) of an approx. 1200 nm thick film of polymer 1a. (a) C=O stretching vibration b) CN/CC stretching vibration c) CH out-of-plan vibration.

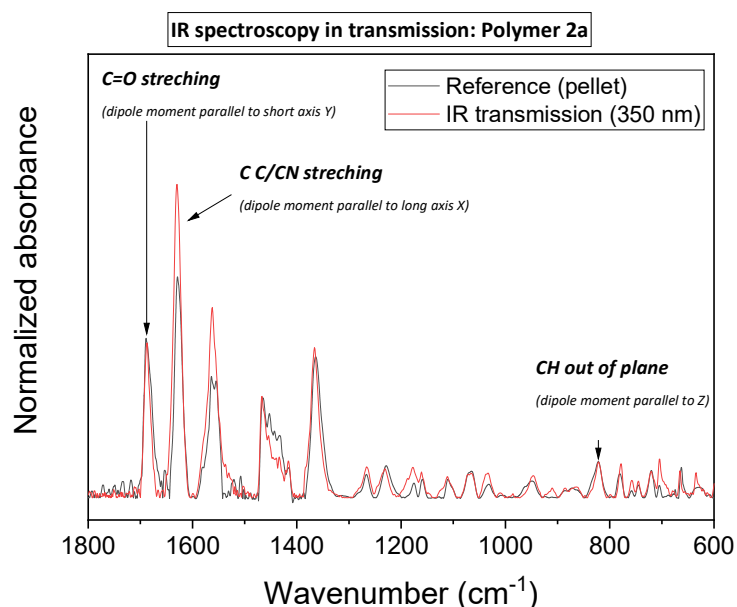


**figure S5.** Polymer 2c: IR spectra in transmission (polar angle 0°) of an approx. 1200 nm thick film of polymer 1a. (a) C=O stretching vibration b) CN/CC stretching vibration c) CH out-of-plan vibration.

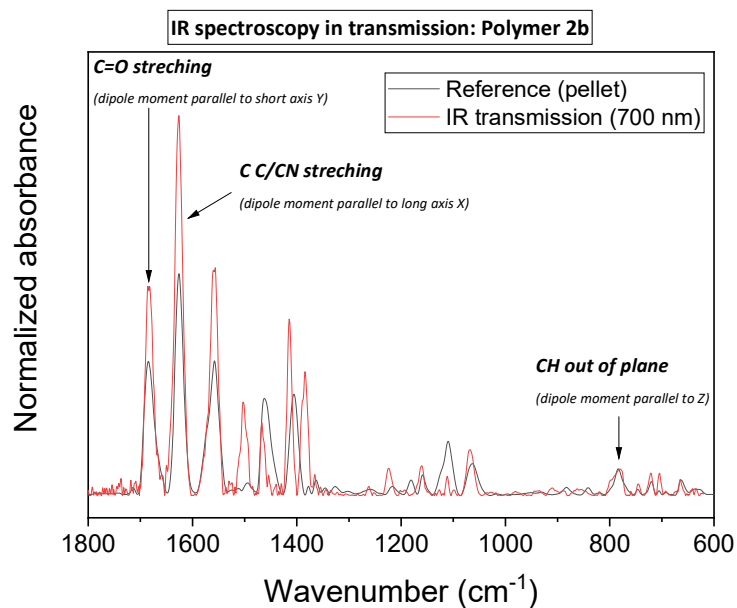
## Comparison of IR spectra in transmission of films to the reference (pellet) for polymers 1b, 2a, 2b and 2c



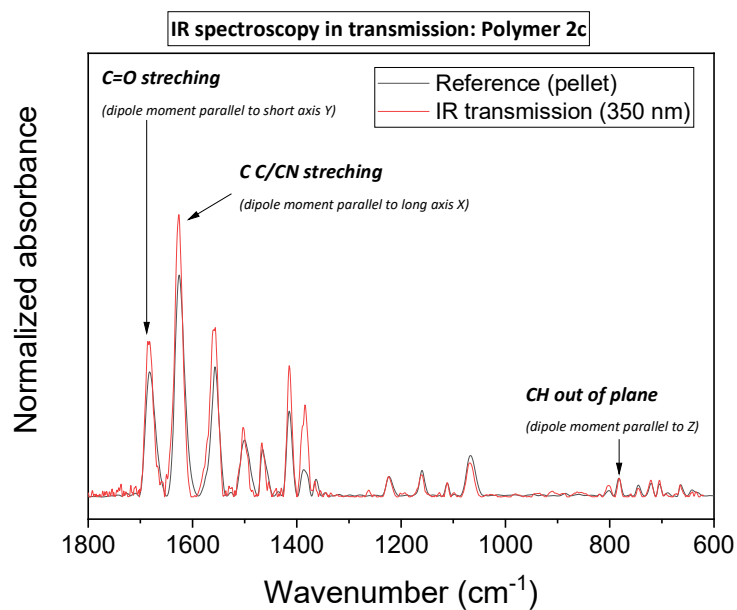
**Figure S6.** IR spectra in transmission (normal incidence, polymer 1b) in the wavelength region between 600 and 1800  $\text{cm}^{-1}$ . Comparison of the transmission spectrum of an approx. 700 nm thick film (red) to the reference of a randomly ordered sample (black, powder pressed in KBr). All spectra are normalized to the out of plane CH vibration at 822  $\text{cm}^{-1}$ .



**Figure S7.** IR spectra in transmission (normal incidence, polymer 2a) in the wavelength region between 600 and 1800  $\text{cm}^{-1}$ . Comparison of the transmission spectrum of an approx. 350 nm thick film (red) to the reference of a randomly ordered sample (black, powder pressed in KBr). All spectra are normalized to the out of plane CH vibration at 822  $\text{cm}^{-1}$ .



**Figure S8.** IR spectra in transmission (normal incidence, polymer 2b) in the wavelength region between 600 and 1800  $\text{cm}^{-1}$ . Comparison of the transmission spectrum of an approx. 700 nm thick film (red) to the reference of a randomly ordered sample (black, powder pressed in KBr). All spectra are normalized to the out of plane CH vibration at 822  $\text{cm}^{-1}$ .



**Figure S9.** IR spectra in transmission (normal incidence, polymer 2c) in the wavelength region between 600 and 1800  $\text{cm}^{-1}$ . Comparison of the transmission spectrum of an approx. 350 nm thick film (red) to the reference of a randomly ordered sample (black, powder pressed in KBr). All spectra are normalized to the out of plane CH vibration at 822  $\text{cm}^{-1}$ .