About different packing states of alkyl groups in comb-like polymers with rigid backbone

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Experimental Methods

Temperature-dependent X-ray diffraction measurements in reflection mode were performed using an Empyrean diffractometer (PANalytical) equipped with the temperature chamber TTK 450 (Anton Paar). The emitted radiation is parallelized and monochromatized using a parallel beam mirror (λ = 1.54 Å). The scattered intensity passes a parallel plate collimator (0.27°) and is detected by a Pixel 3D detector with 19 channels of 0.055 µm size combined to be used as a receiving slit. The scan range was 0.2 $Å^{-1} < q < 2.0Å^{-1}$, the step size 0.05° and the counting time per step 1 s. PPAOTs were prepared according to the thermal program mentioned in Ref.[1] whereas data for rreg P3ATs are taken from Ref.[2].

Materials

Average molecular weight M_w and polydispersity index PDI of alkoxylated poly(2,5-dialkyloxy-1,4-phenylenevinylenes) (AOPPVs) and polydispersity index as obtained from gel permeation chromatography (GPC) against polystyrene standards are given in Table A1. The melting temperatures are estimated based on temperature-dependent x-ray diffraction measurements. Further details about the synthesis of AOPPVs can be found in Ref.[3]. The synthesis and sample characteristics of poly(1,4-phenylene-2,5-dialkyloxy tere-phthalates) (PPAOTs) are reported in Ref.[1]. The rreg poly(3-alkylthiophenes) (P3ATs) were purchased from Rieke Metals and have high molecular weights (M_w > 100 kg/mol).[1]

Table A1. Sample characteristics for AOPPVs

label	*C*	M_w (kg/mol)	PDI	T_m (°C)
HOPPV	6	5.02	1.69	≈ 230
OOPPV	8	5.92	1.67	≈ 235
DOPPV	10	4.48	1.37	≈ 210
DDOPPV	12	3.58	1.30	≈ 210

Table A2. Sample characteristics for PPAOTs

label	*C*	M_w (kg/mol)	PDI	T_m (°C)
PPHOT	6	183	1.02	≈ 230
PPOOT	8	78	6.30	≈ 220
PPDOT	10	95	6.50	≈ 230
PPDDOT	12	5.2	2.01	≈ 170

Structural parameters and unit cell fit of PPAOTs and AOPPVs based on XRD

Table A2. Structural parameters of PPAOTs [1] and AOPPVs [3]

label	*C*	d^a_{100}	d^b_{alkyl}	d^a_{020}	d^a_{001}	V^c_{CH2}
PPHOT	6	13.9	7.2	3.54	11.6	24.6
PPOOT	8	16.2	9.5	3.65	11.6	25.1
PPDOT	10	18.9	12.2	3.63	11.8	26.1
PPDDOT	12	21.0	14.3	3.64	11.9	25.8
HOPPV	6	14.6	9.3	3.89	6.3	19.0
OOPPV	8	18.1	12.8	3.96	6.3	20.0
DOPPV	10	21.2	15.9	4.02	6.3	20.1
DDOPPV	12	24.1	18.8	4.04	6.3	19.9

[a] estimated based on Bragg's law $d_{hkl} = 2\pi/q_{hkl}$ using the relevant scattering peaks at q_{hkl}; [b] $d_{alkyl} = d_{100} - d_{mc}$; [c] estimated by $V_{CH2} = (d_{100} - d_{mc}) * 2d_{020} * d_{001}/4C$

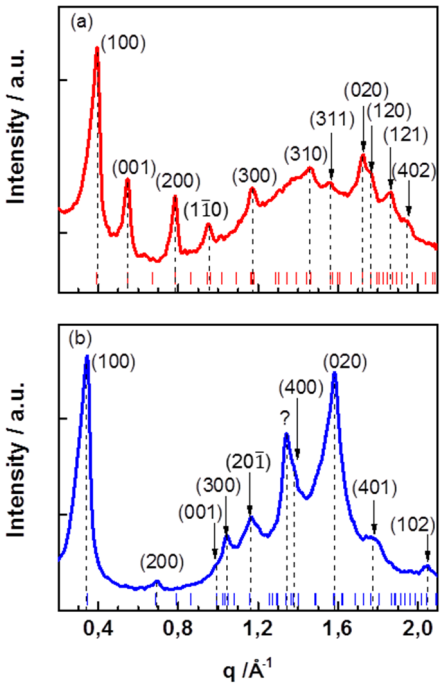

Figure A1. Scattering pattern for octyl members (C=8) of (a) the PPAOT series exhibiting modification A along with peak indexing using an orthorhombic unit cell and (b) the AOPPV series with peak indexing for a monoclinic unit cell. The used patterns are measured at room temperature.

References

1 T. Babur, J. Balko, H. Budde, and M. Beiner, *Polymer*, 2014, **55**, 6844-6852.
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