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Figure S1. TM-AFM height image of PEO-49Py (d_{film} = 7 nm) recorded at room temperature. With decreasing film thickness the inclination angles of the lamellae observed decrease until eventually at 10 nm - 20 nm thickness, depending on the crystallization temperature, the lamellae become thicker than the original average film thickness. Lamellae for these very thin films lie exactly in the plane of the film. Films thinner than 15 nm tend to break up and crystallize with a dendritic habit, as shown here.

Figure S2. Transmission mode FT-IR spectra of different PEO films on oxidized silicon crystallized isothermally at 44°C. All films show a pronounced preferential orientation of the PEO helices along the surface normal direction as concluded from the dominance of the perpendicularly polarized bands at e.g. 1360 cm^{-1}, 1278 cm^{-1}, and 947 cm^{-1} over the corresponding parallel polarized bands.

Figure S3. Logarithmic plot of excimer / monomer emission intensity vs. film thickness for thin films of PEOpy-49 crystallized isothermally at 44°C on oxidized silicon. This dependence of the excimer-to-monomer emission intensity ratio on film thickness may be attributed to the decrease in crystallinity as detected by GIR FT-IR (Figure 6) or to the increase in T_g of the ultrathin PEO films. Any increase in T_g as a result of interactions with the oxide-covered silicon substrates would slow down the motions of the PEO considerably and thus may reduce the fraction of pyrene moieties that could fluoresce as excimers. However, based on our *in situ* AFM work we can estimate the increase in T_g to

be of the order of only 30 – 35 K in the thinnest films. The corresponding difference in molecular mobility at temperatures ca. 140 K above T_g can thus hardly account for the observed reduction in excimer fluorescence. Hence, it is more reasonable to attribute the observed behavior to a dilution effect. As mentioned, a decrease in crystallinity with decreasing film thickness was detected by GIR FT-IR (Figure 6). With an increasing fraction of amorphous phase in films with decreasing thickness, the chromophores become more and more diluted. This dilution results in a decrease of the pyrene excimer emission. Given the fact that the detected reduction of the degree of crystallinity with decreasing film thickness is only qualitative in nature, we did not attempt a more thorough analysis.

Figure S4. (a) Normalized steady state fluorescence emission spectra recorded during the heating and melting of a 130 nm film of PEOpy-49 on oxidized silicon at different temperatures (top). The temperatures are indicated in the order of the spectra shown. (b) Normalized excimer emission intensity at λ_{em} = 480 nm vs. temperature (bottom). These fluorescence spectra reveal the first order phase transition as shown for the melting transition. The subsequently captured spectra show the changes of excimer-to-monomer emission at different temperatures. While the relative excimer fluorescence increases steadily up to a temperature of ca. 50°C, there is an abrupt decrease at 55°C that coincides with the onset of the melting transition. The general observations can be tentatively ascribed to the onset of significant molecular motions and rearrangements leading to the melting of the PEO lamellar crystals. After complete melting the

chains ends diffuse away from each other leading to a reduction in excimer emission relative to the monomer emission.

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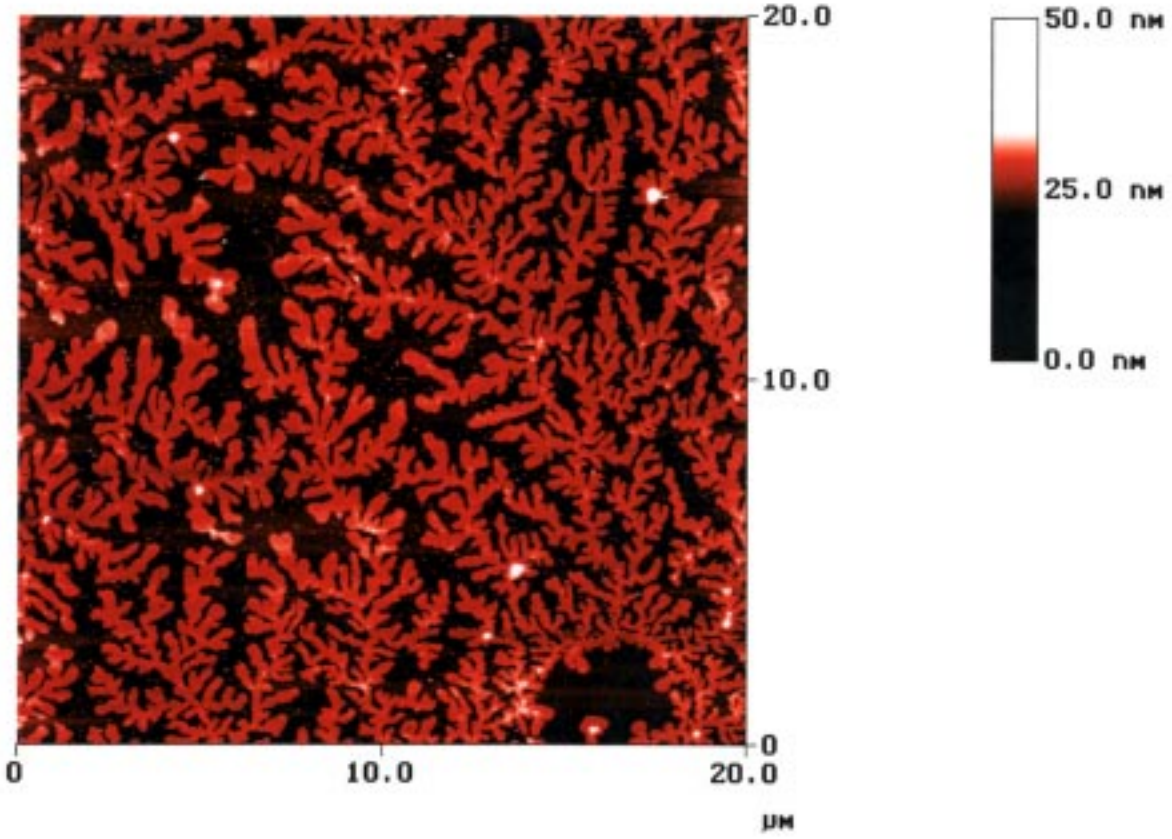
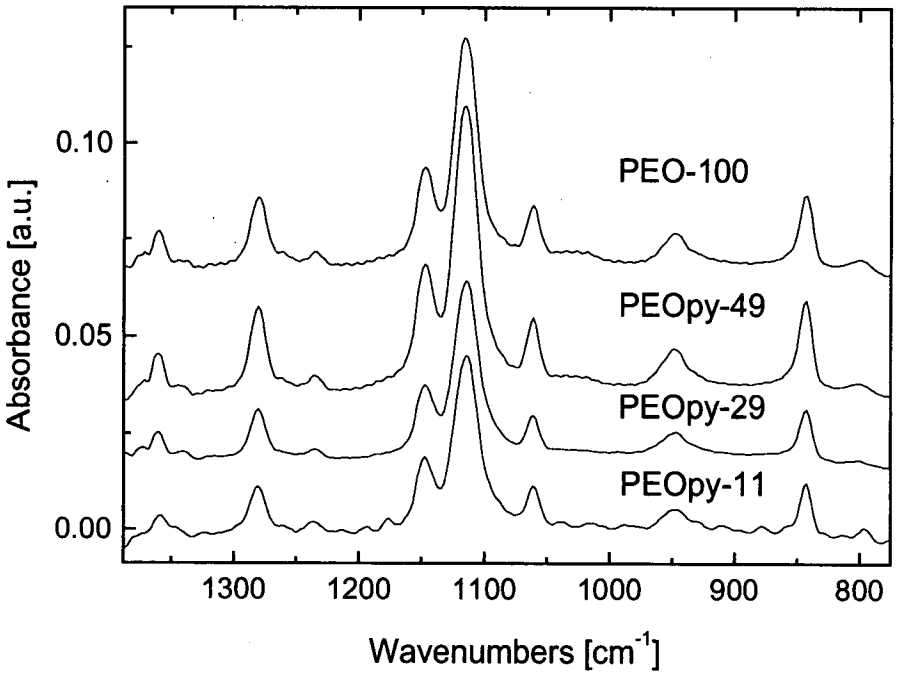
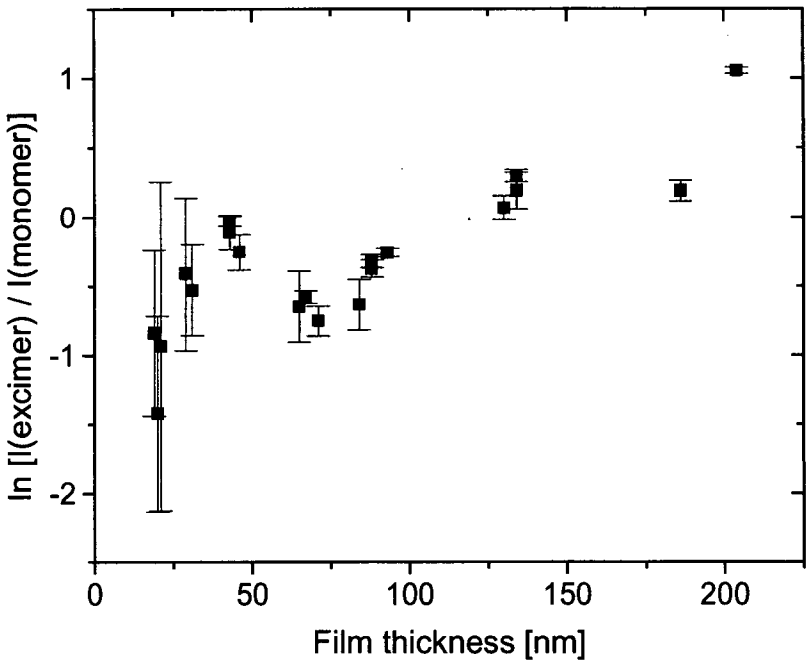
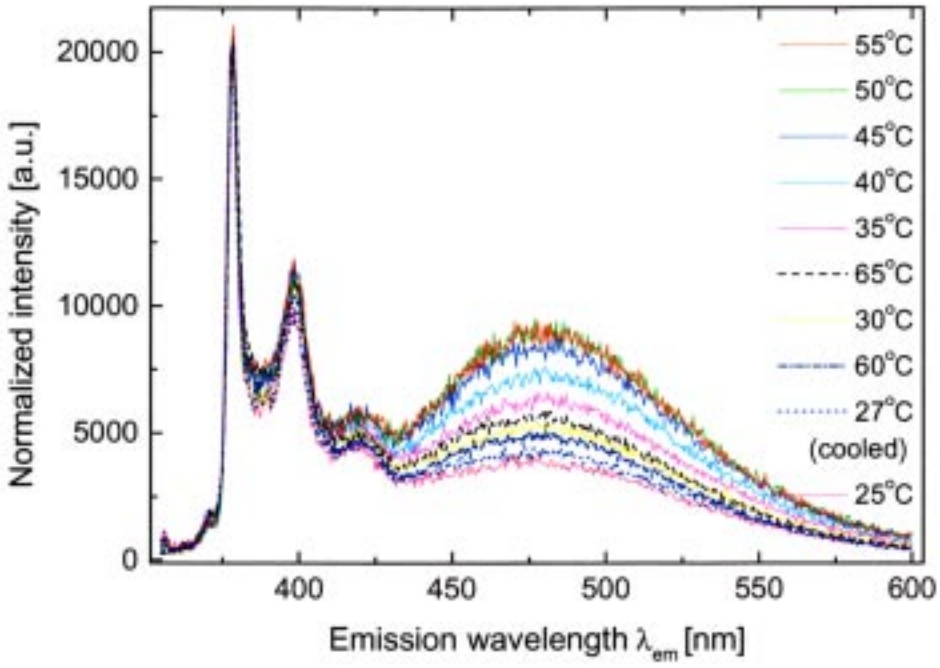
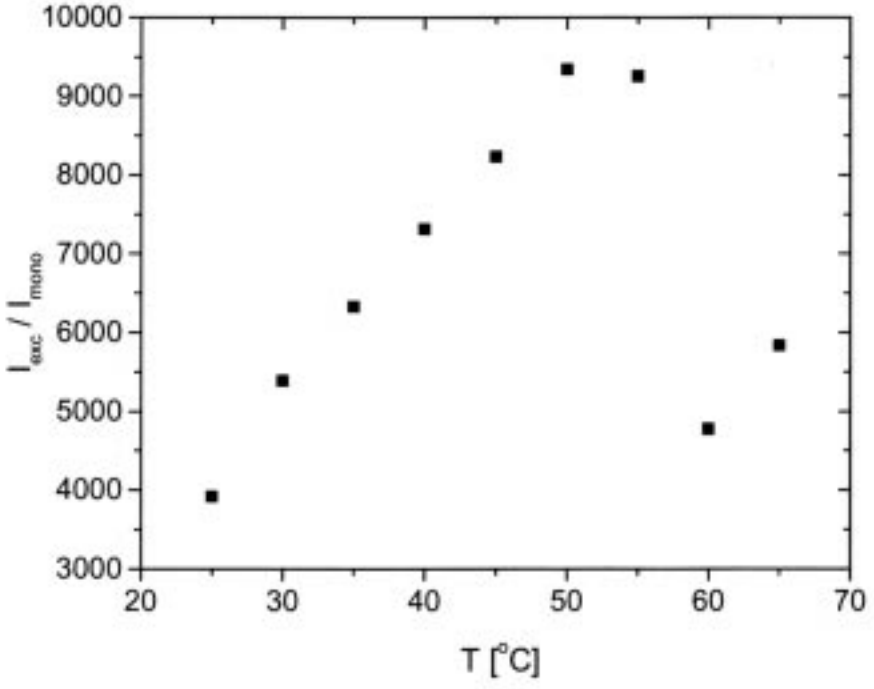



0.10
0.05
0.00
Absorbance [a.u.]
PEO-100
PEOpy-49
PEOpy-29
PEOpy-11
1300
1200
1100
1000
900
800
Wavenumbers [cm-1]


ln [I(excimer) / I(monomer)]
1
0
-1
-2
0
50
100
150
200
Film thickness [nm]


Normalized intensity [a.u.]
20000
15000
10000
5000
0
400
450
500
550
600
Emission wavelength λem [nm]
55°C
50°C
45°C
40°C
35°C
65°C
30°C
60°C
27°C
(cooled)
25°C

a


Iexc / Imono
10000
9000
8000
7000
6000
5000
4000
3000
20
30
40
50
60
70
T [°C]

b