Effect of side-chain asymmetry on the intermolecular structure and order-disorder transition in alkyl-substituted polyfluorenes

We study relations among the side-chain asymmetry, structure, and order-disorder transition (ODT) in hairy-rod-type poly(9,9-dihexylfluorenone) (PF6) with two identical side chains and atactic poly(9-octyl-9-methyl-fluorenone) (PF1-8) with two different side chains per repeat. PF6 and PF1-8 organize into alternating side-chain and backbone layers that transform into an isotropic phase at TODT(PF6) and TODT(PF1−8). We interpret polymers in terms of monodisperse and bidisperse brushes and predict scenarios TODT<TODTbi for high and low grafting densities (the side-chain length above or below the average grafting distance). Calorimetry and x-ray scattering indicate the condition TODT(PF6)∼TODTbi(PF1−8) following the low grafting prediction. PF6 side chains coming from the alternating backbone layers appear as two separate layers with thickness H(PF6), whereas PF1-8 side chains appear as an indistinguishable bilayer with a half thickness Hbi layer(PF1−8)/2=H(PF6). The low grafting density region is structurally possible but not certain for PF6 and confirmed for PF1-8.

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