Supplementary Information for:

Molecular Mapping of Poly(methyl methacrylate) Super-helix Stereocomplexes

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Quadruple helix model of the *it*-/*st*-PMMA stereocomplex

The quadruple helix model of the *it*-/*st*-PMMA stereocomplex was proposed by Yashima and colleagues[1] in 2007 as an alternative to the triple helix model that still satisfied the atomic force microscopy results and maintained the *it*:*st* stoichiometry of 1:2 (Figure S1).

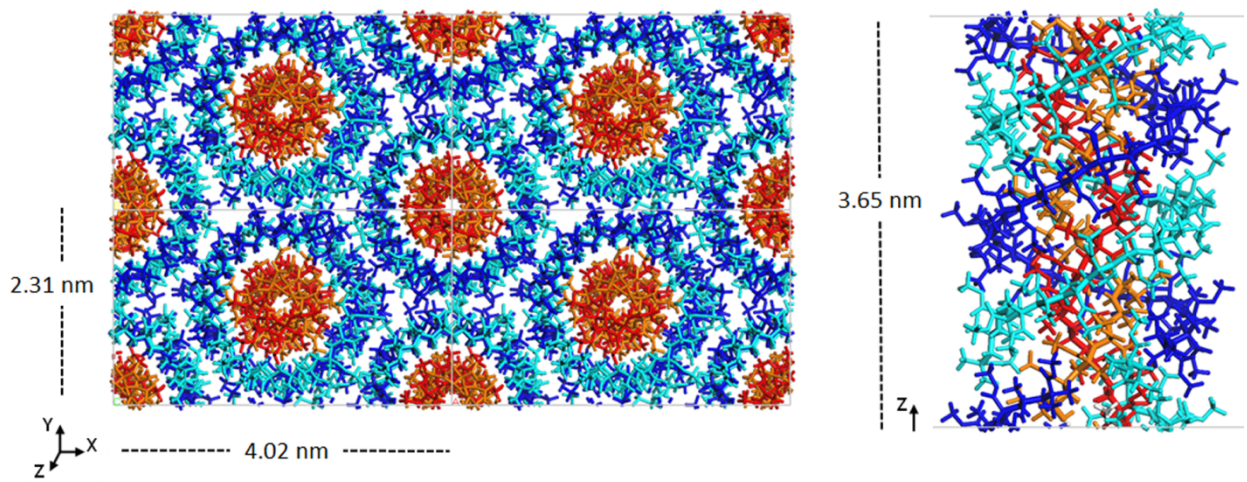

Figure S1. Optimized crystal structure model of the 9_1-*it*-/2x40mer-*st*-PMMA quadruple helix in the Right Down packing motif.

Quadruple helix *it*-/*st*-PMMA stereocomplex models were constructed in a manner similar to the triple helix models, with each unit cell containing two *it*-PMMA double helices surrounded by two 40-unit *st*-PMMA helices of the same sense and direction in a hexagonal packing arrangement with initial cell dimensions of 3.98 and 2.36 nm in the *x*- and *y*-directions. The length along the *z*-direction depended on the helical pitch of the *it*-PMMA double helix; 4.2 and 3.68 nm for the 10_1-*it*/2x40mer-*st* and 9_1-*it*/2x40mer-*st* models respectively.

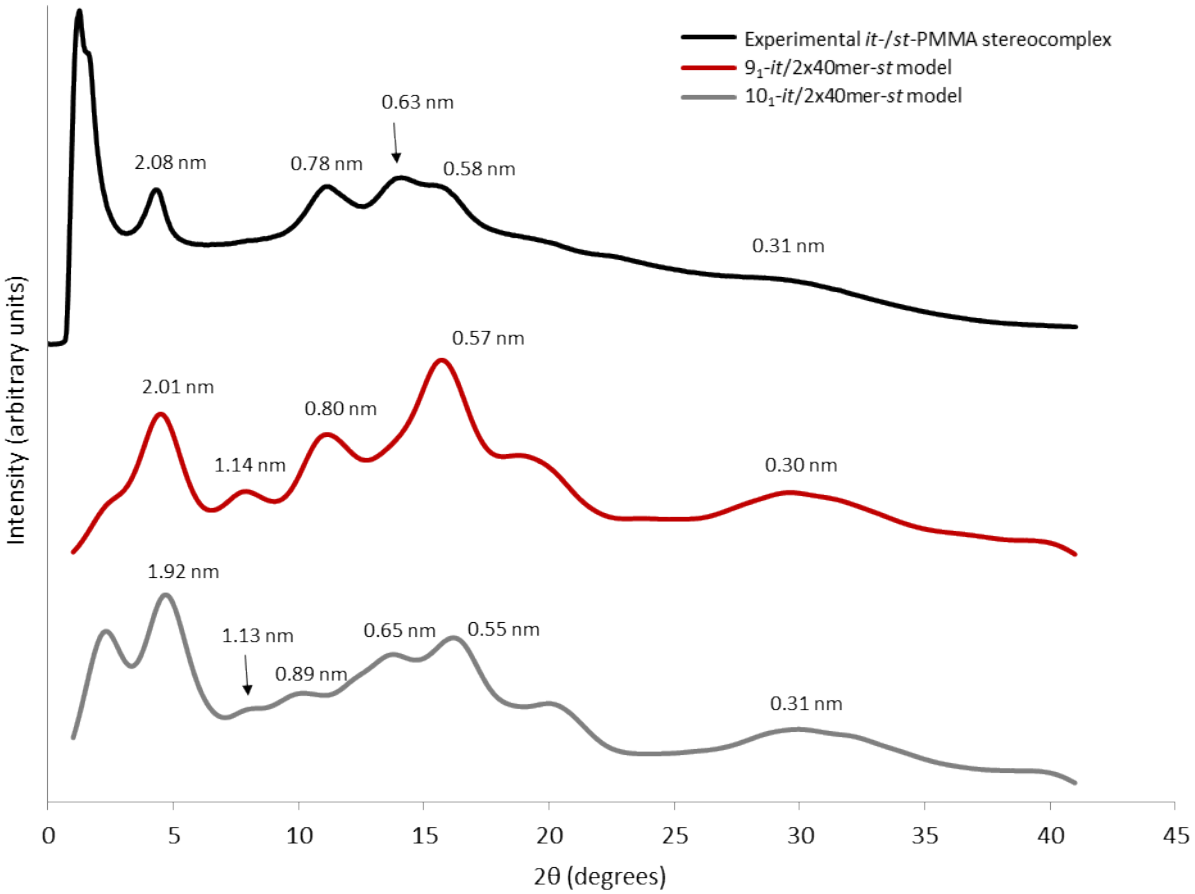

Figure S2. Wide angle X-ray scattering data obtained from powder diffraction experiments and molecular dynamic simulation for the quadruple helix *it*-/*st*-PMMA stereocomplex in the Right Down packing motif.

Table S1. Simulated and experimental structural and thermodynamic properties of *it*-/*st*-PMMA stereocomplex crystals of Right Down (RD) packing motif.

Description	Density (g/cm^3)	Helical Pitch *st*-PMMA (nm)	Cohesive Energy Density (J/cm^3)	Chain Width (nm)	Sum of Differences[a] (nm)
Experiment	1.215[2]	0.92 ± 0.02[1]	361[b]		
9_1-*it*/2x40mer-*st*	1.189	0.90	436	1.86	0.11*
10_1-*it*/2x40mer-*st*	1.168	0.99	427	1.83	0.33*

[a] Sum of Differences refers to the sum of the numerical value differences between the peak positions of the simulated structures and the experimental X-ray diffraction. Thus, a smaller value indicates a better agreement with experiment. [b] Experimental cohesive energy density of PMMA with unspecified tacticity.[3] * In addition to the sum of differences, both models exhibited a peak at ~ 1.1 nm not found in the experimental X-ray diffraction profile, and the 9_1-*it*/2x40mer-*st* model did not exhibit the experimental peak at 0.63 nm.

References

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2 K. E. Min and D. R. Paul, *J. Polym. Sci. Pol. Phys.*, 1988, **26**, 1021-1033.

3 H. J. Vandenburg, A. A. Clifford, K. D. Bartle, R. E. Carlson, J. Carroll and I. D. Newton, *Analyst*, 1999, **124**, 1707-1710.