Ab initio prediction of polymer tacticity produced by bulk radical polymerization

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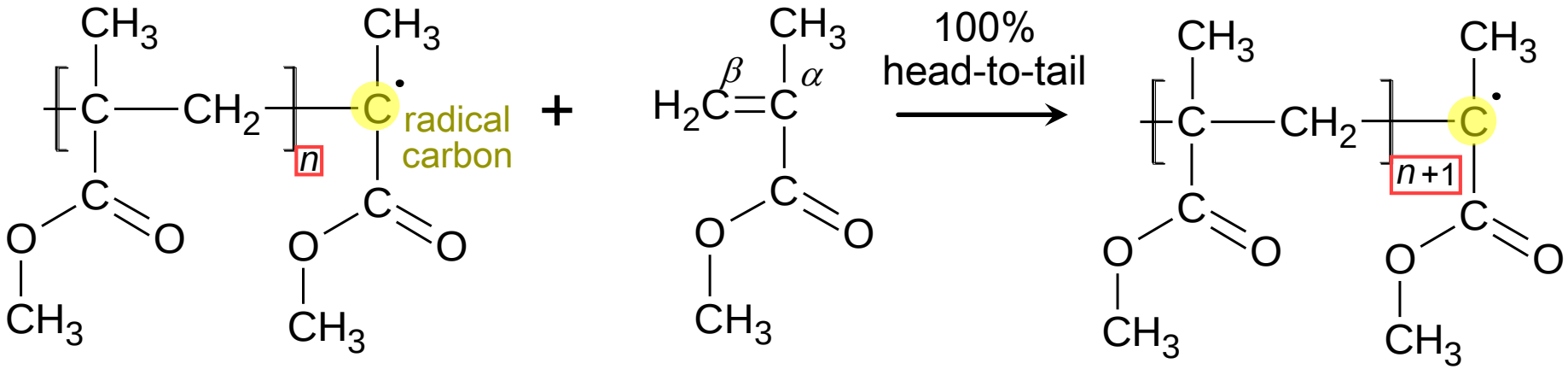
Radical polymerization of Poly(methyl methacrylate) (PMMA) and its product polymer tacticity



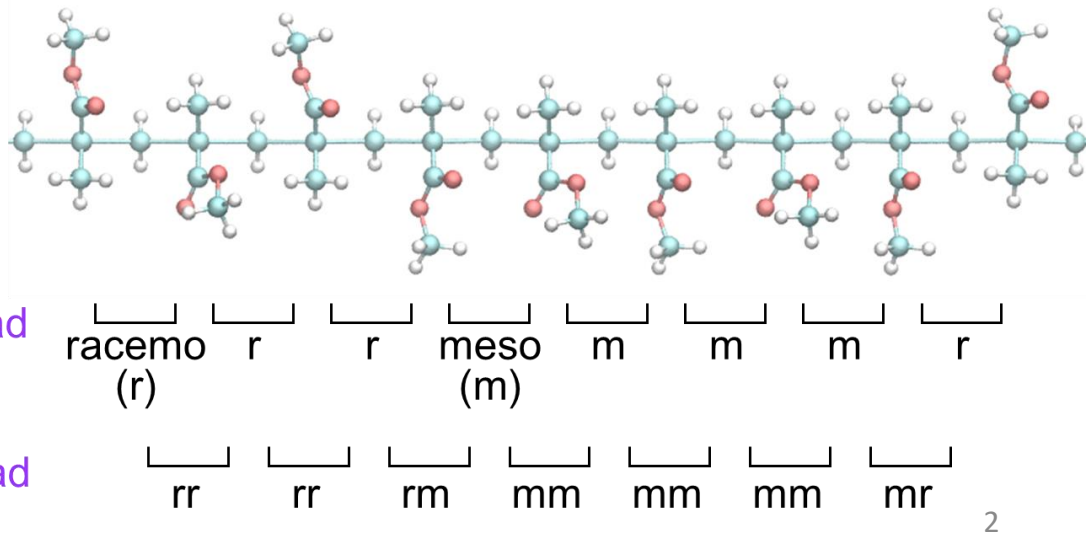
PMMA radical terminal

MMA (methyl methacrylate) monomer

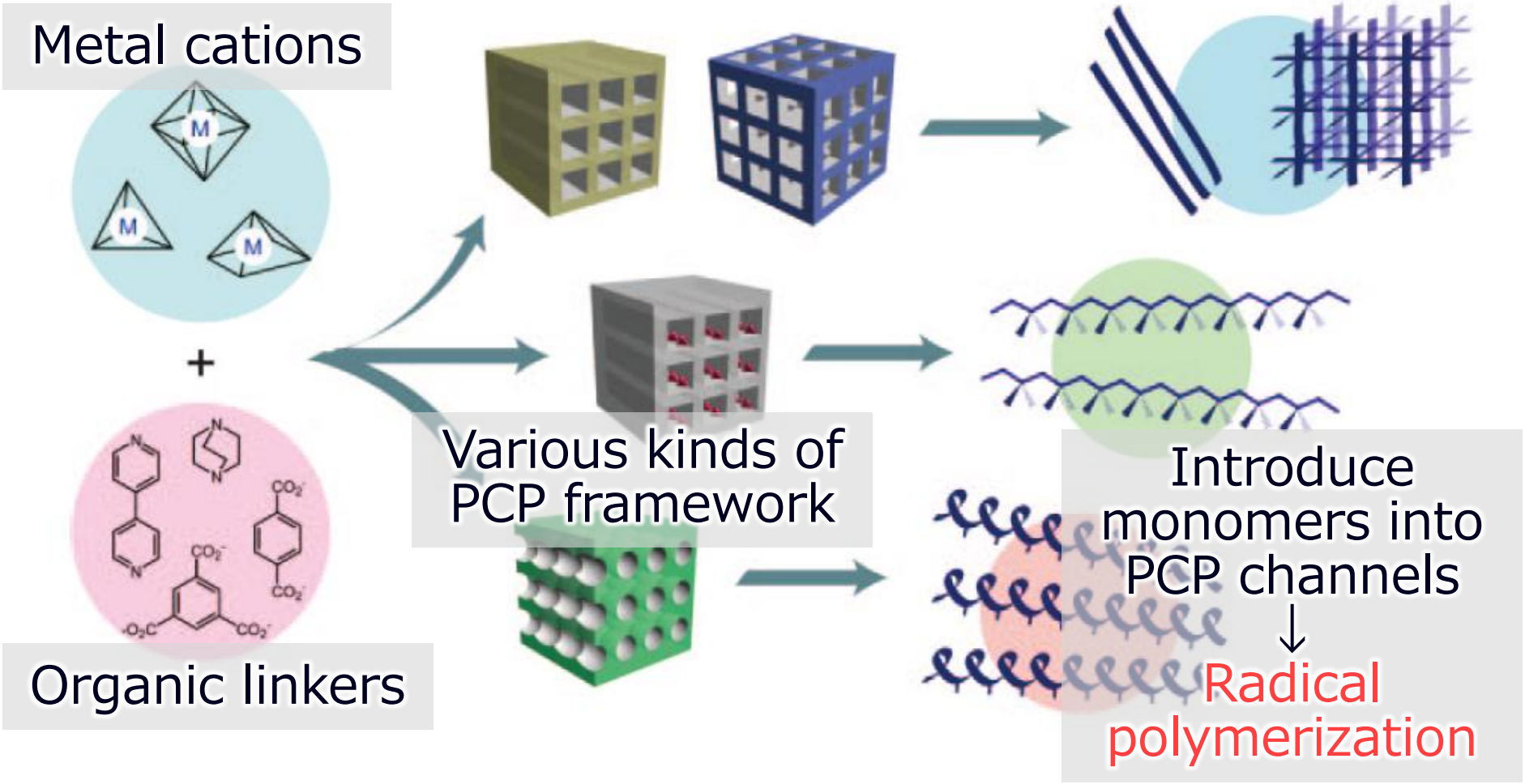
Elongated PMMA

Tacticity of PMMA

Bulk radical polymerization: meso ratio ~20%



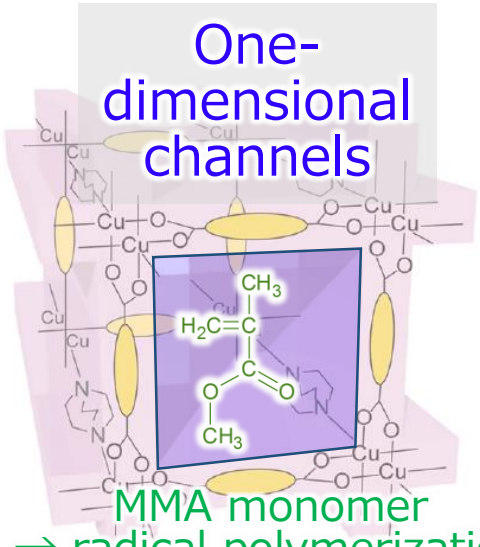
Polymer synthesis in PCP channels



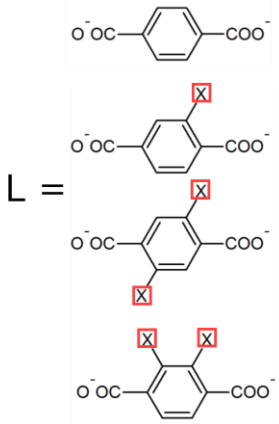
Radical polymerization in PCP channels

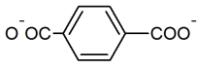
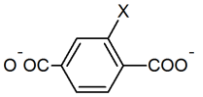
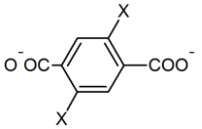
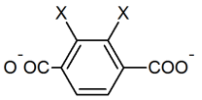
Uemura, T. *BCSJ*, **2011**, *84*, 1169

Tacticity control by polymerization in PCP channels



MOF [$Cu_2(L)_2$ted]



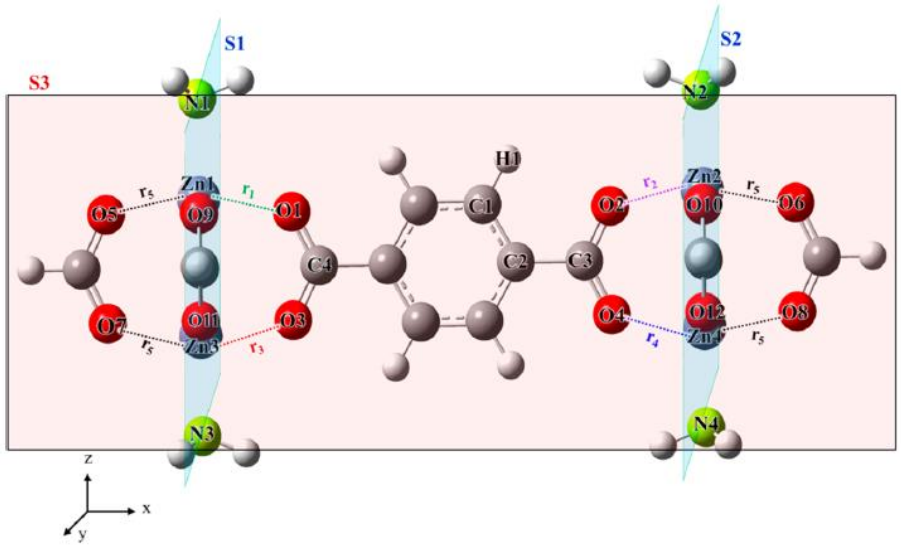
L	X	tacticity (%) mm:mr:rr (m)
Bulk polymerization		5:35:60 (22)
		8:40:52 (28)
	F OCH_3	9:41:50 (30) 13:44:43 (35)
	F OCH_3	10:45:45 (32) 28:53:19 (55)
	F OCH_3	8:40:52 (28) 8:39:53 (28)

meso ratio increase >30%

Significant control of tacticity > 30%

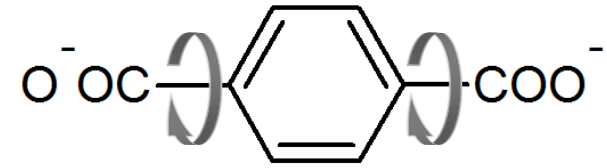
Uemura, T. et al. *Macromolecules* **2008**, *41*, 87.
Uemura, T. et al. *J. Am. Chem. Soc.* **2010**, *132*, 4917.

Ligand rotational flexiblity



DFT calculation
model system

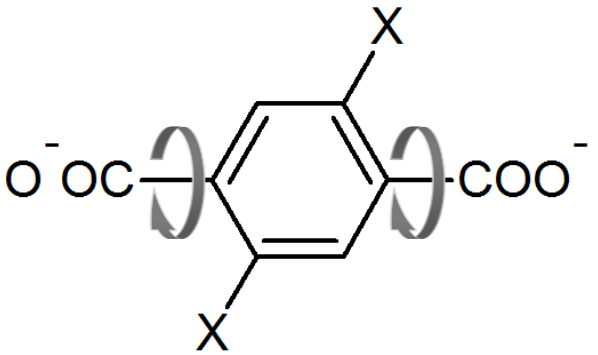
B3LYP-D3 or M06-2X/cc-pVDZ



Planar structure

High rotational barrier
~15 kcal/mol

PCP framework is fixed
→ First target system



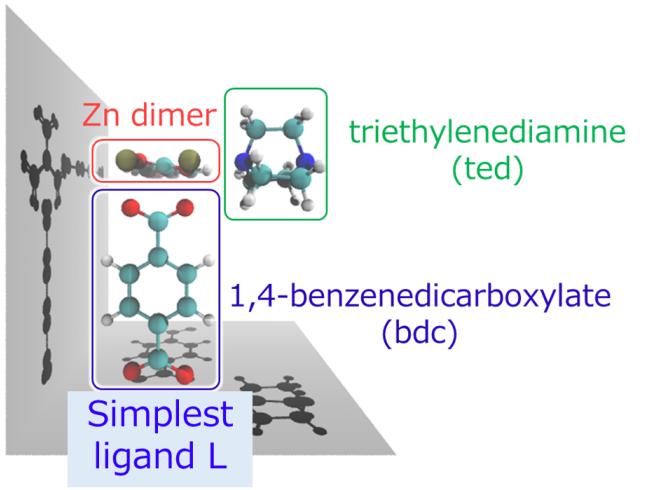
Planar or non-planar structure

Low rotational barrier
2-10 kcal/mol

PCP framework is flexible

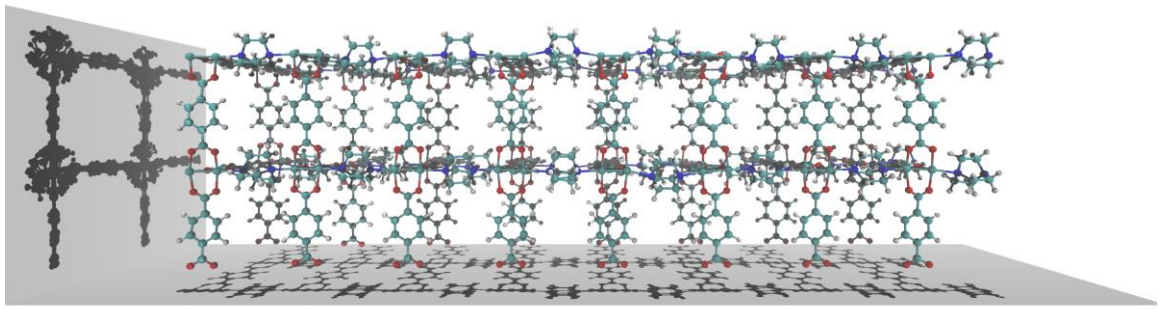
J. Phys. Chem. C **2015**, *119*, 28789-28799.

Target PCP [$Zn_2(bdc)_2(ted)$]



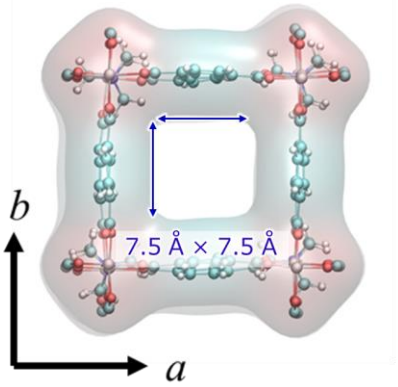
Use reported
flexible force field

JACS **2012**, *134*, 4207

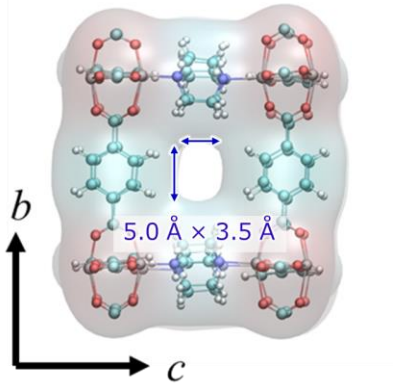


Lattice constant
(10.948 Å, 10.948 Å, 9.804 Å)

1-dimensional channels along *c*-axis

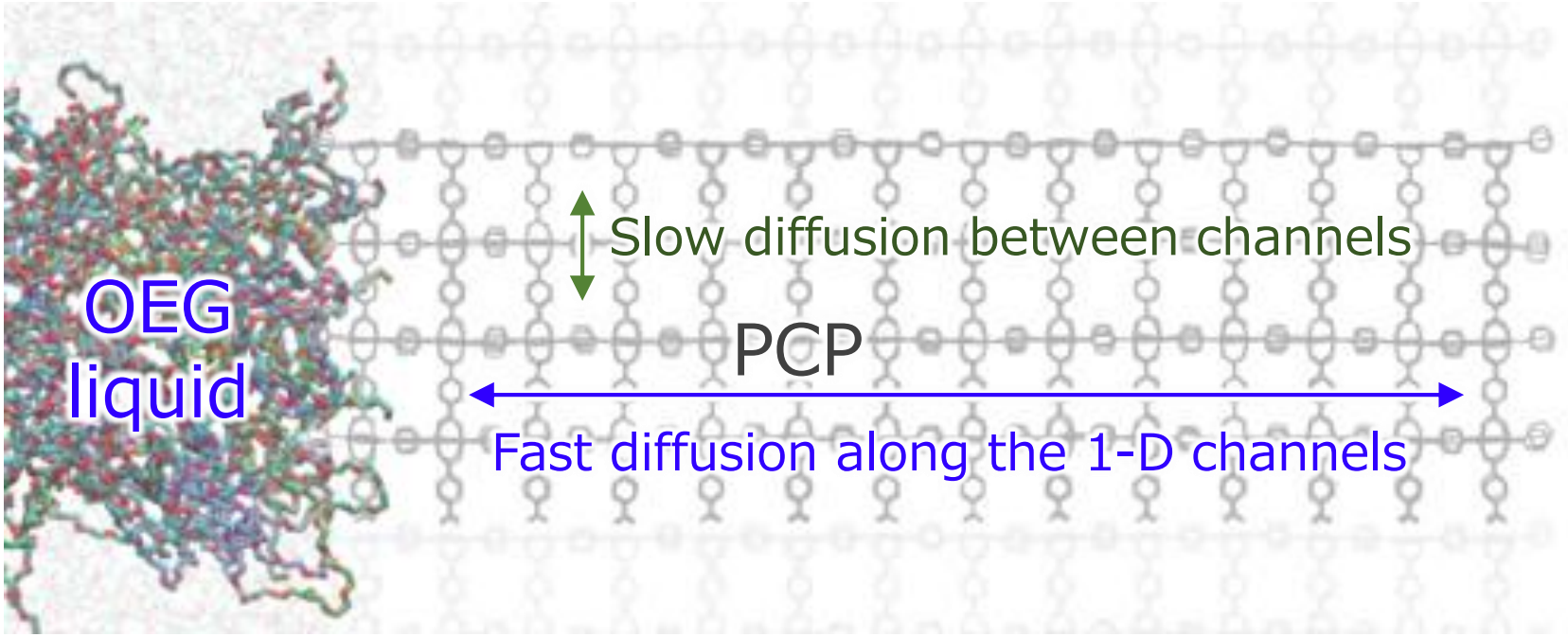


Wide channel
along *c*-axis

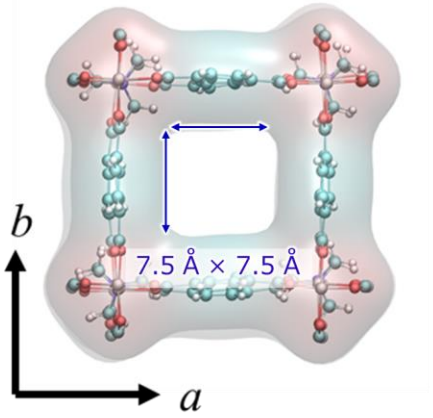


Narrow aperture
along *a*- and *b*-axes

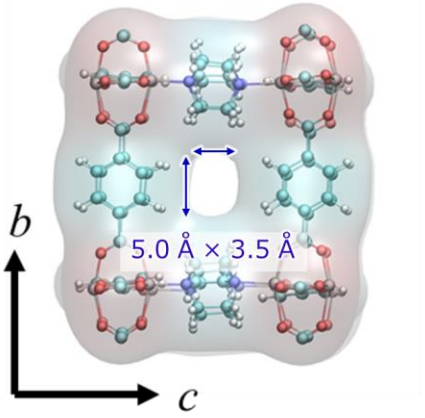
OEG permeation from (001) surface: Movie



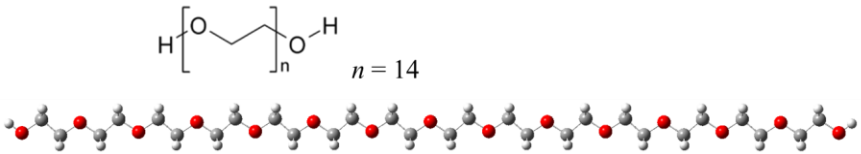
Temperature 363 K



Wide channel
along *c*-axis



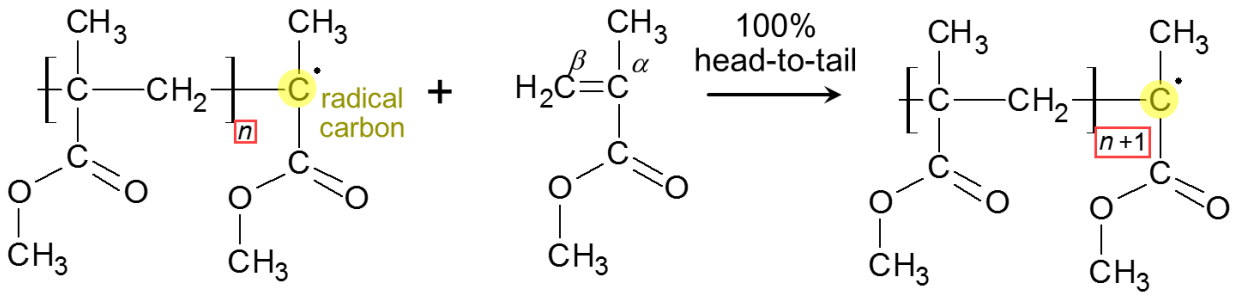
Narrow aperture
along *a*- and *b*-axes



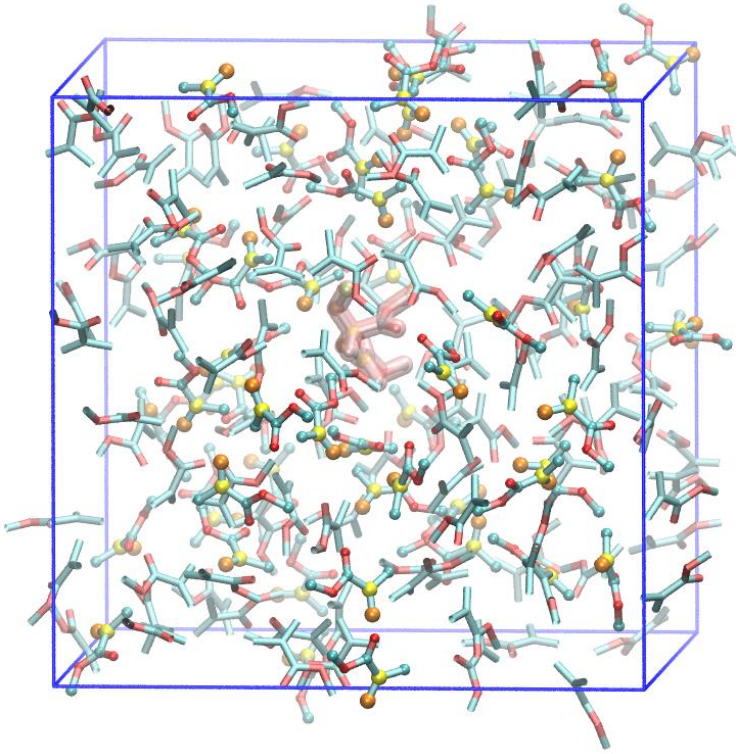
Guest molecule:
oligo(ethylene glycol) (OEG)

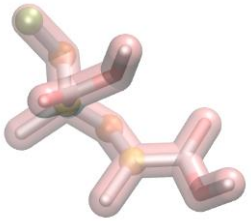
J. Phys. Chem. C **2015**, *119*, 21504–21514.

Simulate bulk radical polymerization by hybrid MC/MD reaction method

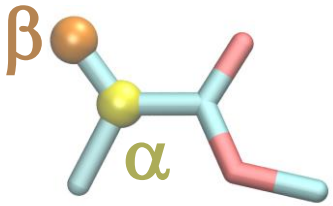


As a first step, investigate why meso ratio is ~20% by bulk radical polymerization



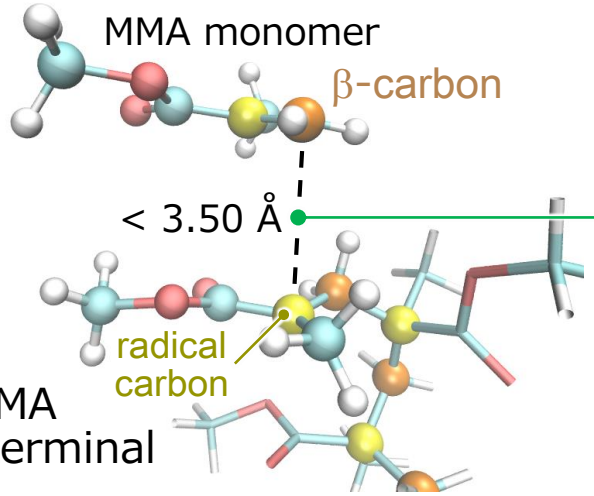


MMA dimer radical
× 1

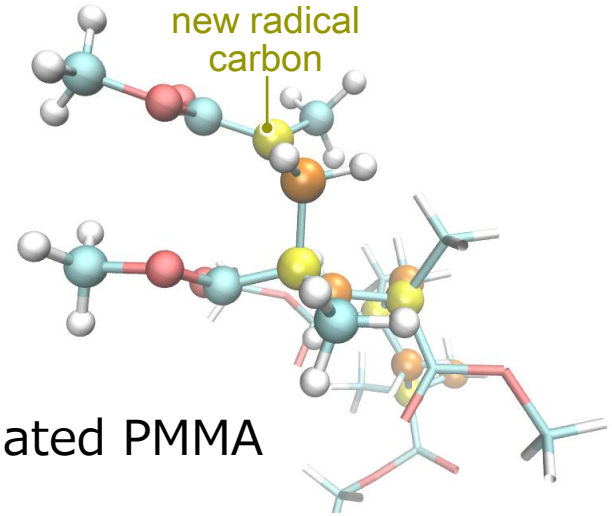


MMA monomer
×158

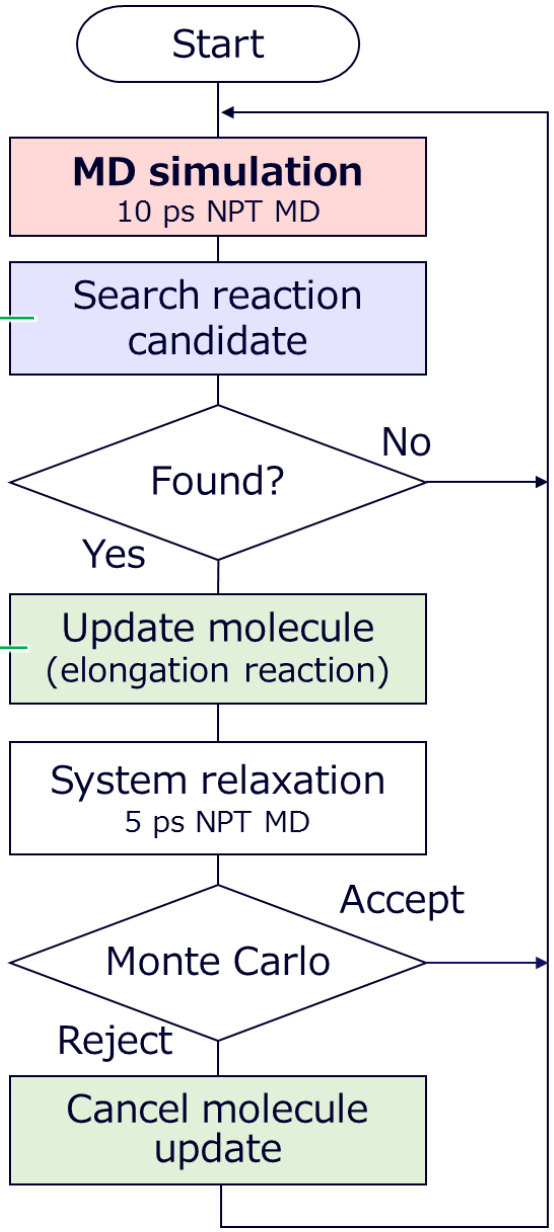
MC/MD cycle of polymerization simulation



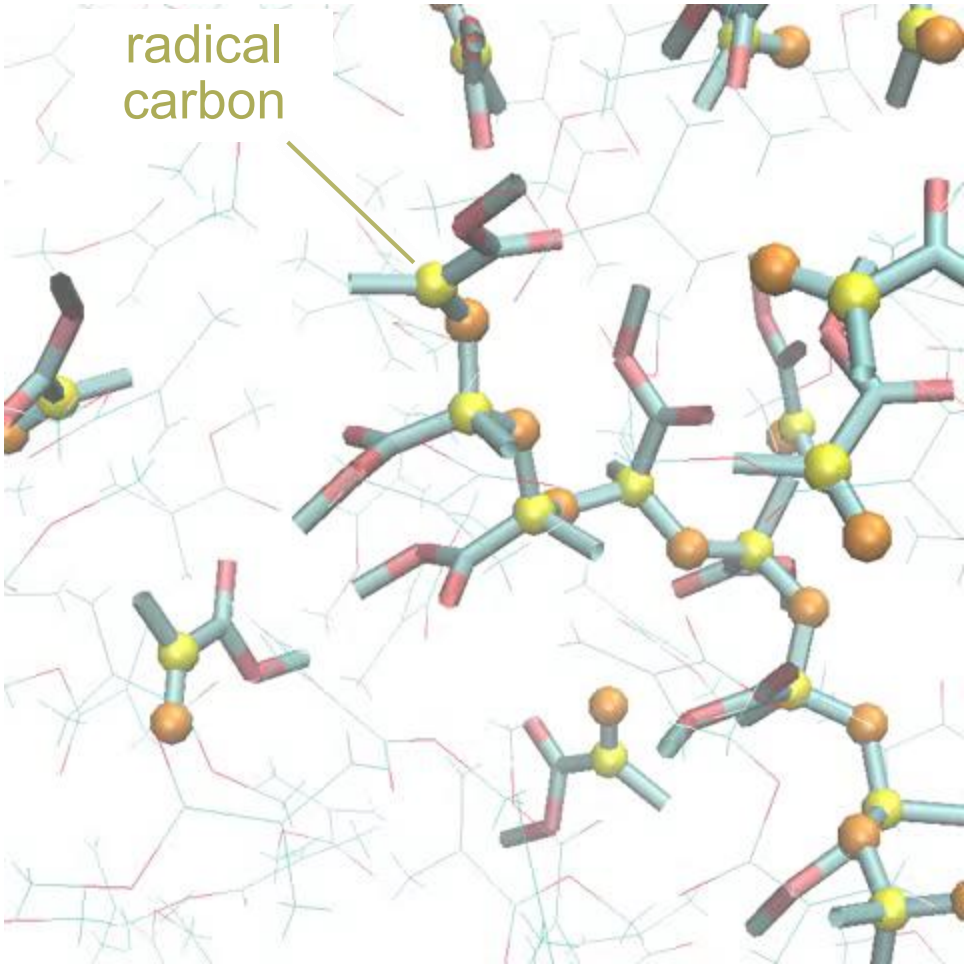
When radical—β-carbon distance is <3.5 Å



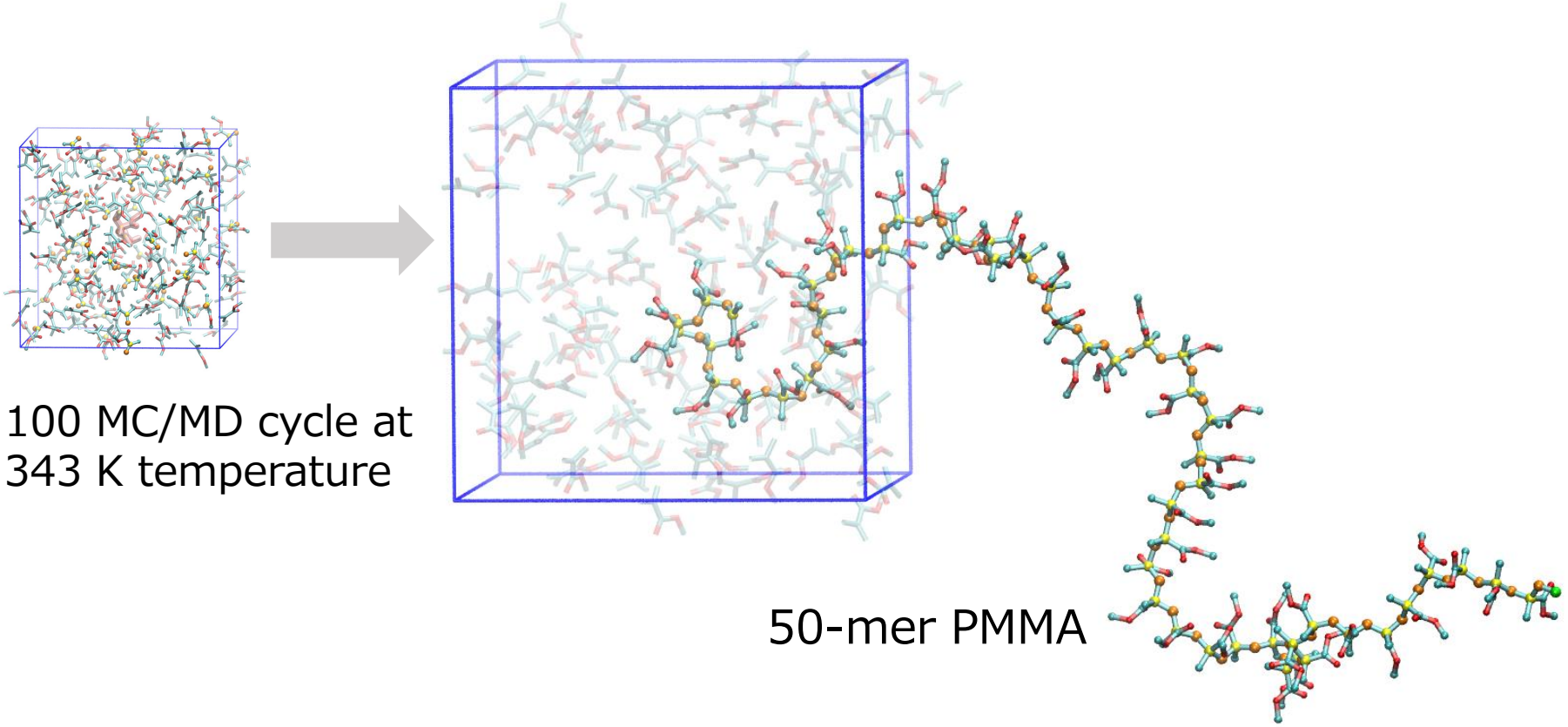
Try the elongation reaction



Trajectory of bulk radical polymerization



PMMA produced by hybrid MC/MD simulation



100 MC/MD cycle at
343 K temperature

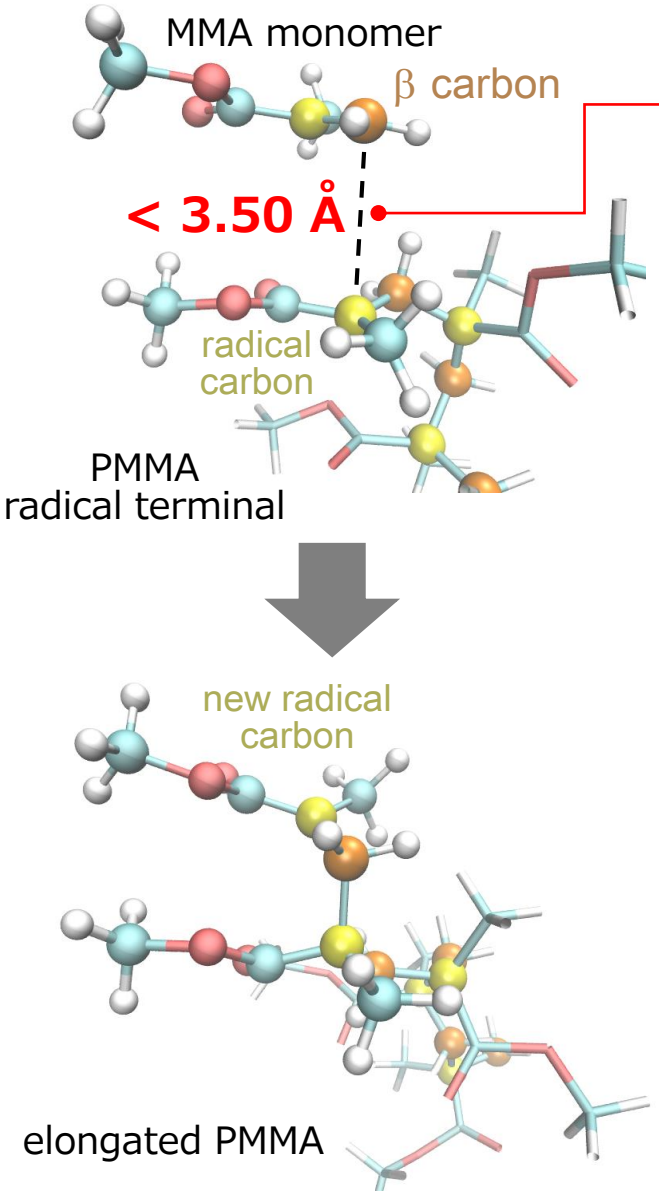
50-mer PMMA

Succeeded in producing PMMA. However...

Tacticity is racemo:meso = ~50%:50%

Could not reproduce actual value ~20%:80%

Reaction condition would not be correct

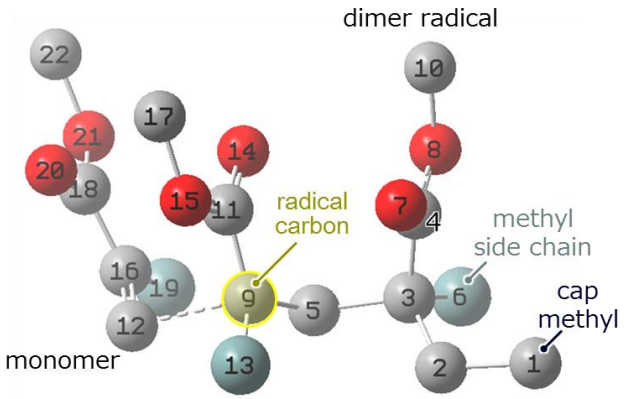


Simple distance condition can be not appropriate to reproduce the tacticity.

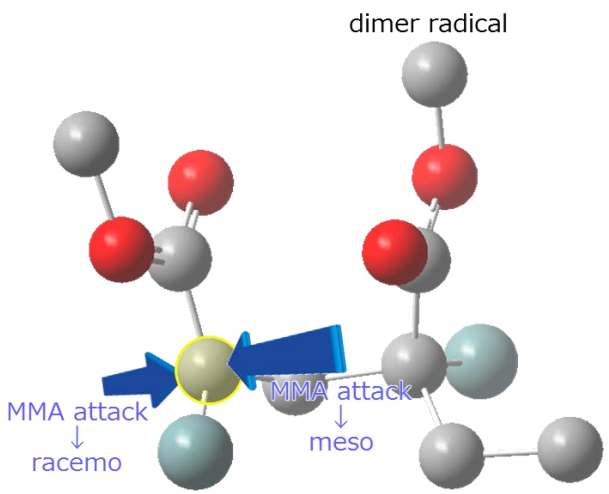
↓

Investigate the reaction barrier by calculating transition state (TS) structures by DFT calculations to produce racemo and meso diads.

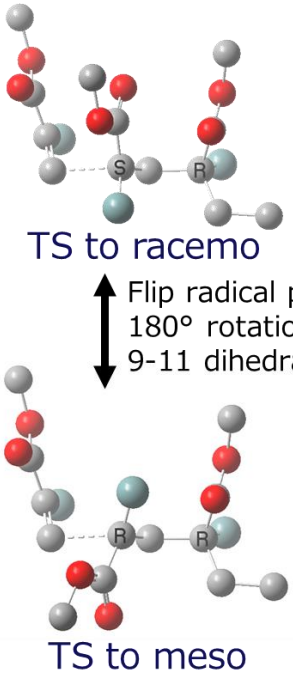
DFT calculations to obtain reaction barriers of PMMA elongation reaction



MMA monomer + MMA dimer radical at UM06/6-31+G(d)



Tacticity is determined by the radical addition direction

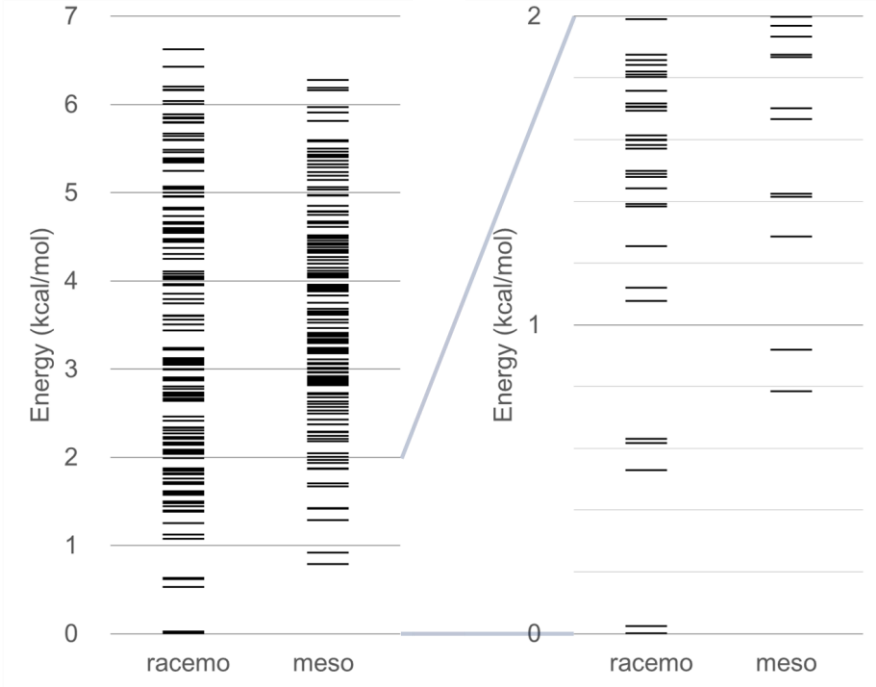


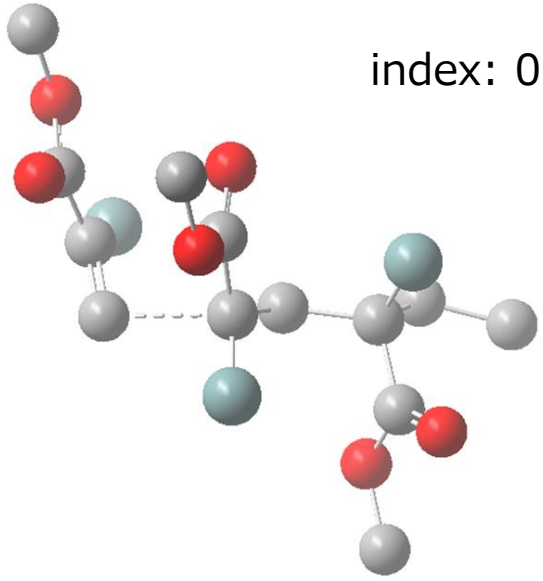
Starting from the combinations of dihedral angles in the right table, we executed **288** (= $2^5 \times 3^2$) TS optimizations.

Index of the above conformation: 2110-000

Dihedral angle	Initial value (degrees)	Index
φ_1(2-3-5-**9**)	-180, -60, 60	0, 1, 2
φ_2(3-5-**9**-11)	-90, 90	0, 1
φ_3(5-**9**-12-16)	-180, -60, 60	0, 1, 2
φ_4(**9**-12-16-18)	-90, 90	0, 1
ψ_1(6-3-4-8)	0, 180	0, 1
ψ_2(13-9-11-15)	0, 180	0, 1
ψ_3(19-16-18-21)	0, 180	0, 1

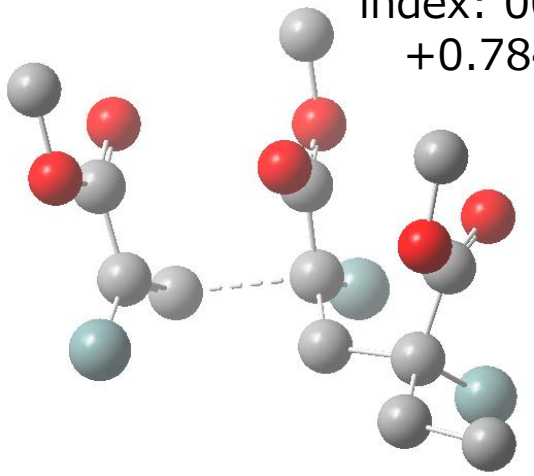
Energy distribution of 288 TS conformations to racemo and meso





index: 0110-100
0 kcal/mol

Most stable conformation to racemo



index: 0021-100
+0.784 kcal/mol

Most stable conformation to meso

Estimate PMMA tacticity from Boltzmann factors

	TS index	E(kcal/mol)	diad	Boltzmann factor	Probability	Accumulated probability
1	0110-100	0.000	r	1.0000	10.18%	10.18%
2	0110-000	0.023	r	0.9667	9.84%	20.01%
3	0101-010	0.529	r	0.4600	4.68%	24.69%
4	0101-110	0.616	r	0.4052	4.12%	28.81%
5	2110-000	0.629	r	0.3974	4.04%	32.86%
6	0021-100	0.784	m	0.3165	3.22%	36.08%
7	2021-000	0.918	m	0.2599	2.64%	38.72%
8	2110-100	1.076	r	0.2063	2.10%	40.82%
9	2101-100	1.119	r	0.1935	1.97%	42.79%
10	0100-100	1.253	r	0.1590	1.62%	44.41%
11	2021-100	1.285	m	0.1519	1.55%	45.95%
12	0110-011	1.382	r	0.1317	1.34%	47.29%
13	0110-101	1.391	r	0.1299	1.32%	48.62%
14	0021-000	1.415	m	0.1255	1.28%	49.89%
15	0000-010	1.423	m	0.1240	1.26%	51.15%
30	0100-110	1.717	r	0.0806	0.82%	65.81%
50	2101-001	2.073	r	0.0477	0.49%	77.79%
90	0121-001	2.705	r	0.0189	0.19%	90.01%
125	0010-101	3.063	m	0.0112	0.11%	95.06%
288	1120-000	6.619	r	0.0001	0.0006%	100.00%

at 343 K

$$\text{ratio(racemo)} = \frac{\sum_{n \in \text{racemo TS}} \exp\left(\frac{-E_n}{k_B T}\right)}{\sum_{n \in \text{all TS}} \exp\left(\frac{-E_n}{k_B T}\right)}$$

$$\text{ratio(meso)} = \frac{\sum_{n \in \text{meso TS}} \exp\left(\frac{-E_n}{k_B T}\right)}{\sum_{n \in \text{all TS}} \exp\left(\frac{-E_n}{k_B T}\right)}$$

Predicted r:m
73.93%:26.07%

Experimental r:m
78%:22%

Good ab initio prediction of experimental tacticity

Estimate polysthyrene (PS) tacticity

	index	E (kcal /mol)	diad	Boltzmann factor	Probability	Accumulated probability
1	0110_1	0.000	r	1.0000	16.10%	16.10%
2	0111_0	0.307	m	0.6459	10.40%	26.50%
3	0120_0	0.347	m	0.6098	9.82%	36.32%
4	0101_1	0.433	r	0.5392	8.68%	45.00%
5	0121_0	0.564	m	0.4475	7.20%	52.20%
6	0021_1	0.763	m	0.3369	5.42%	57.63%
7	0000_0	0.837	r	0.3034	4.89%	62.51%
8	1021_1	0.871	m	0.2891	4.65%	67.17%
9	0000_1	1.078	m	0.2150	3.46%	70.63%
10	0121_1	1.100	r	0.2084	3.35%	73.98%
11	1000_1	1.231	m	0.1730	2.79%	76.77%
12	2110_1	1.269	r	0.1639	2.64%	79.41%
13	2021_1	1.501	m	0.1176	1.89%	81.30%
14	2101_1	1.529	r	0.1131	1.82%	83.12%
15	0111_1	1.639	r	0.0967	1.56%	84.68%
72	2111_0	14.903	m	0.0000	0.00%	100.00%

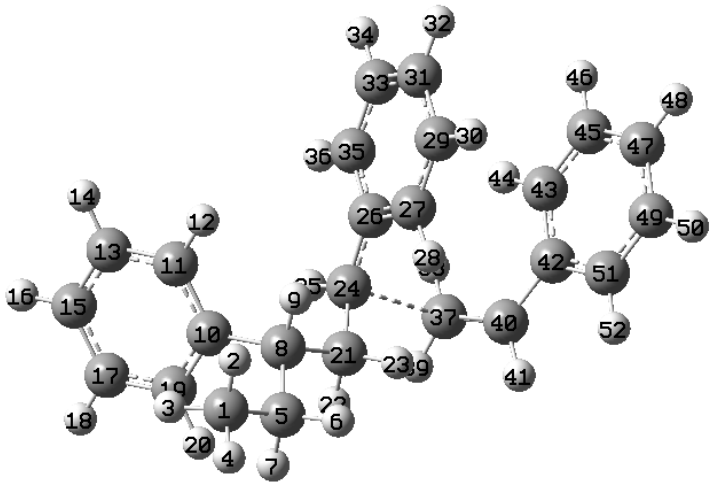
at 343 K

Predicted r:m
48.29%:51.71%

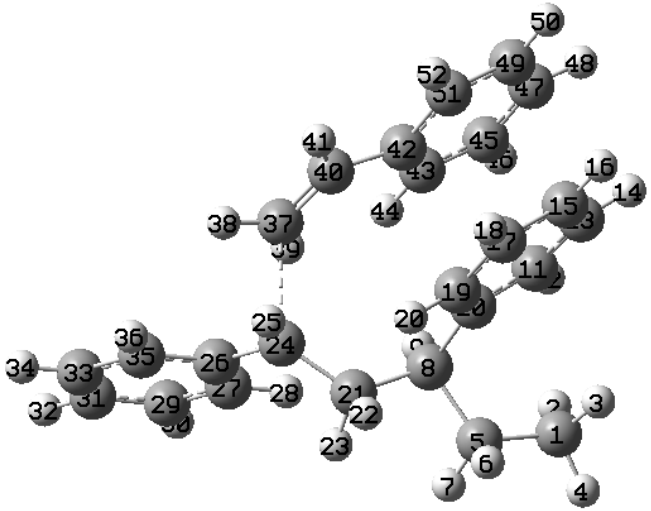
Experimental r:m
~65%:35%

Prediction is not good

Need further investigation



0110_1 to racemo (most stable TS)



0111_0 to meso (+0.307 kcal/mol)