Controlled Radical Polymerization of 3-Methylenecyclopentene with N-Substituted Maleimides To Yield Highly Alternating and Regiospecific Copolymers

Daisuke Yamamoto[†] **and Akikazu Matsumoto***[,‡]
[†]*Department of Applied Chemistry and Bioengineering, Graduate School of Engineering, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan*
[‡]*Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai-shi, Osaka 599-8531, Japan*

CONTENTS

Table S1. Radical Copolymerization of MCP with RMIs

time (h)	MMI			CHMI			PhMI		
	yield (%)	$M_n/10^5$	M_w/M_n	yield (%)	$M_n/10^5$	M_w/M_n	yield (%)	$M_n/10^5$	M_w/M_n
0.5	20.3	1.28	1.96	18.6	3.48	2.03	36.7	1.74	2.88
1.0	40.3	1.23	1.91	35.8	3.61	2.15	56.7	1.98	2.24
1.5	57.2	0.96	2.33	48.3	3.53	2.24	73.0	1.92	2.43
2.0	66.5	1.04	2.03	58.9	3.45	2.22	77.9	1.97	2.32
3.5	87.8	0.84	2.42	84.3	2.92	2.49	93.7[b]	1.69[b]	2.65[b]
6.0	99.3	0.77	2.42	97.1	2.31	2.84	97.3	1.47	2.97

[a] Copolymerization conditions: ([MCP]+[RMI]) = 0.5 mol/L, [AIBN] = 1.0 mmol/L in 1,2-dichloroethane at 60 ºC. [b] Polymerized for 4 h.

Table S2. Production of Alternating Copolymer and Diels-Alder Adduct During Reaction of IP with PhMI in $CDCl_3$ at 60 ºC[a]

time (h)	PhMI conversion (%)	copolymer yield (%)	Diels-Alder adduct yield (%)	$M_n/10^3$	$M_w/10^3$	M_w/M_n
0.5	68.1	8.7	59.9	34.6	56.9	1.65
1.0	79.8	10.2	69.6	26.8	46.1	1.72
1.5	85.0	12.3	74.4	23.3	43.9	1.88
2.0	87.6	13.1	76.9	23.9	39.9	1.67
3.0	91.2	14.9	80.3	28.4	46.1	1.62

[a] [IP] = [PhMI] = 0.50 mol/L, [AIBN] = 10 mmol/L.

Table S3. Solubility of Poly(MCP-*alt*-RMI)s

solvent RMI =	MMI	BMI	CHMI	PhMI
acetone	swelling	insoluble	insoluble	swelling
acetonitrile	swelling	insoluble	insoluble	swelling
chloroform	soluble	soluble	soluble	soluble
dichloromethane	soluble	soluble	soluble	soluble
1,2-dichloroethane	soluble	soluble	swelling	soluble
N,N-dimethylformamide	soluble	insoluble	insoluble	soluble
dimethyl sulfoxide	soluble	insoluble	insoluble	soluble
tetrahydrofuran	soluble	soluble	soluble	soluble
toluene	swelling	swelling	soluble	insoluble

Table S4. Radical Copolymerization of MCP and IP with PhMI for Determination of Monomer Reactivity Ratios in 1,2-Dichloroethane at 60 ºC

diene monomer	PhMI mol% in feed	time (h)	yield (%)	$M_n/10^4$	M_w/M_n	PhMI mol% in copolymer
MCP	10.0	0.2	5.4	7.3	1.93	47.9
	30.0	0.5	8.0	12.4	1.67	48.4
	50.0	0.2	3.1	45.3	1.58	49.6
	70.0	0.5	7.1	16.9	1.76	49.7
	90.0	0.2	2.4	4.5	1.94	51.9
IP	10.0	2.0	1.4	10.5	1.56	32.2
	30.0	2.0	4.9	19.1	1.97	43.6
	50.0	1.5	12.2	20.4	1.75	49.4
	70.0	0.5	13.5	80.6	1.71	51.7
	90.0	0.17	5.0	79.2	1.80	56.1

[a] Copolymerization conditions: ([diene]+[PhMI]) = 1.0 mol/L, [AIBN] = 10 mmol/L in 1,2-dichloroethane at 60 ºC.

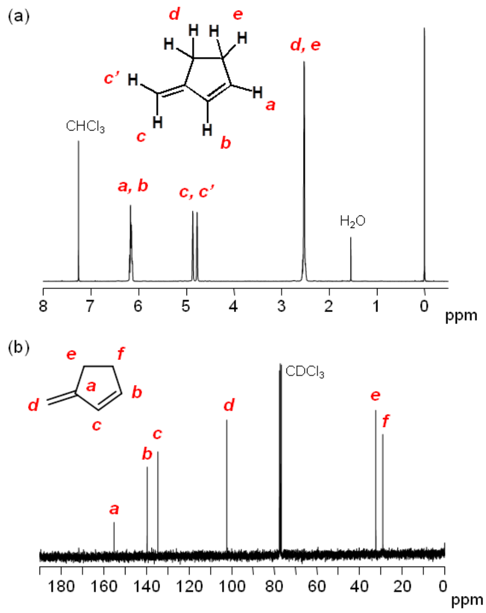

Figure S1. (a) ^{1}H and (b) ^{13}C NMR spectra of MCP synthesized by the ring-close metathesis reaction of myrcene. Measurement solvent, $CDCl_3$.

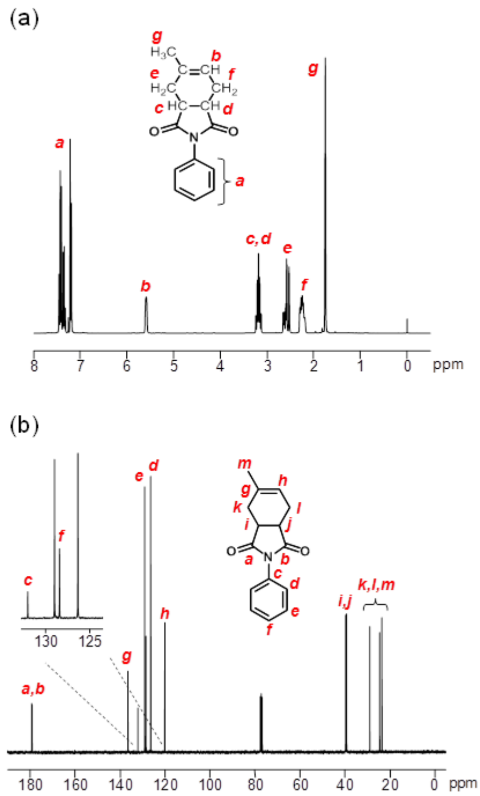

Figure S2. (a) ^{1}H and (b) ^{13}C NMR spectra of the isolated IP-PhMI ~~DA-~~ Diels-Alder adduct in $CDCl_3$ at room temperature.

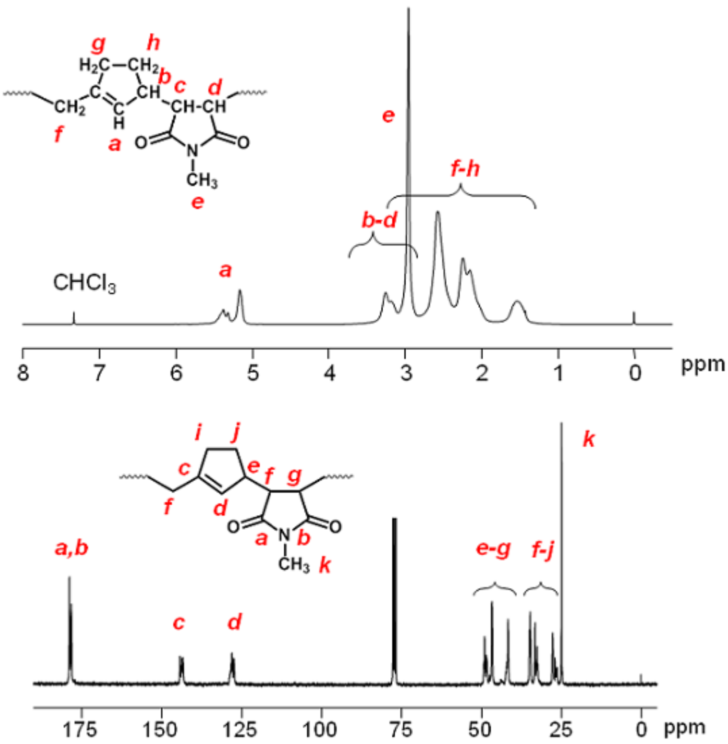

Figure S3. ^{1}H and ^{13}C NMR spectra of poly(MCP-*alt*-MMI). Measurement solvent, $CDCl_3$.

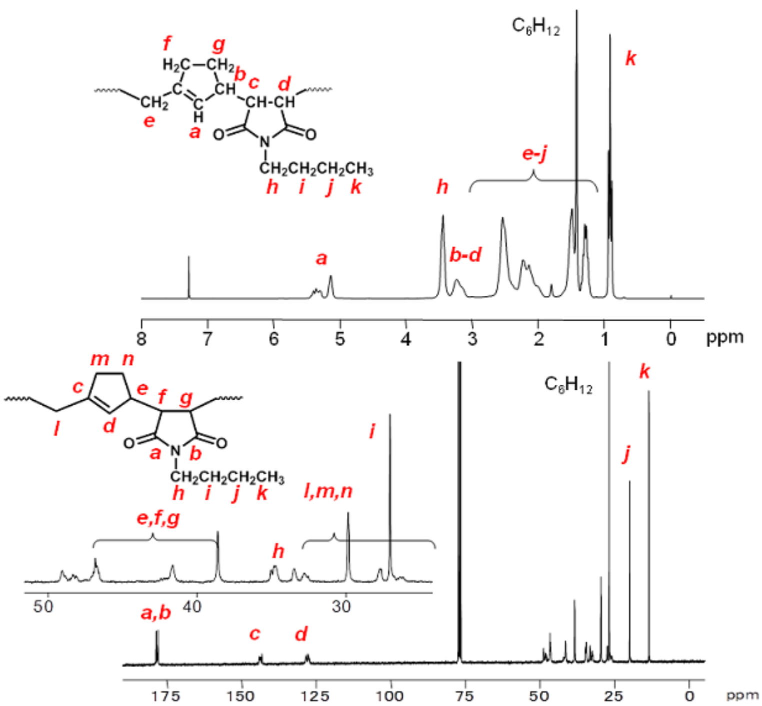

Figure S4. ^{1}H and ^{13}C NMR spectra of poly(MCP-*alt*-BMI). Measurement solvent, $CDCl_3$.

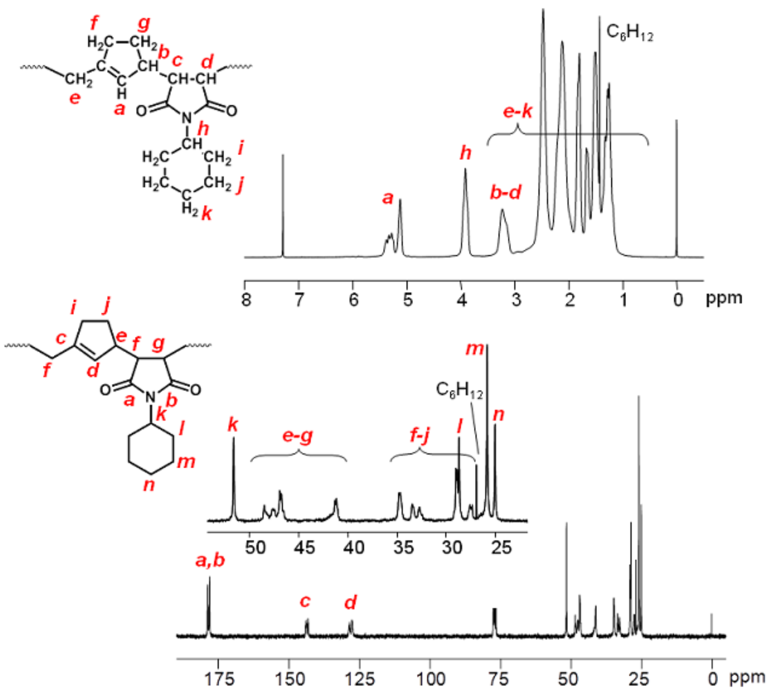

Figure S5. ^{1}H and ^{13}C NMR spectra of poly(MCP-*alt*-CHMI). Measurement solvent, $CDCl_3$.

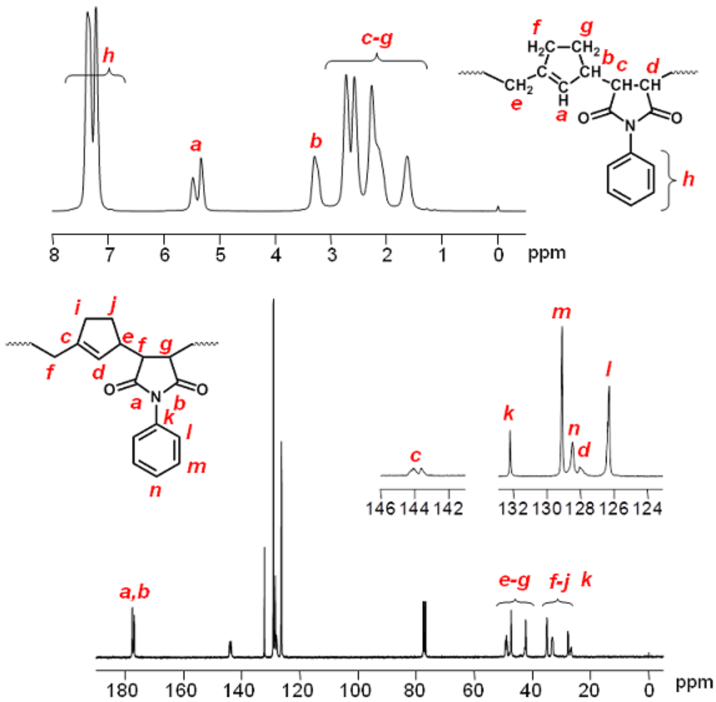

Figure S6. ^{1}H and ^{13}C NMR spectra of poly(MCP-*alt*-PhMI). Measurement solvent, $CDCl_3$.

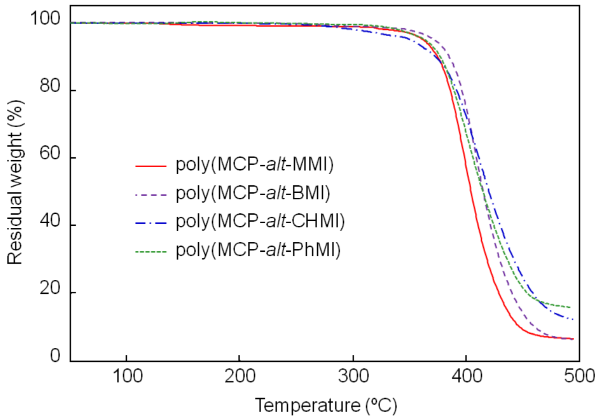

Figure S7. TG curves for poly(MCP-*alt*-RMI)s in a nitrogen stream at the heating rate of 10 ºC/min.

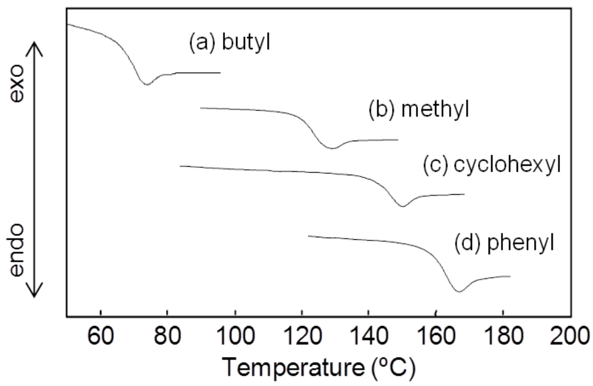

Figure S8. DSC curves of the poly(MCP-*alt*-RMI)s at the heating rate of 10 ºC/min. (a) poly(MCP-*alt*-BMI), (b) poly(MCP-*alt*-MMI), (c) poly(MCP-*alt*-CHMI), and (d) poly(MCP-*alt*-PhMI).

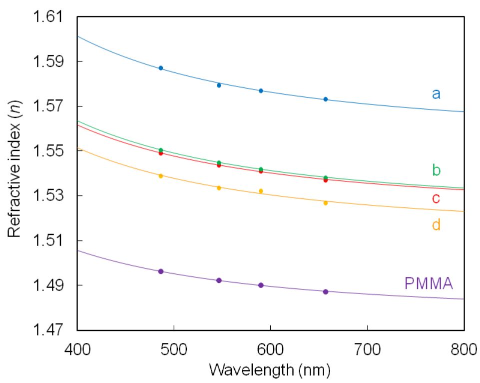

Figure S9. Wavelength dispersion of poly(MCP-*alt*-RMI)s: (a) poly(PhMI-*alt*-MCP), (b) poly(MCP-*alt*-CHMI), (c) poly(MCP-*alt*-MMI), (d) poly(MCP-*alt*-BMI), and (e) PMMA. Curves indicate fitting results by the simplified Cauchy formula using the two parameters, D and n_∞.

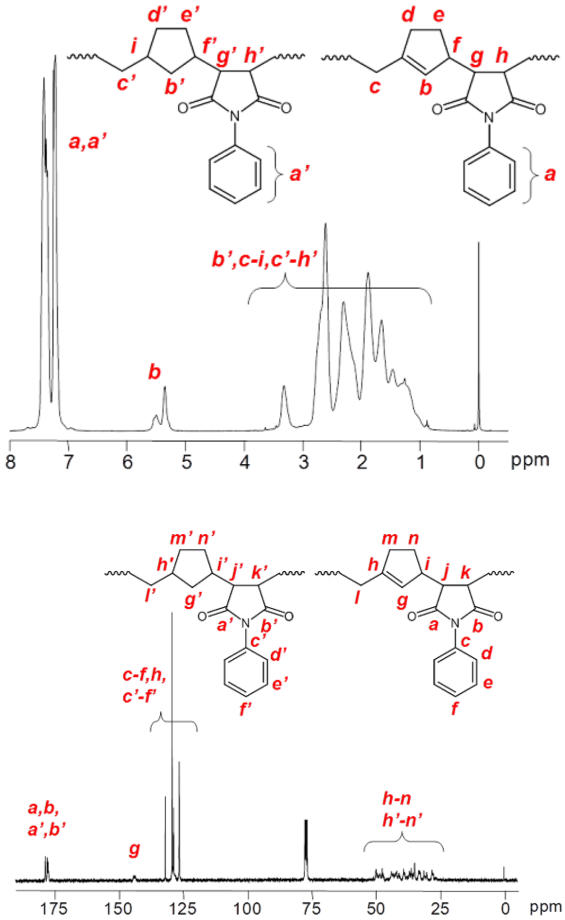

Figure S10. ^{1}H and ^{13}C NMR spectra of the hydrogenated poly(MCP-*alt*-PhMI) in $CDCl_3$ at room temperature. The conversion was 61%.

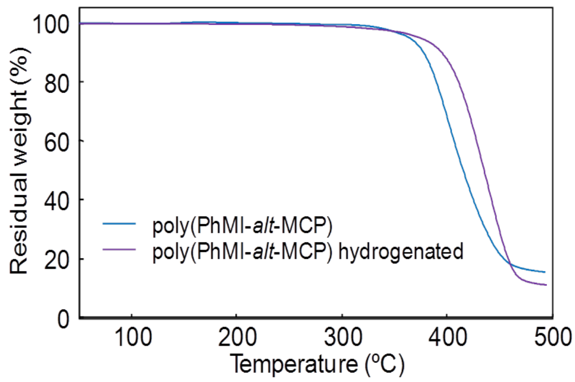

Figure S11. TG curves of poly(MCP-*alt*-PhMI) and the hydrogenated poly(MCP-*alt*-PhMI) at the heating rate of 10 ºC/min. The conversion was 61%.

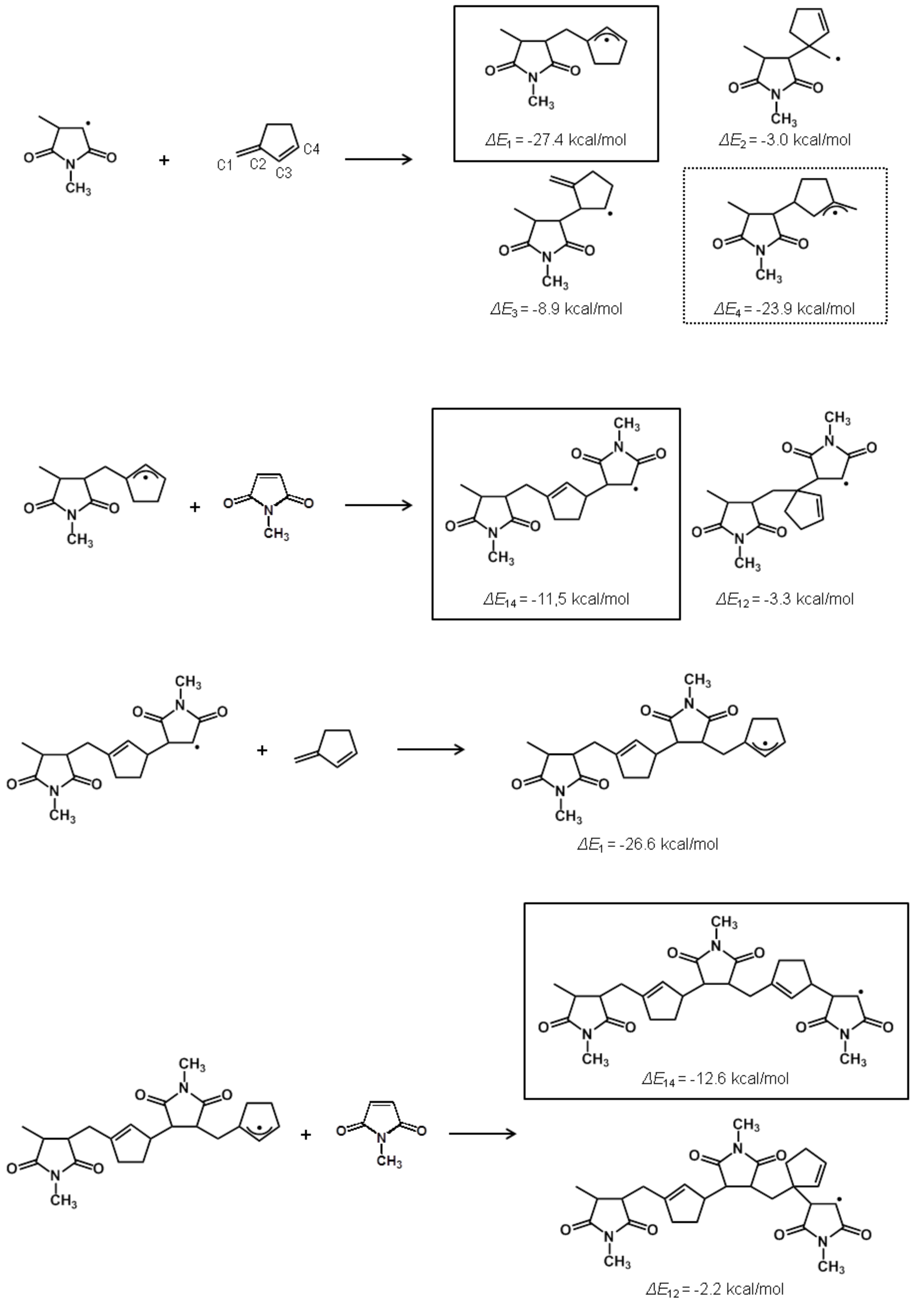

Figure S12. DFT calculation results for the model reactions related to the preferred regiospecific propagation during the radical copolymerization of MCP with the RMIs.

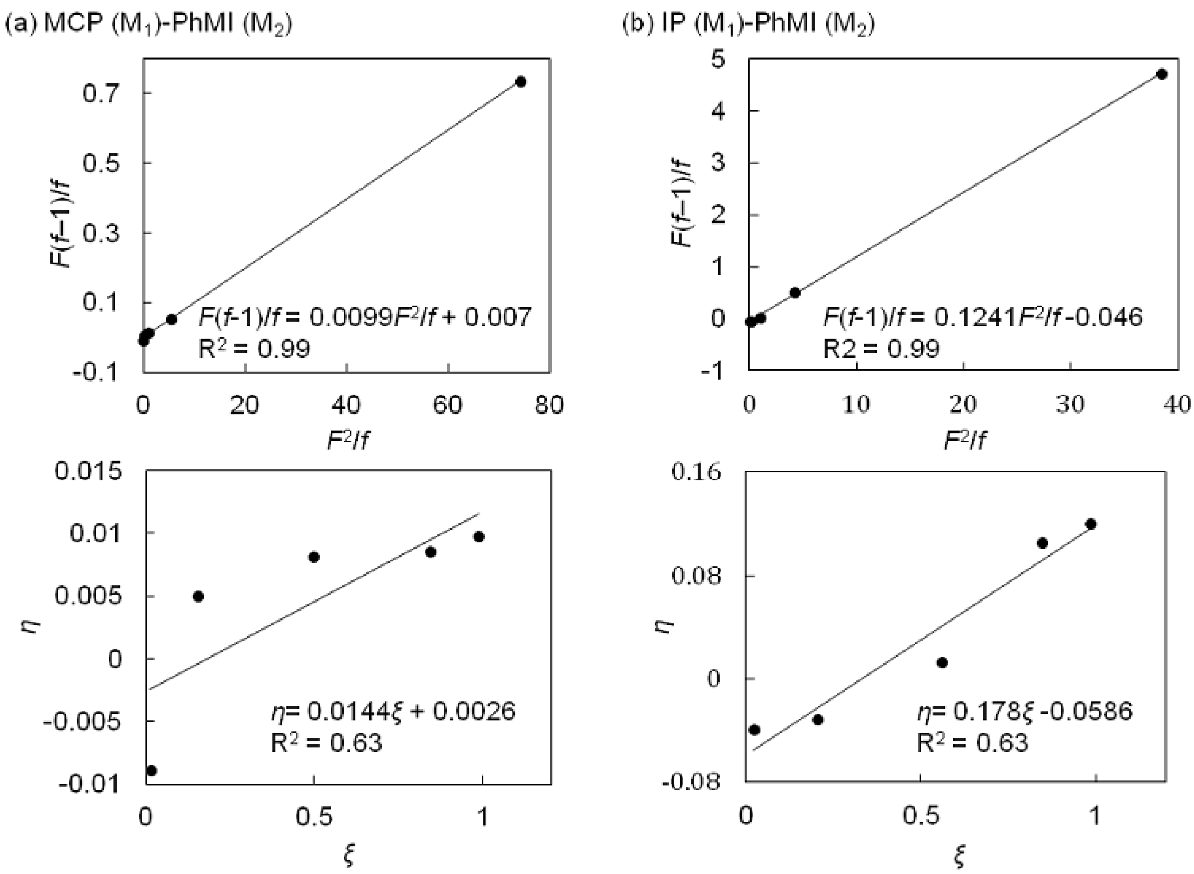

Figure S13. Fineman-Ross and Kelen-Tüdõs plots for (a) MCP (M_1)–PhMI (M_2) and (b) IP (M_1)–PhMI (M_2) copolymerization systems.

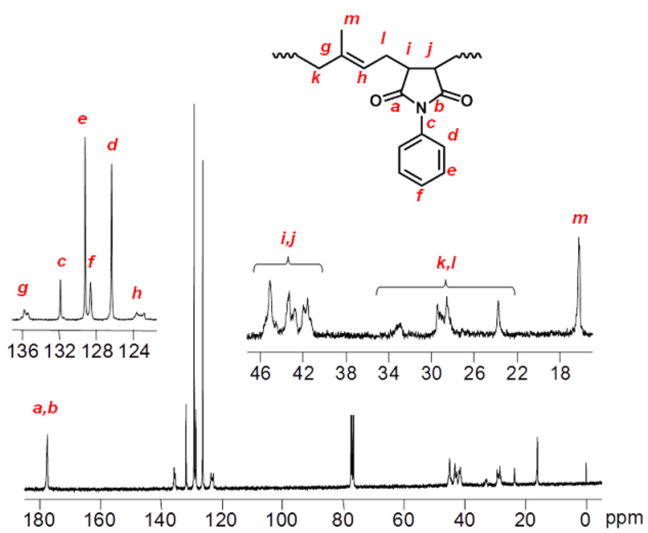

Figure S14. ^{13}C NMR spectrum of poly(IP-*alt*-PhMI). Measurement solvent, $CDCl_3$.

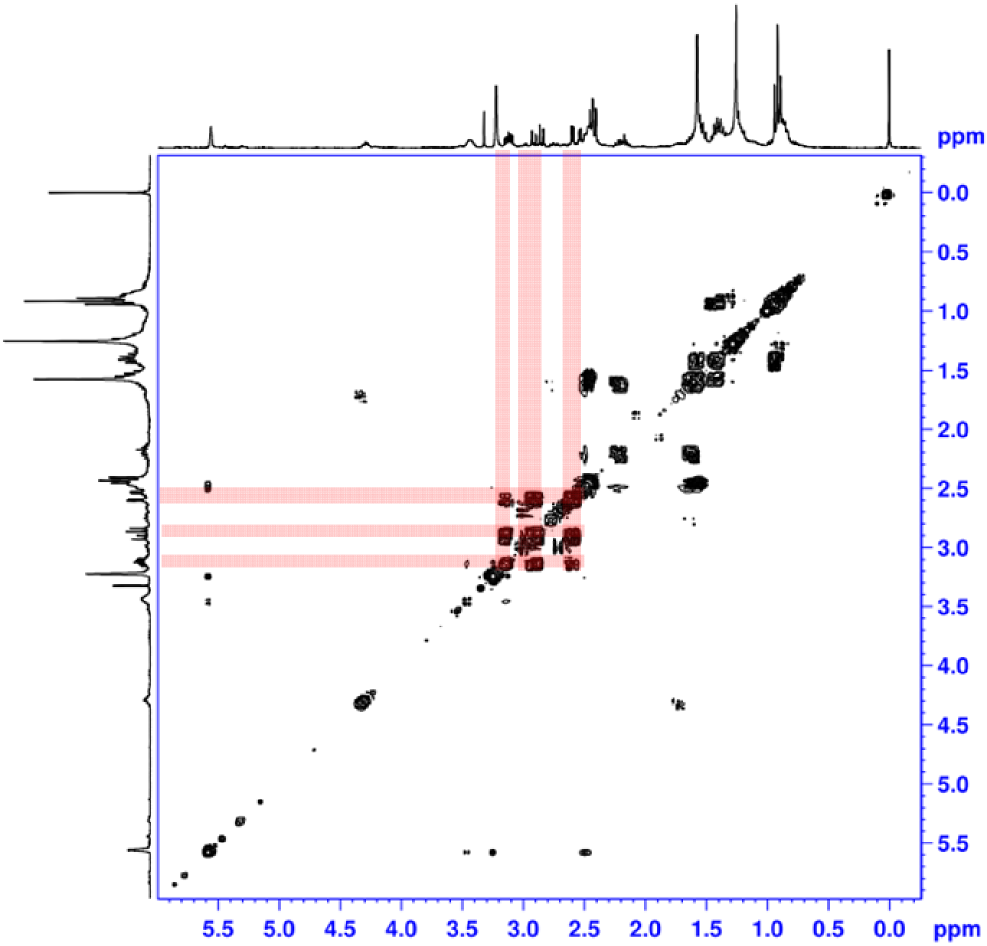

Figure S15. HHCOSY spectrum of BT/MCP/PhMI-1,4-adduct (Isomer II) separated from the telomerization mixture by preparative SEC, followed by purification using silica gel column chromatography. For Isomer I, see Figure 12.

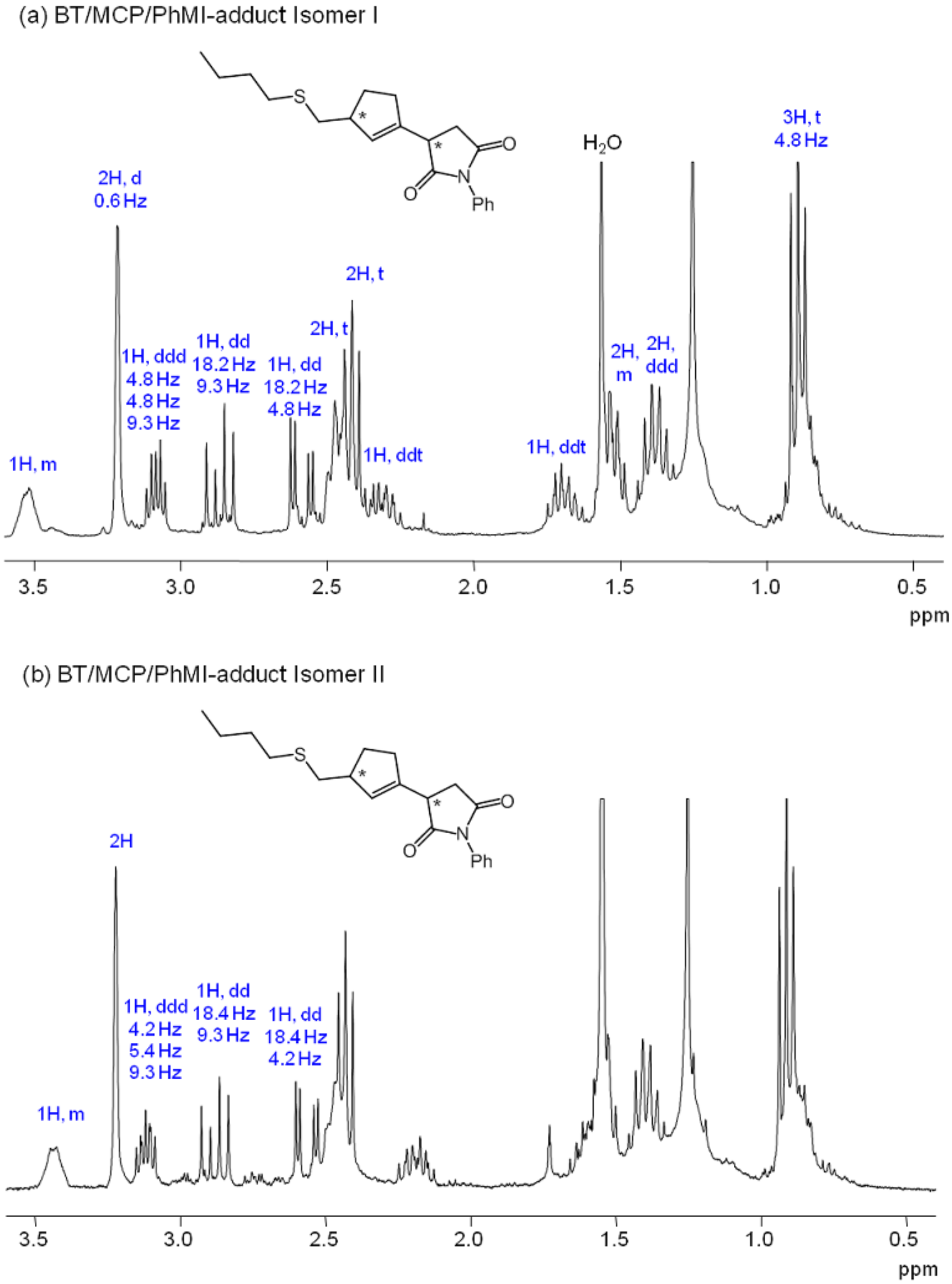

Figure S16. Expanded ^{1}H NMR spectra of BT/MCP/PhMI-1,4-adducts: (a) Isomer I and (b) Isomer II. Separated from the telomerization mixture by preparative SEC, followed by purification using silica gel column chromatography.