## Supplementary Information

## Sequence-regulated vinyl polymers via iterative atom transfer radical additions and acyclic diene metathesis polymerization

Masato Miyajima,<sup>1</sup> Kotaro Satoh,<sup>1,2</sup> and Masami Kamigaito<sup>\*,1</sup>

<sup>1</sup>Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan <sup>2</sup>Department of Chemical Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, 2-12-1-H120 Ookayama, Meguro-ku, Tokyo 152-8550, Japan e-mail: kamigait@chembio.nagoya-u.ac.jp

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**Fig. S1.** <sup>1</sup>H and <sup>13</sup>C NMR spectra (CDCl<sub>3</sub>, 25 °C) of **M1**.



Fig. S2. <sup>1</sup>H and <sup>13</sup>C NMR spectra (CDCl<sub>3</sub>, 25 °C) of M2.



Fig. S3. SEC curves of poly(M1) (A) and poly(M2) (B) before and after purification by preparative SEC.



Fig. S4. <sup>13</sup>C NMR spectra (CDCl<sub>3</sub>, 55 °C) of poly(M1) (A) and poly(M1)-H<sub>2</sub>.



Fig. S5. <sup>13</sup>C NMR spectra (CDCl<sub>3</sub>, 55 °C) of poly(M2) (A) and poly(M2)-H<sub>2</sub>.



Fig. S6. Hydrogenation of poly(M1) (A) and poly(M2) (B).



Fig. S7. MALDI-TOF-MS spectra of poly(M1)(A) and  $poly(M1)-H_2(B)$ .

Table S1. ADMET	poly	ymerization	of M1	under	various	conditions <sup>4</sup>
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Entry	[M] <sub>0</sub>	Catalyst	Temperature	e Pressure	Time	Conversion <sup>b</sup>	Isomerization <sup>b</sup>	<i>M</i> <sub>n</sub> <sup>c</sup>	<i>M</i> <sub>w</sub> <sup>c</sup>	$M_{\rm w}/M_{\rm n}^{c}$
1	bulk	G2	50 °C	1.01 x 10 <sup>5</sup> Pa(1 atm)	400 h	81%	26%	1000	1300	1.26
2	bulk	G2	50 °C	< 200 Pa (< 0.002 atm)	300 h	91%	22%	1900	3200	1.68
3	bulk	G2	100 °C	< 200 Pa (< 0.002 atm)	270 h	95%	25%	2700	5300	1.96
4	bulk	G2	120 °C	< 200 Pa (< 0.002 atm)	360 h	96%	32%	4000	9400	2.35
5	bulk	HG2	120 °C	< 200 Pa (< 0.002 atm)	360 h	99%	49%	4700	12000	2.52
6	bulk	G3	120 °C	< 200 Pa (< 0.002 atm)	360 h	98%	61%	2500	4900	1.94
7	1500	G2	50 °C	0.02 MPa (0.03 atm)	30 min	83%	>1%	1600	2800	1.75
8	1500	G2	50 °C	0.02 MPa (0.03 atm)	18 h	98%	9%	2900	9800	3.40



<sup>*a*</sup> Polymerization condition:  $[M1]_0/[Catalyst]_0 = 400$ . <sup>*b*</sup> Determined by <sup>1</sup>H NMR. <sup>*c*</sup> Determined by SEC using polystyrene standards.