Supporting Information

Achieving High Molecular Weight Alternating Copolymers of 1-Octene with Methyl Acrylate via Lewis Acid Catalyzed Copolymerization

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Supporting Information

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Table S1. Effect of different $Sc(OTf)_3$ dosage on ^{13}C NMR Chemical shift of MA.

carbon	$n(Sc(OTf)_3)/n(MA)$	Chemical shift(ppm)	Δδ(ppm)[a]
	0	130.57	/
1	0.1	131.88	1.31
	0.3	135.40	4.83
	0	128.06	/
2	0.1	127.67	0.39
	0.3	126.75	1.31
	0	166.49	/
3	0.1	167.58	1.09
	0.3	170.62	4.13
	0	51.50	/
4	0.1	52.19	0.69
	0.3	54.36	2.86

a: Δδ represents the change in chemical shift of MA after adding different molar ratios of $Sc(OTf)_3$.

Table S2. Copolymer Constitutions at Different 1,7-Octadiene Addition Amount.

#	n(1,7-octadiene)/n(MA)	n(Initiator)/n(Monomer) (%)	$n(Sc(OTf)_3)$/n(MA)	Solvent	Solvent amount (ml)	Temp. (°C)	$F_{1\text{-octene}}$ (%)	F_{MA} (%)	$M_n \times 10^{-4}$ (g/mol)	$M_w \times 10^{-4}$ (g/mol)	PDI[b]
1	0.00	0.1	0.1	CH_2Cl_2	50	45	48.50	51.50	2.59	4.34	1.68
2	0.00	0.1	0.2	CH_2Cl_2	50	45	43.00	57.00	2.85	5.28	1.85
3	0.00	0.3	0.1	CH_2Cl_2	50	45	45.04	54.96	2.16	3.82	1.77
4	0.00	0.3	0.2	CH_2Cl_2	50	45	42.43	57.57	3.17	5.71	1.80
5	0.00	0.5	0.1	CH_2Cl_2	50	45	43.46	56.54	1.84	3.64	1.98
6	0.00	0.5	0.1	CH_2Cl_2	50	45	45.43	54.57	1.79	3.20	1.79
7	0.00	0.5	0.2	CH_2Cl_2	50	45	42.24	57.76	2.34	4.63	1.98
8	0.01	0.05	0.1	PhCl	30	60	38.28	60.90	4.77	8.78	1.84
9	0.01	0.1	0.1	PhCl	30	60	38.53	60.87	4.17	8.32	1.99
10	0.01	0.1	0.1	PhCl	30	50	40.95	58.33	6.77	13.45	1.99
11	0.01	0.1	0.1	PhCl	50	60	38.47	60.96	4.09	8.72	2.13
12	0.01	0.1	0.1	PhCl	50	50	37.46	62.09	5.72	10.53	1.84
13	0.01	0.1	0.1	PhCl	90	50	38.65	60.46	5.75	10.92	1.89
14	0.01	0.1	0.1	1,4-Dioxane	30	40	35.43	63.69	6.17	10.50	1.70
15	0.03	0.1	0.1	CH_2Cl_2	50	45	40.86	59.10	4.22	7.33	1.73
16	0.03	0.1	0.1	PhCl	50	60	40.18	59.60	4.48	9.60	2.14

(Continued table on the following page)

(Table S2 continued)

#	n(1,7-octadiene)/ n(MA)	n(Initiator)/ n(Monomer) (%)	n(Sc(OTf)$_3$)/ n(MA)	Solvent	Solvent amount (ml)	Temp. (°C)	$F_{1\text{-octene}}$ (%)	F_{MA} (%)	$M_n \times 10^{-4}$ (g/mol)	$M_w \times 10^{-4}$ (g/mol)	PDI[b]
17	0.03	0.1	0.2	CH_2Cl_2	50	45	41.31	57.89	3.84	7.89	2.05
18	0.03	0.5	0.1	PhCl	50	60	39.80	60.06	3.86	8.65	2.24
19	0.03	0.5	0.2	PhCl	50	60	41.25	58.07	2.87	6.38	2.22
20	0.04	0.1	0.1	CH_2Cl_2	50	45	49.71	49.37	3.01	5.56	1.84
21	0.04	0.1	0.2	CH_2Cl_2	50	45	42.34	56.80	4.12	8.40	2.04
22	0.04	0.5	0.1	PhCl	50	60	38.15	60.31	2.93	8.37	2.86
23	0.04	0.5	0.2	PhCl	50	60	40.82	57.19	2.41	6.34	2.63
24	0.05	0.1	0.1	CH_2Cl_2	50	45	40.31	58.80	3.81	7.49	1.96
25	0.05	0.1	0.2	CH_2Cl_2	50	45	43.47	55.66	3.83	8.12	2.12
26	0.05	0.1	0.2	CH_2Cl_2	50	45	38.74	60.43	3.92	10.88	2.84
27	0.05	0.5	0.1	PhCl	50	60	38.83	60.14	3.56	8.82	2.48
28	0.05	0.5	0.2	PhCl	50	60	40.45	58.05	2.28	5.45	2.39

Table S3. Copolymer Constitutions of Relationship between molecular weight of copolymer and gel content.

#	n(1,7-octadiene)/ n(MA)	n(Initiator)/ n(Monomer) (%)	$n(Sc(OTf)_3)$/ n(MA)	Solvent	Solvent amount (ml)	Temp. (°C)	$M_n \times 10^{-4}$ (g/mol)	Gel (g)
1	0.005	0.1	0.1	PhCl	30	50	5.92	0.24
2	0.01	0.05	0.1	PhCl	30	60	4.77	0.69
3	0.01	0.1	0.1	PhCl	50	60	4.09	0.82
4	0.01	0.1	0.1	PhCl	30	60	4.17	0.81
5	0.01	0.1	0.1	PhCl	50	50	5.72	0.40
6	0.01	0.1	0.1	PhCl	30	50	7.07	0.42
7	0.01	0.1	0.1	PhCl	30	50	6.77	0.45
8	0.01	0.1	0.1	PhCl	90	50	5.75	0.54
9	0.03	0.1	0.1	PhCl	50	60	4.48	0.55
10	0.03	0.5	0.1	PhCl	50	60	3.86	0.32
11	0.03	0.5	0.2	PhCl	50	60	2.87	1.53
12	0.04	0.5	0.1	PhCl	50	60	2.93	0.52
13	0.04	0.5	0.2	PhCl	50	60	2.41	1.33
14	0.05	0.5	0.1	PhCl	50	60	3.56	0.50
15	0.05	0.5	0.2	PhCl	50	60	2.28	1.84

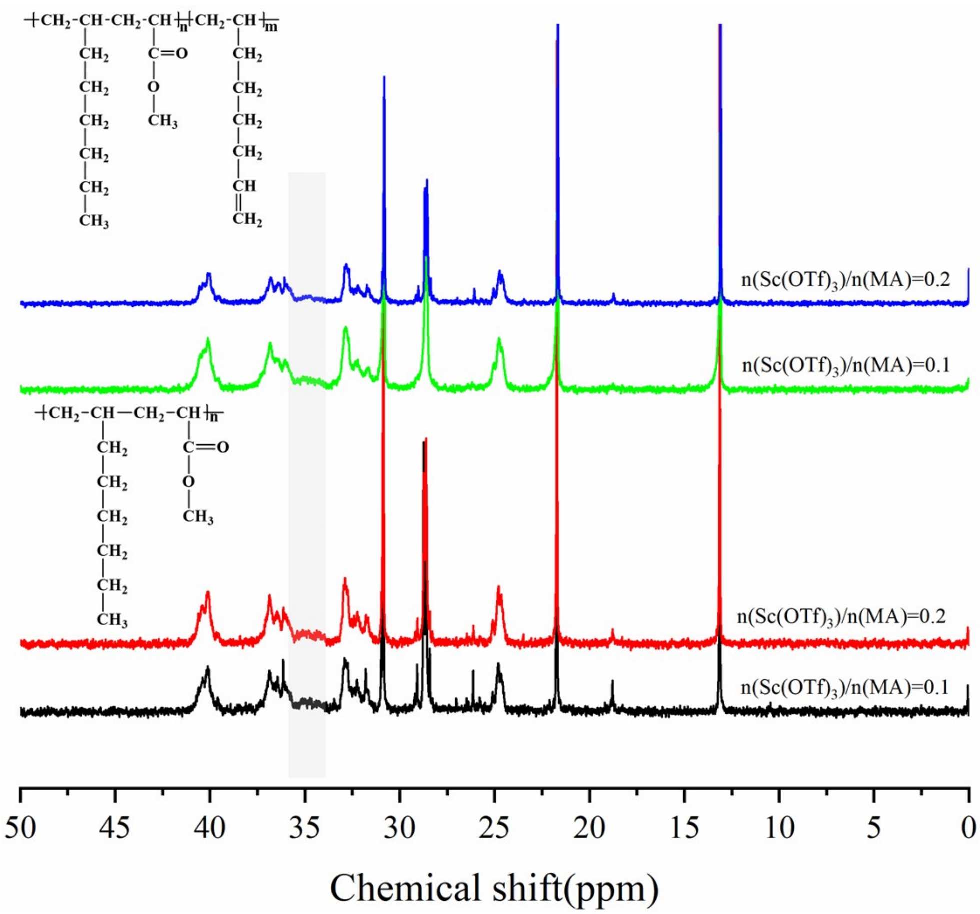

Figure S1. ^{13}C NMR spectrum of copolymer of MA-1-octene-1,7-octadiene and MA-1-octene with different $Sc(OTf)_3$ dosage.

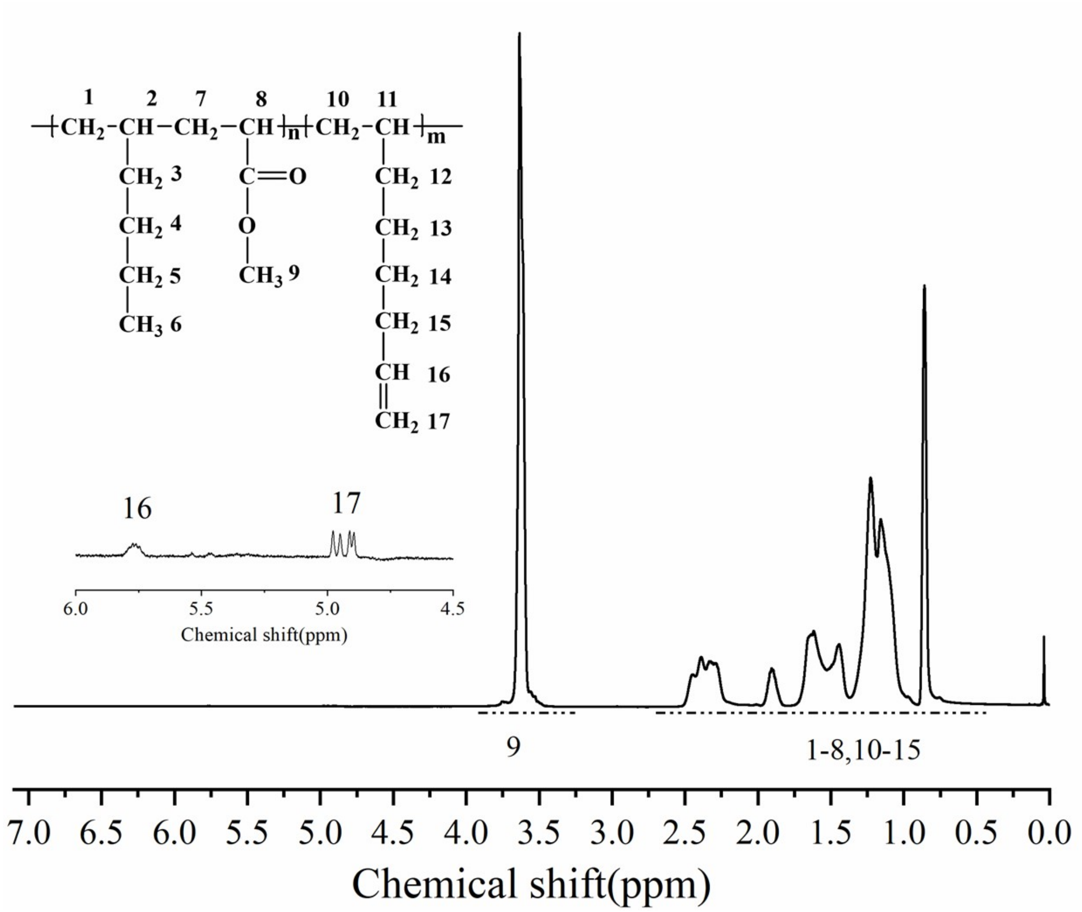

Figure S2. ^{1}H NMR spectrum of copolymer of MA, 1-hexene and 1,7-octadiene in $CDCl_3$.

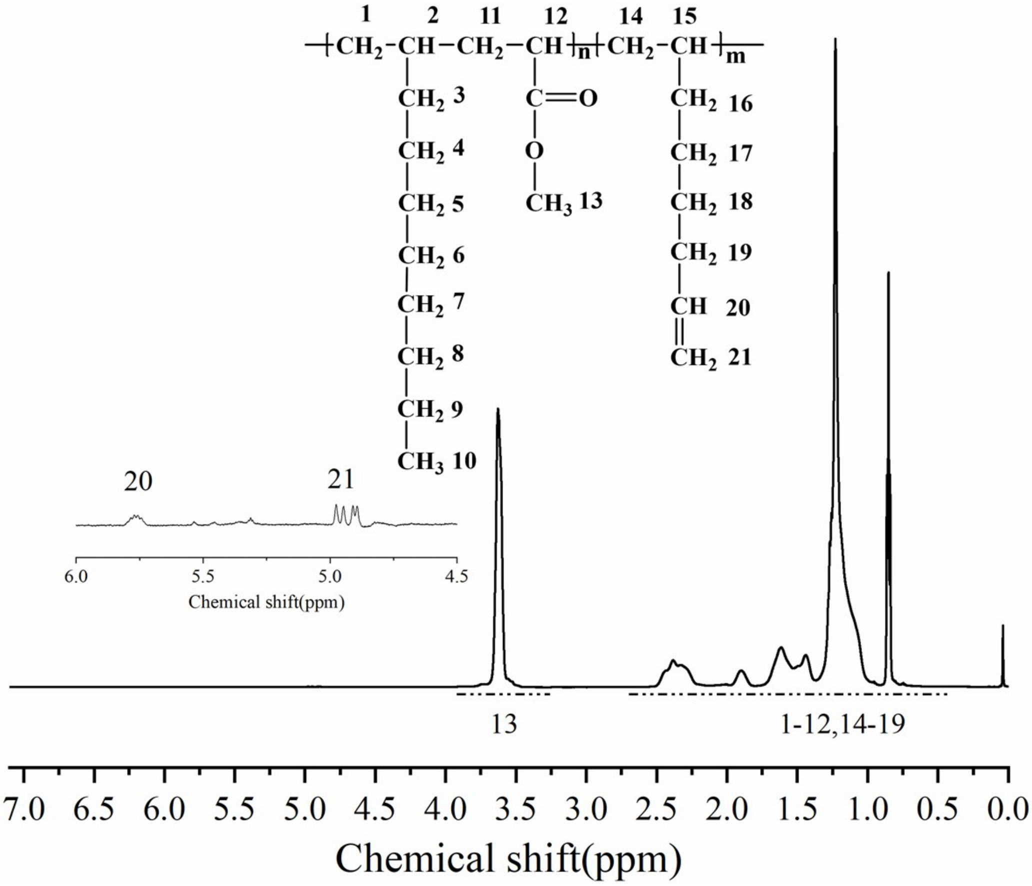

Figure S3. ^{1}H NMR spectrum of copolymer of MA, 1-decene and 1,7-octadiene in $CDCl_3$.

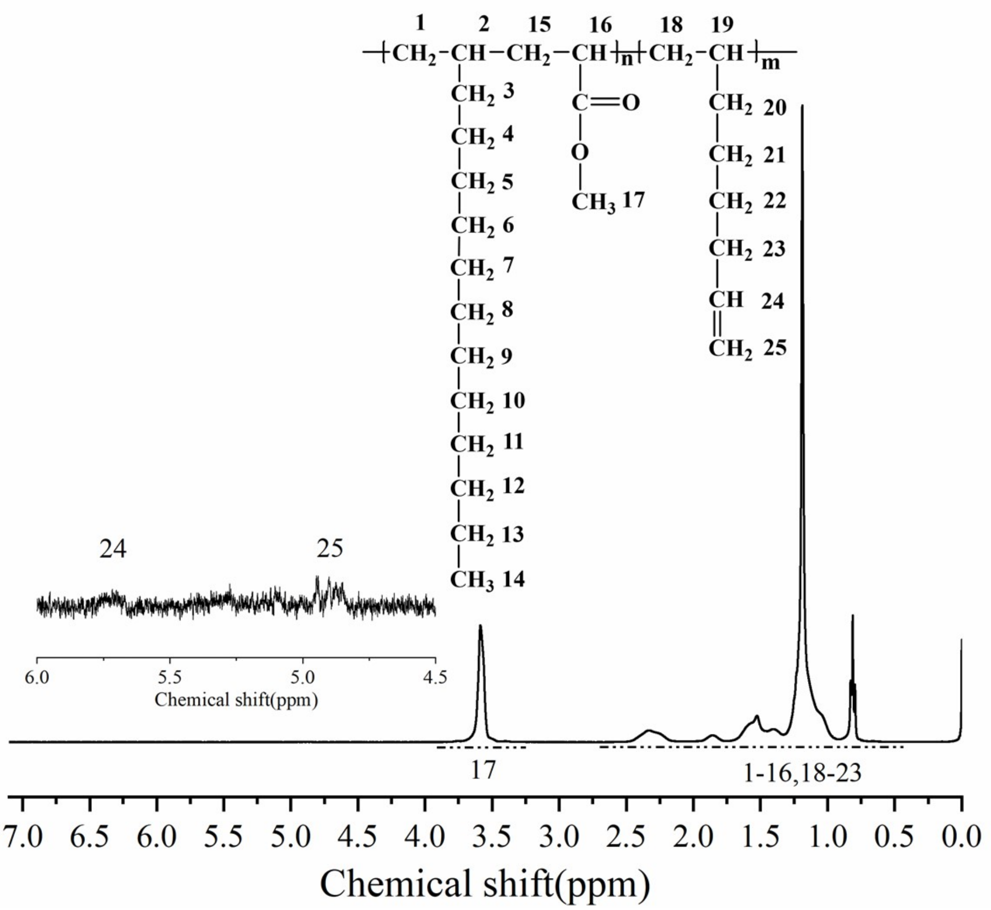

Figure S4. ^{1}H NMR spectrum of copolymer of MA, 1-tetradecane and 1,7-octadiene in $CDCl_3$.

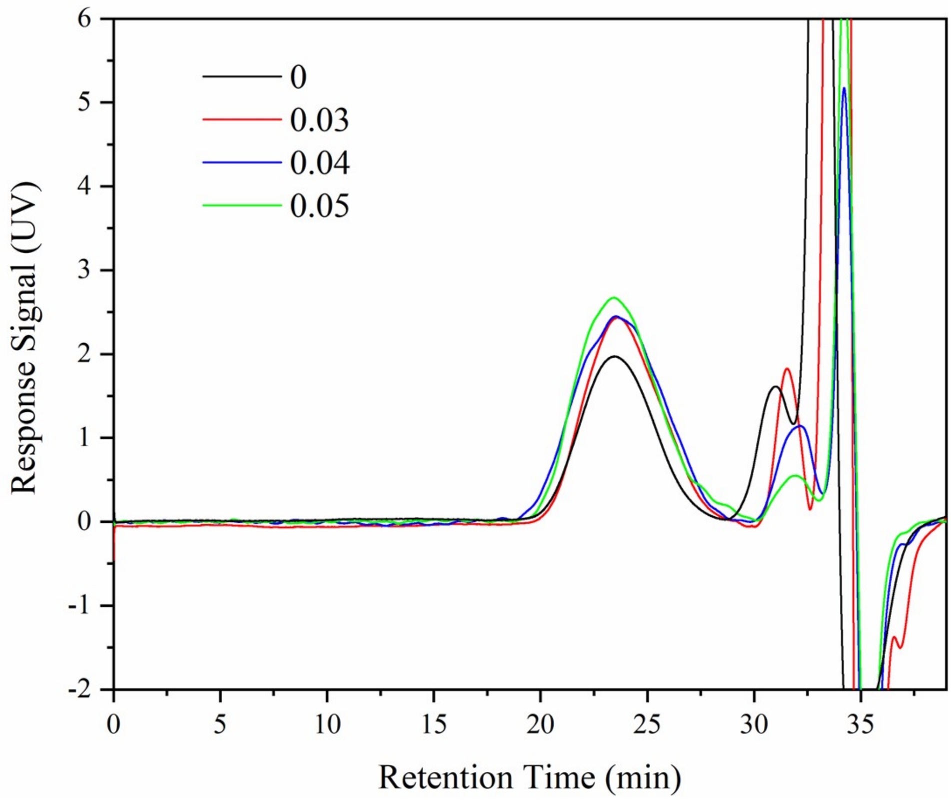

Figure S5. GPC curves of copolymers with different 1,7-octadiene/MA molar ratio. Reaction conditions: n($Sc(OTf)_3$)/n(MA)=0.1; n(1-octene)/n(MA) =2.87; n(ABVN)/n(Monomer)=0.001; temperature 45 °C.

Equation S1. The equations for calculating the composition of the obtained MA, 1-octene and 1,7-octadiene copolymer.

$$F_{MA} = \frac{\frac{S_{11}}{3}}{\frac{S_{11}}{3} + \frac{S_{1-10,12-17} - S_{18} \times 11 - S11}{16} + S_{18}} \times 100\% \quad \text{Eq. S1-1}$$

$$F_{1-octene} = \frac{\frac{S_{1-10,12-17} - S_{18} \times 11 - S11}{16}}{\frac{S_{11}}{3} + \frac{S_{1-10,12-17} - S_{18} \times 11 - S11}{16} + S_{18}} \times 100\% \quad \text{Eq. S1-2}$$

$$F_{1,7-octadiene} = \frac{S_{18}}{\frac{S_{11}}{3} + \frac{S_{1-10,12-17} - S_{18} \times 11 - S11}{16} + S_{18}} \times 100\% \quad \text{Eq. S1-3}$$

F_{MA}: molar content of MA units in the copolymer, $F_{1\text{-octene}}$: molar content of 1-octene units in the copolymer, $F_{1,7\text{-octadiene}}$: molar content of 1,7-octadiene units in the copolymer. S_{11} represents the integrated area of H on C_{11}, S_{18} represents the integrated area of H on C_{18}, and $S_{1\text{-}10,12\text{-}17}$ represents the integrated area of H on C_1-C_{10} and C_{12}-C_{17}.

Equation S2. The equations for calculating the composition of the obtained MA, 1-hexene and 1,7-octadiene copolymer.

$$F_{MA} = \frac{\frac{S_{9}}{3}}{\frac{S_{9}}{3} + \frac{S_{1-8,10-15} - S_{16} \times 11 - S9}{12} + S_{16}} \times 100\% \quad \text{Eq. S2-1}$$

$$F_{1-hexene} = \frac{\frac{S_{1-8,10-15} - S_{16} \times 11 - S9}{12}}{\frac{S_{9}}{3} + \frac{S_{1-8,10-15} - S_{16} \times 11 - S9}{12} + S_{16}} \times 100\% \quad \text{Eq. S2-2}$$

$$F_{1,7-octadiene} = \frac{S_{16}}{\frac{S_{9}}{3} + \frac{S_{1-8,10-15} - S_{16} \times 11 - S9}{12} + S_{16}} \times 100\% \quad \text{Eq. S2-3}$$

F_{MA}: molar content of MA units in the copolymer, $F_{1\text{-hexene}}$: molar content of 1-hexene units in the copolymer, $F_{1,7\text{-octadiene}}$: molar content of 1,7-octadiene units in the copolymer. S_9 represents the integrated area of H on C_9, S_{16} represents the integrated area of H on C_{16}, and $S_{1\text{-}8,10\text{-}15}$ represents the integrated area of H on C_1-C_{10} and C_{10}-C_{15}.

Equation S3. The equations for calculating the composition of the obtained MA, 1-decene and 1,7-octadiene copolymer.

$$F_{MA}=\frac{\frac{S_{13}}{3}}{\frac{S_{13}}{3}+\frac{S_{1-12,14-19}-S_{20}\times 11-S13}{20}+S_{20}}\times 100\%$$ Eq. S3-1

$$F_{1-decene}=\frac{\frac{S_{1-12,14-19}-S_{20}\times 11-S13}{20}}{\frac{S_{13}}{3}+\frac{S_{1-12,14-19}-S_{20}\times 11-S13}{20}+S_{20}}\times 100\%$$ Eq. S3-2

$$F_{1,7-octadiene}=\frac{S_{20}}{\frac{S_{13}}{3}+\frac{S_{1-12,14-19}-S_{20}\times 11-S13}{20}+S_{20}}\times 100\%$$ Eq. S3-3

F_{MA}: molar content of MA units in the copolymer, $F_{1\text{-decene}}$: molar content of 1-decene units in the copolymer, $F_{1,7\text{-octadiene}}$: molar content of 1,7-octadiene units in the copolymer. S_{13} represents the integrated area of H on C_{13}, S_{20} represents the integrated area of H on C_{20}, and $S_{1-12,14-19}$ represents the integrated area of H on C_1-C_{12} and C_{14}-C_{19}.

Equation S4. The equations for calculating the composition of the obtained MA, 1-tetradecane and 1,7-octadiene copolymer.

$$F_{MA}=\frac{\frac{S_{17}}{3}}{\frac{S_{17}}{3}+\frac{S_{1-16,18-23}-S_{24}\times 11-S17}{28}+S_{24}}\times 100\%$$ Eq. S4-1

$$F_{1-tetradecane}=\frac{\frac{S_{1-16,18-23}-S_{24}\times 11-S17}{28}}{\frac{S_{17}}{3}+\frac{S_{1-16,18-23}-S_{24}\times 11-S17}{28}+S_{24}}\times 100\%$$ Eq. S4-2

$$F_{1,7-octadiene}=\frac{S_{24}}{\frac{S_{17}}{3}+\frac{S_{1-16,18-23}-S_{24}\times 11-S17}{28}+S_{24}}\times 100\%$$ Eq. S4-3

F_{MA}: molar content of MA units in the copolymer, $F_{1\text{-tetradecane}}$: molar content of 1-tetradecane units in the copolymer, $F_{1,7\text{-octadiene}}$: molar content of 1,7-octadiene units in the copolymer. S_{17} represents the integrated area of H on C_{17}, S_{24} represents the integrated area of H on C_{24}, and $S_{1-16,18-23}$ represents the integrated area of H on C_1-C_{16} and C_{18}-C_{23}.