Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supporting Information

Nitroxide radical-containing polynorbornenes by ring-opening metathesis polymerization as stabilizing agents for polyolefins

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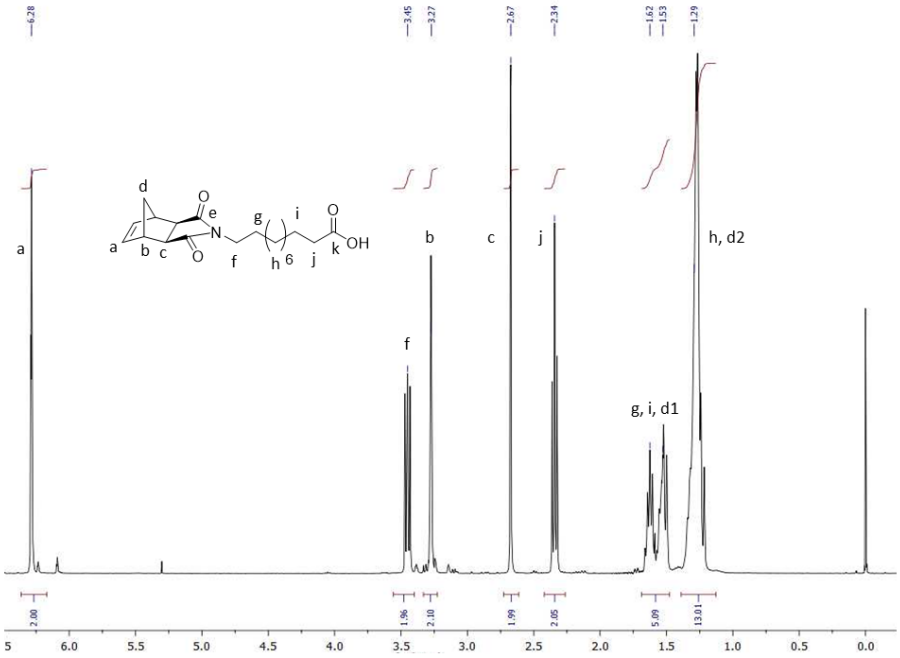

Figure S1. ^{1}H NMR spectrum of **1** in $CDCl_3$

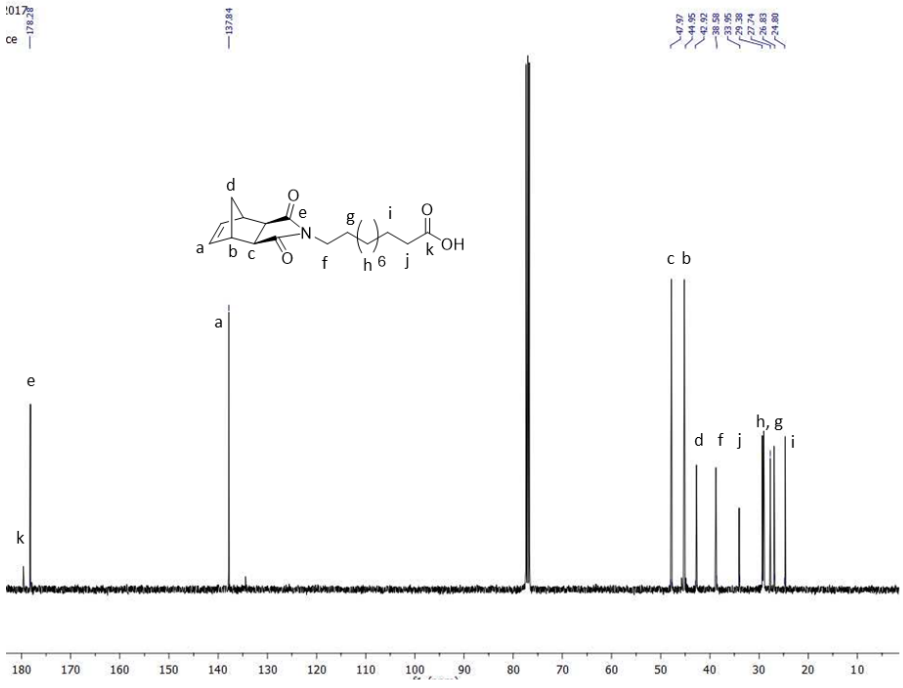

Figure S2. ^{13}C NMR spectrum of **1** in $CDCl_3$

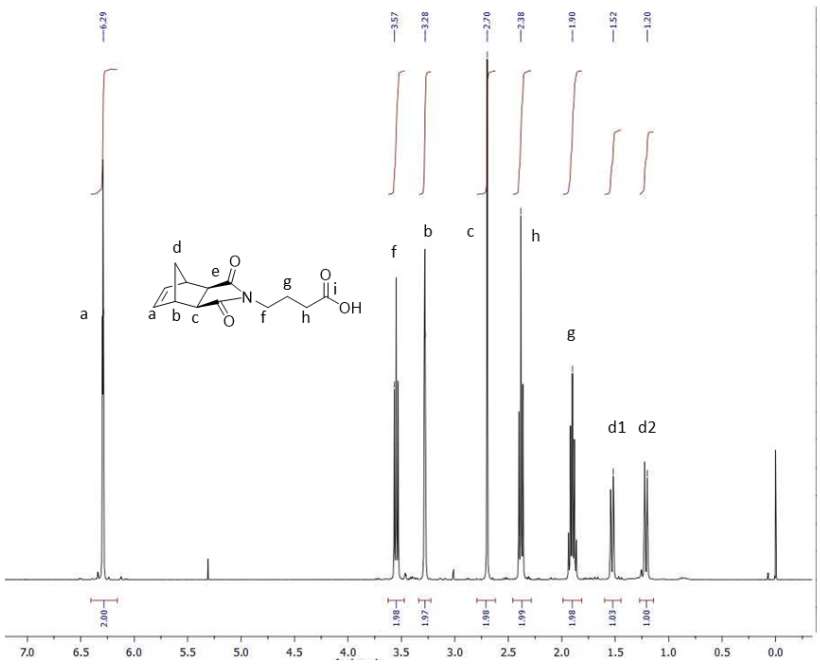

Figure S3. ^{1}H spectrum of **2** in $CDCl_3$

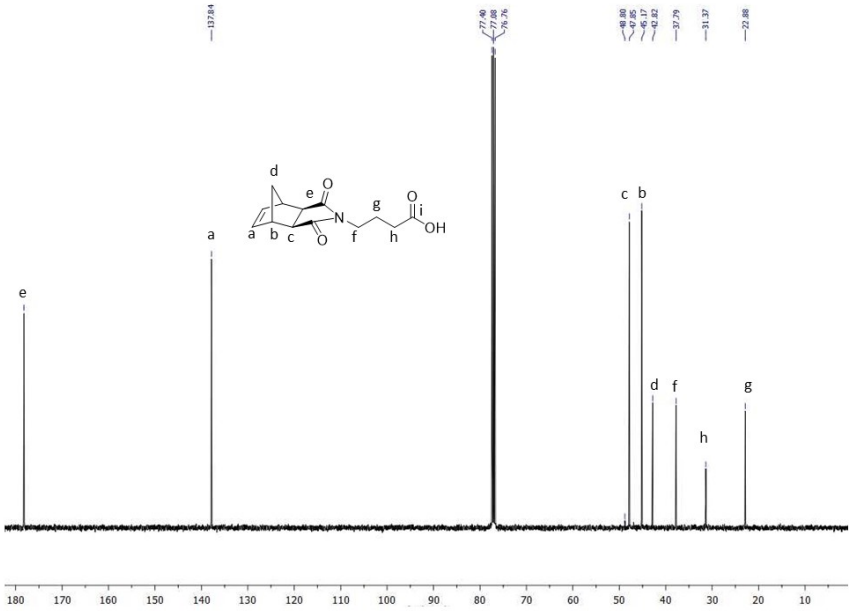

Figure S4. ^{13}C NMR spectrum of **2** in $CDCl_3$

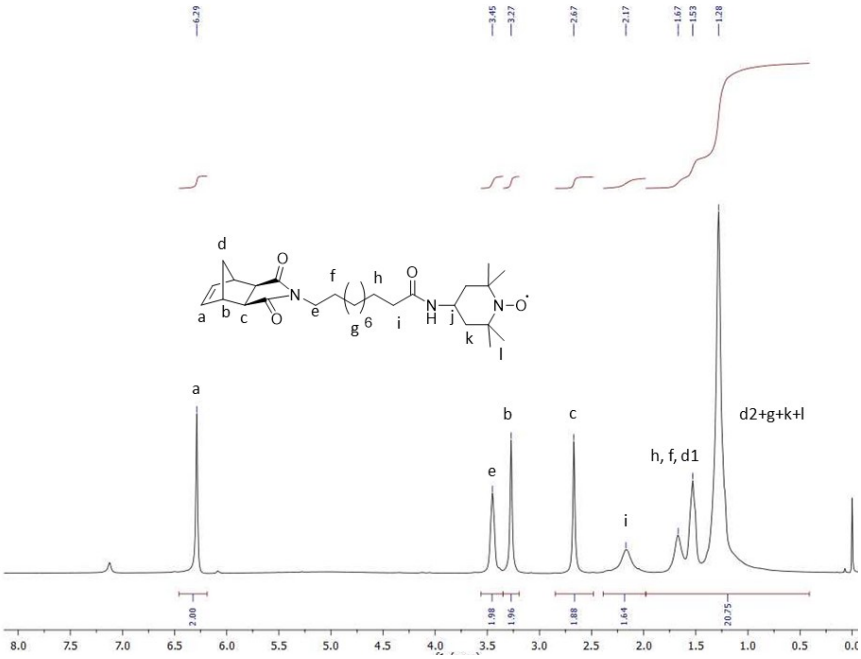

Figure S5. ^{1}H NMR spectrum of $\mathbf{M1}_N$ in $CDCl_3$

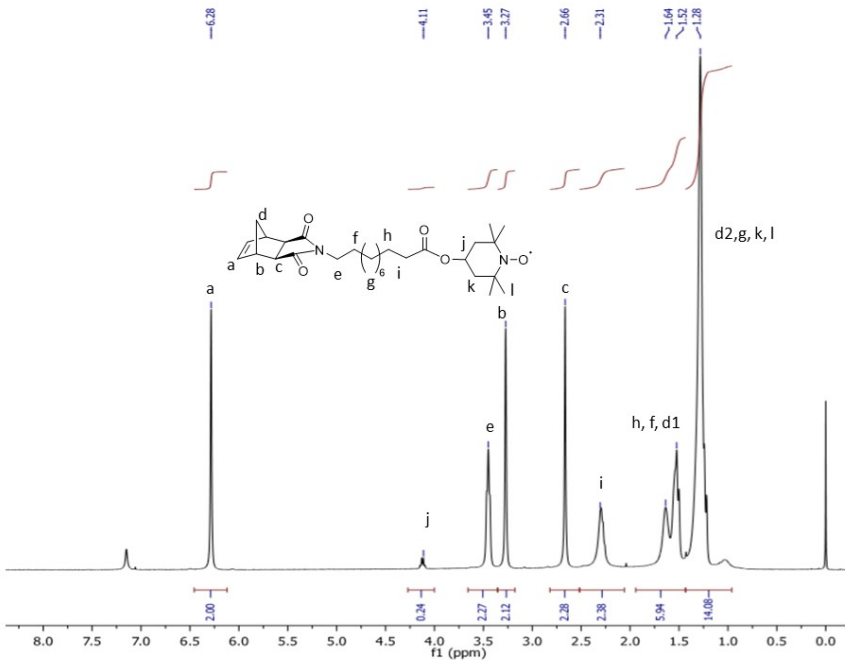

Figure S6. ^{1}H NMR spectrum of $\mathbf{M1}_o$ in $CDCl_3$

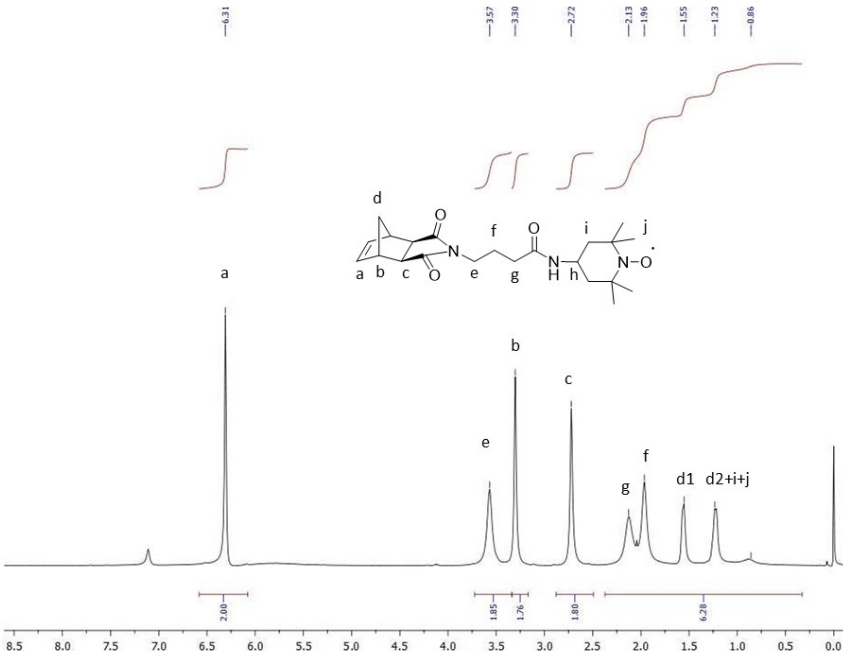

Figure S7. ^{1}H NMR spectrum of **M2**$_N$ in $CDCl_3$

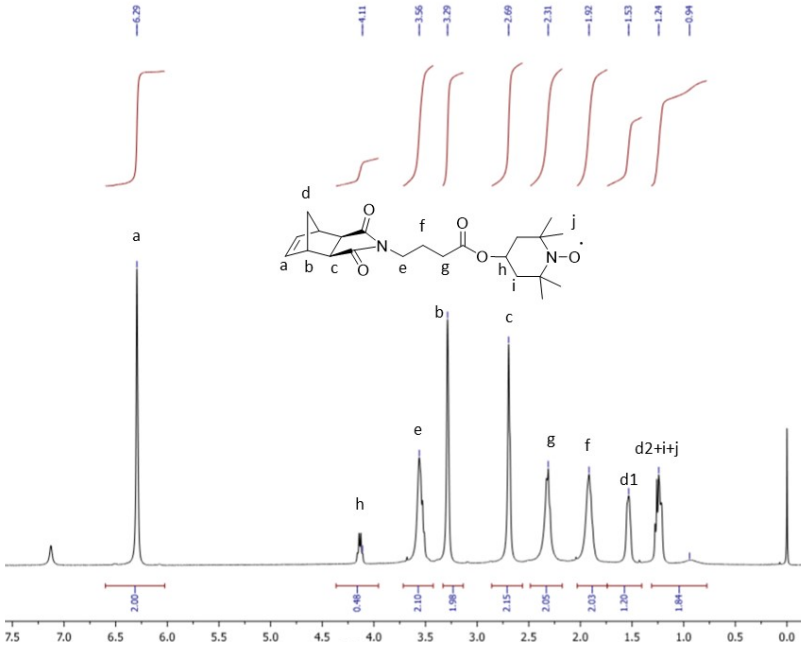

Figure S8. ^{1}H NMR spectrum of **M2**$_O$ in $CDCl_3$

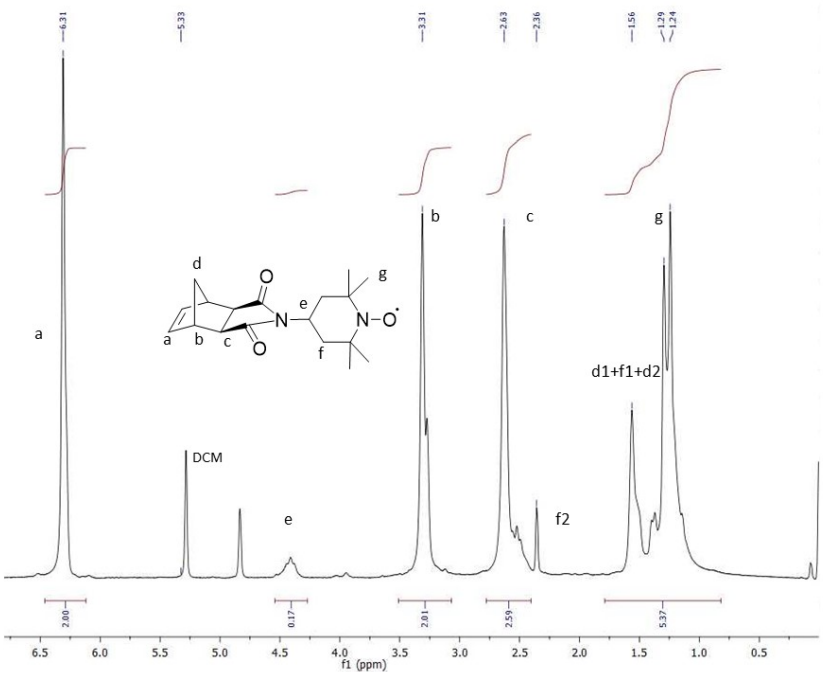

Figure S9. ^{1}H NMR spectrum of **M3** in $CDCl_3$

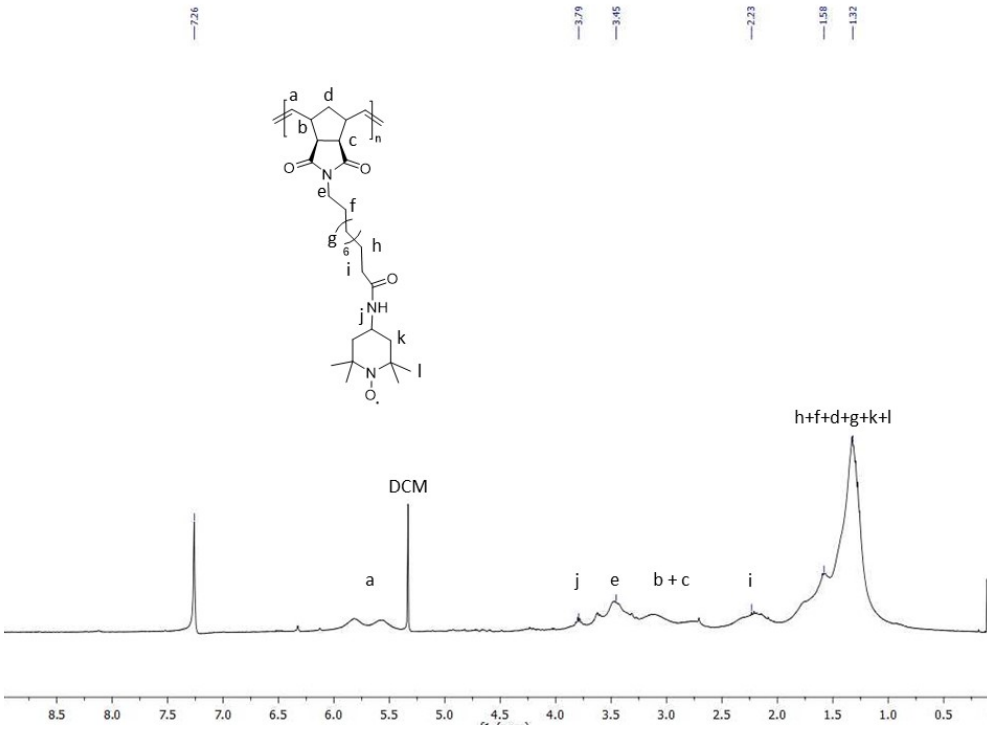

Figure S10. ^{1}H NMR spectrum of **PM1**$_N$ in $CDCl_3$

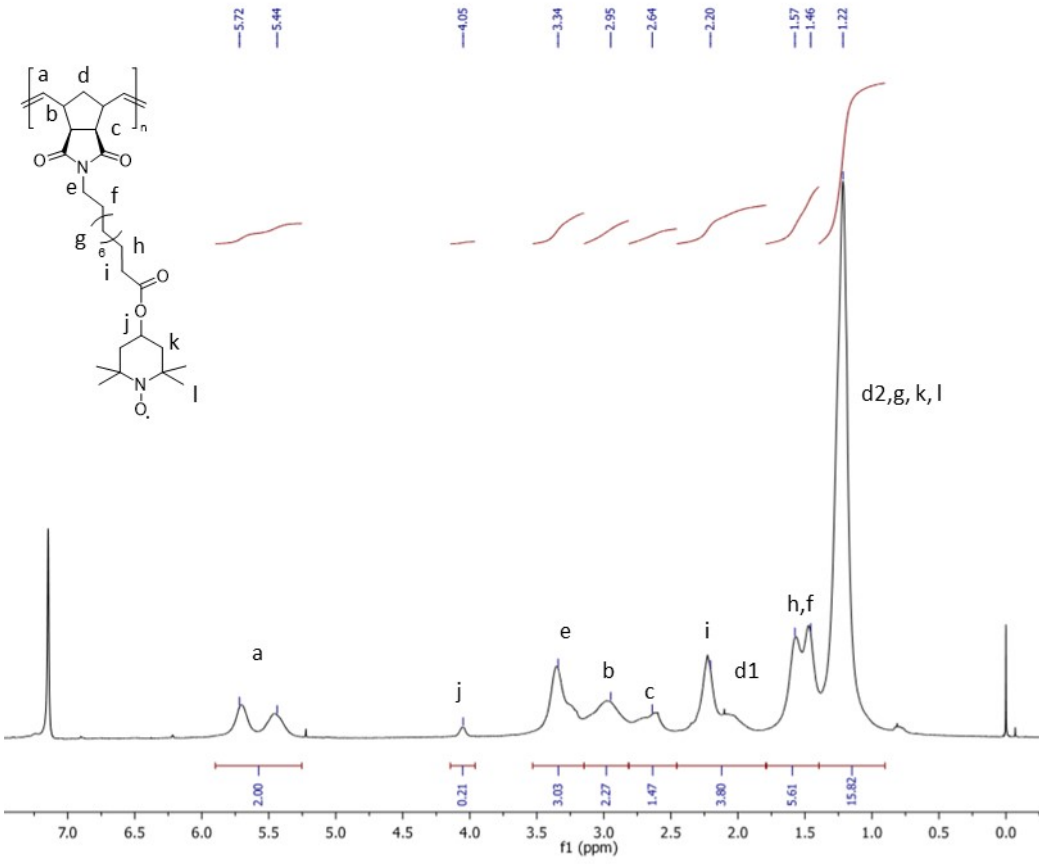

Figure S11. ^{1}H NMR spectrum of **PM1**$_o$ in $CDCl_3$

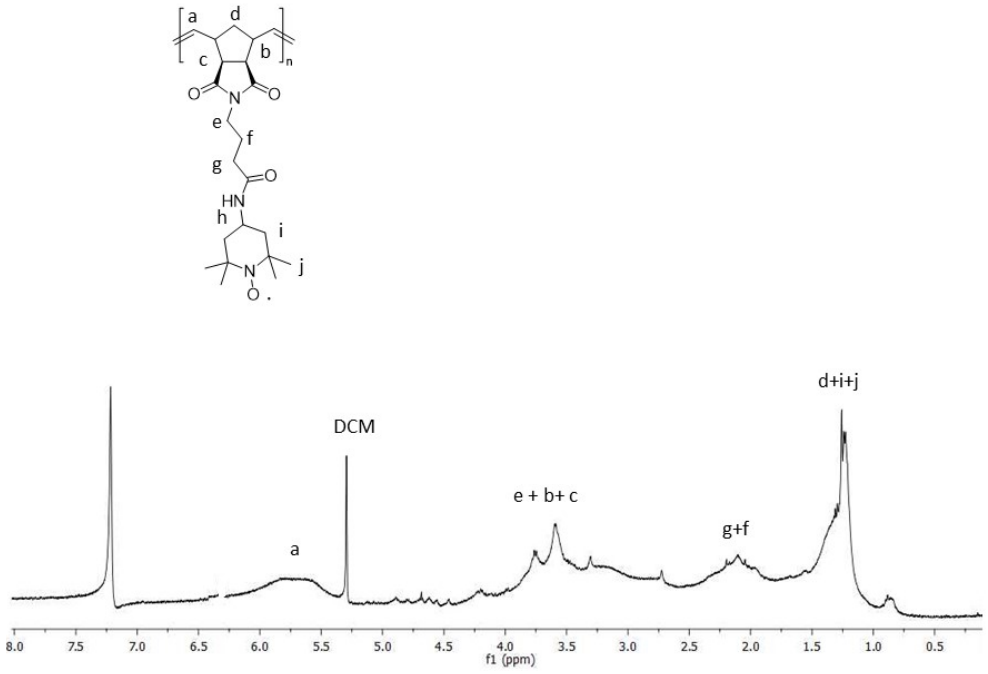

Figure S12. ^{1}H NMR spectrum of **PM2**$_N$ in $CDCl_3$

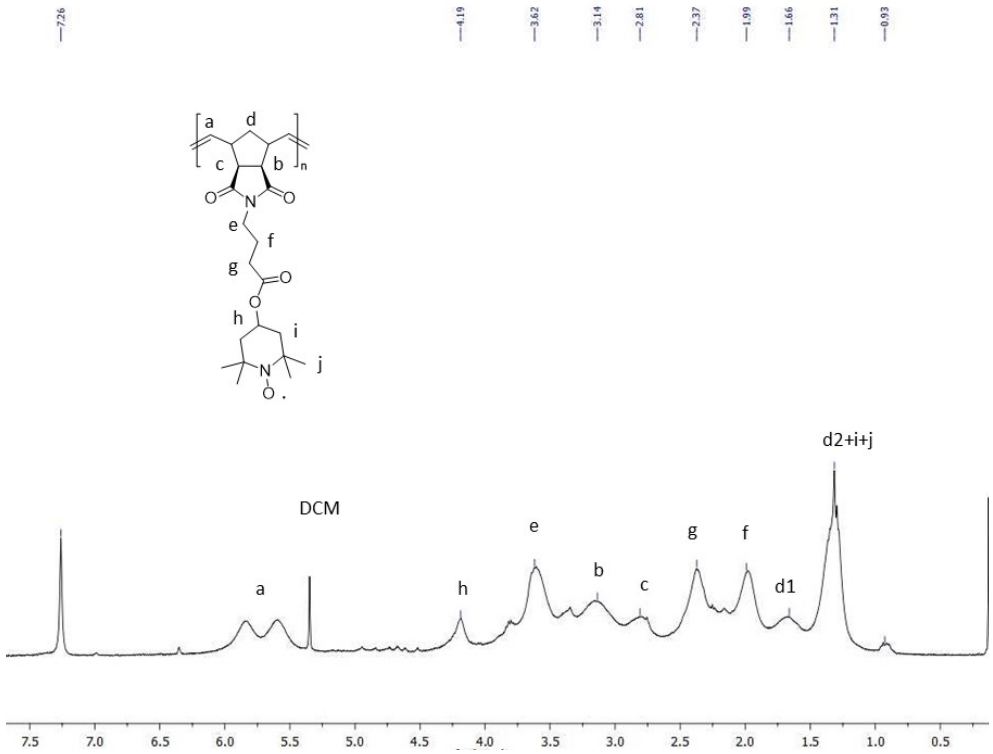

Figure S13. ^{1}H NMR spectrum of **PM2**$_O$ in $CDCl_3$

Table S1. Monitoring of conversions *vs*. time by ^{1}H NMR spectroscopy for ROMP of **M2**$_N$ in DCM at 25 °C using G3' as the initiator with an initial monomer concentration of 0.05 mol.L^{-1} and a monomer-to-initiator molar ratio [**M2**$_N$]$_0$/[**G3'**]$_0$ = 100.

Run	Time (min)	Conv. A[a] (%)	Conv. B[b] (%)	Conv. C[c] (%)
1	1	47	53	56
2	2	74	76	76
3	5	-[d]	97	96
4	7	-[d]	99	99

[a] by comparing the integrations of alkene protons of the norbornene at δ = 6.31 ppm and the alkene protons of polymers at δ = 5.35-6.15 ppm. [b] by comparing the integrations of alkene protons of the norbornene at δ = 6.29 ppm and the aromatic protons of dimethylterephtalate at δ = 8.10 ppm used as internal reference. [c] by comparing the integrations of alkene protons of the norbornene at δ = 6.29 ppm and the aromatic protons of dimethylterephtalate at δ = 8.10 ppm used as internal reference after nitroxide reduction by addition of phenylhydrazine. [d] not determined.

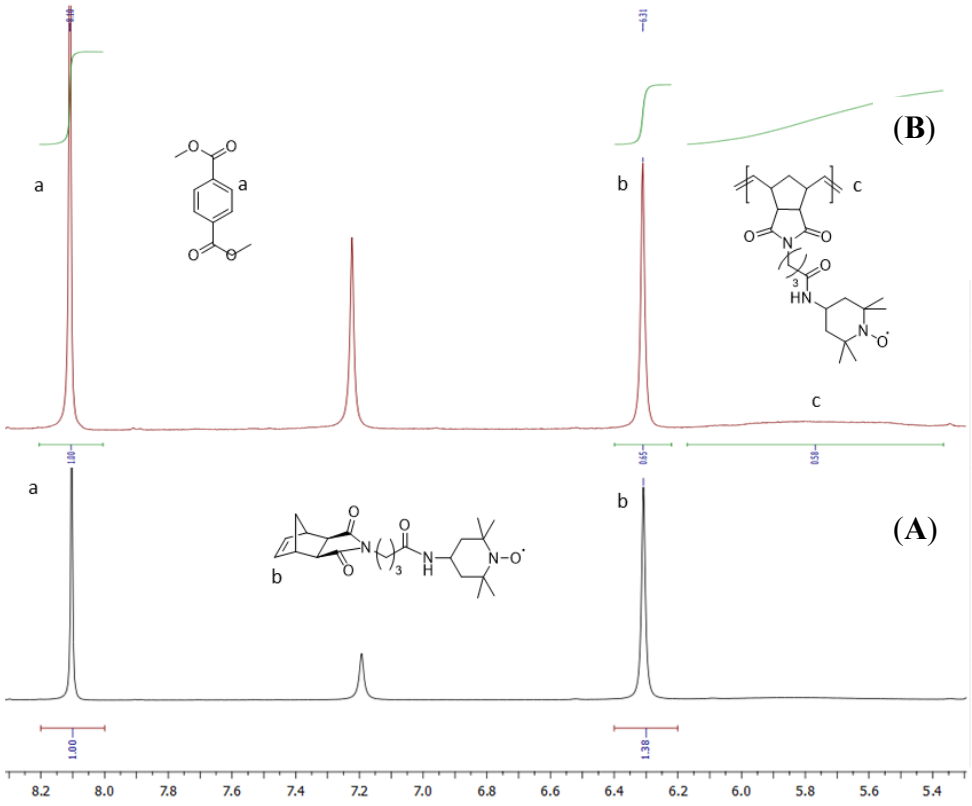

Figure S14. Overlay of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture of the ROMP of **M2**$_N$ in DCM at 25 °C using **G3'** as the initiator with an initial monomer concentration of 0.05 mol.L^{-1} and an initial concentration ratio [**M2**$_N$]$_0$/[**G3'**]$_0$ = 100 for a reaction time of (A) t = 0 min (Table S1, run 1, conv. A), and (B) t = 1 min; peak of the aromatic protons of dimethylphtalate at δ = 8.10 ppm was used as an internal reference (Table S1, run 1, conv. B).

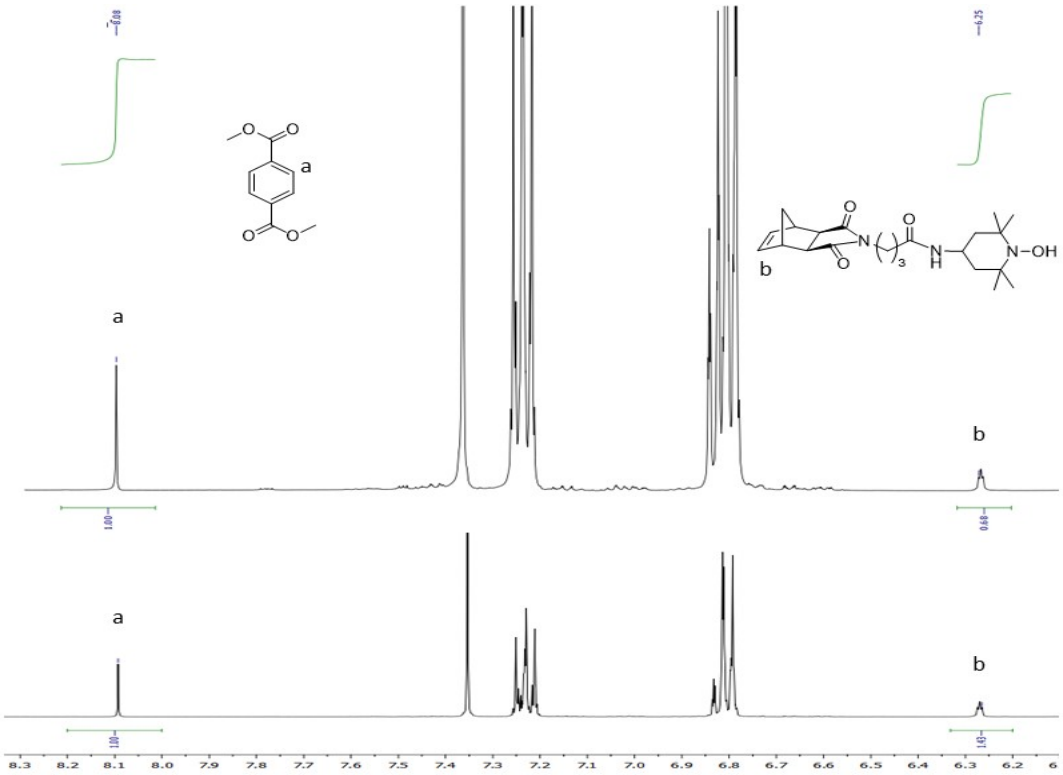

Figure S15. Overlay of ^{1}H NMR spectra in $CDCl_3$ of the reaction mixture of the ROMP of $\mathbf{M2_N}$ in DCM at 25 °C using **G3'** as the initiator with an initial monomer concentration of 0.05 mol.L^{-1} and an initial concentration ratio $[\mathbf{M2_N}]_0/[\mathbf{G3'}]_0 = 100$ after nitroxide reduction by addition of phenylhydrazine for a reaction time of (A) $t = 0$ min and (B) $t = 1$ min; peak of the aromatic protons of dimethylphtalate at $\delta = 8.10$ ppm was used as an internal reference (Table S1, run 1, conv. C).

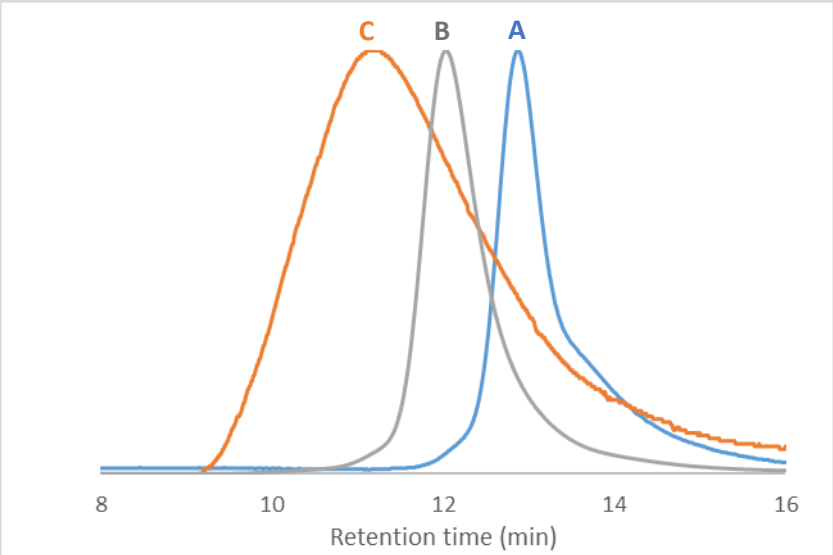

Figure S16. SEC traces of crude polymers **PM1**$_N$ obtained by ROMP of **M1**$_N$ in DCM at 25 °C using G3' as the initiator with an initial monomer concentration of 0.05 mol.L^{-1} and an initial concentration ratio [**M1**$_N$]$_0$/[**G3'**]$_0$(A) = 100 for a reaction time of 10 min (Table 1, run 1), (B) = 250 for a reaction time of 45 min (Table 1, run 2) and (C) = 500 for a reaction time of 300 min (Table 1, run 3).

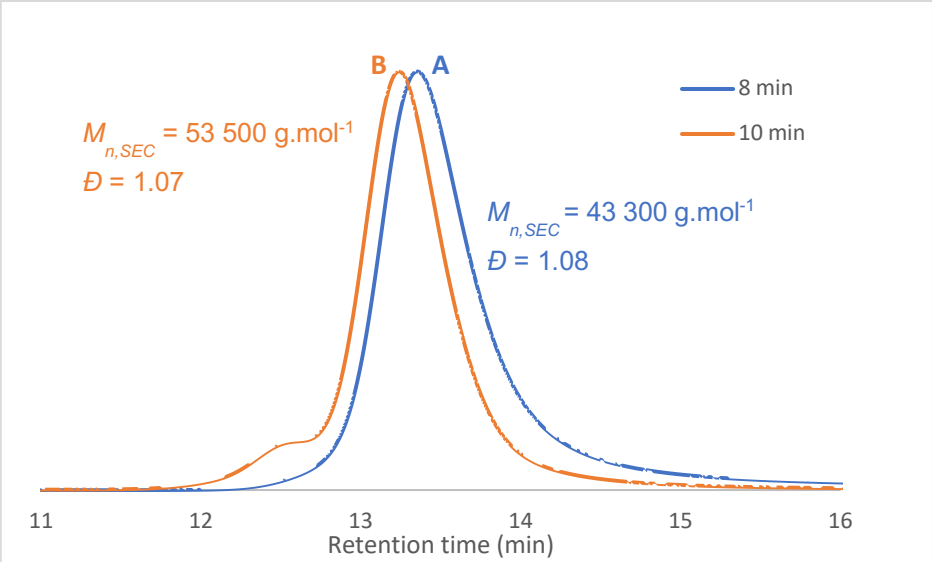

Figure S17. SEC traces of crude polymers **PM1**$_o$ obtained by ROMP of **M1**$_o$ in DCM at 25 °C using G3' as the initiator with an initial monomer concentration of 0.05 mol.L^{-1} and an initial concentration ratio [**M1**$_o$]$_0$/[**G3'**]$_0$= 100 for a reaction time of (A) 8 min (Table 1, run 4) and (B) 10 min.

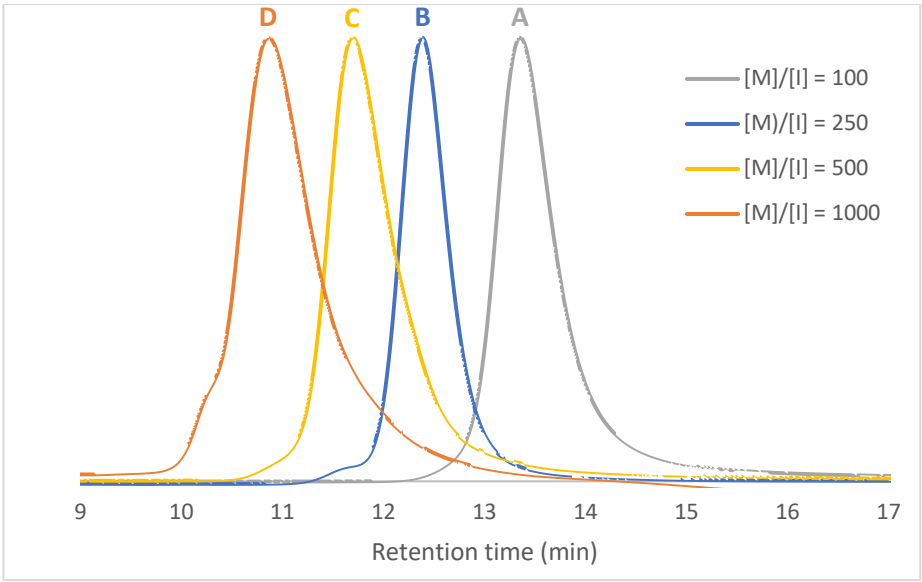

Figure S18. SEC traces of crude polymers **PM1**$_o$ obtained by ROMP of **M1**$_o$ in DCM at 25 °C using G3' as the initiator with an initial monomer concentration of 0.05 mol.L^{-1} and an initial concentration ratio [**M1**$_o$]$_0$/[**G3'**]$_0$(A) = 100 for a reaction time of 10 min (Table 1, run 4), (B) = 250 for a reaction time of 15 min (Table 1, run 5), (C) = 500 for a reaction time of 20 min (Table 1, run 6), and (D) = 1000 for a reaction time of 30 min (Table 1, run 7).

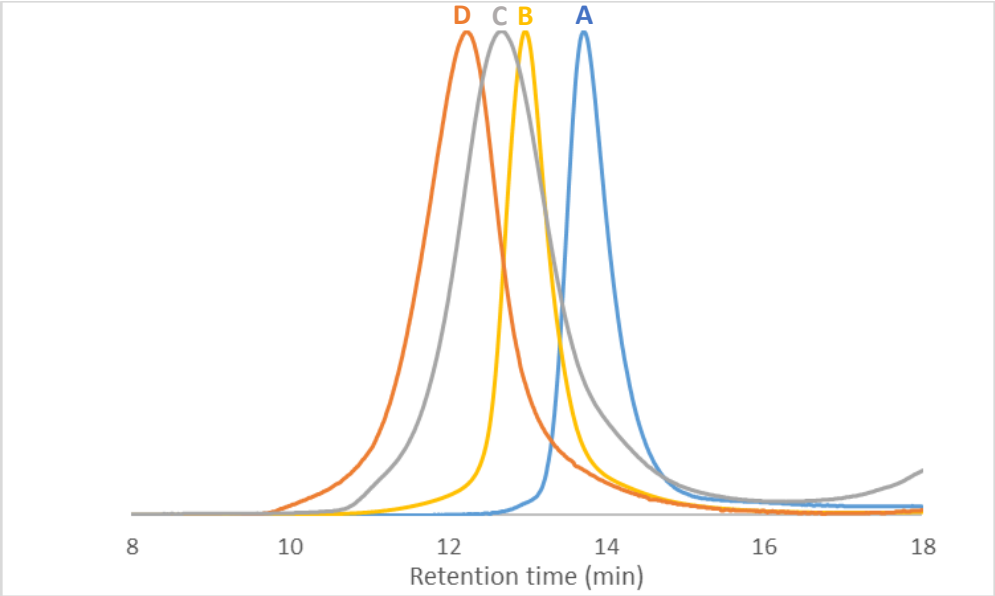

Figure S19. SEC traces of crude polymers **PM2**$_N$ obtained by ROMP of **M2**$_N$ in DCM at 25 °C using **G3'** as the initiator with [**M2**$_N$]$_0$/[**G3'**]$_0$(A) = 100 for a reaction time of 10 min (Table 1, run 8), (B) = 250 for a reaction time of 15 min (Table 1, run 9), (C) = 500 for a reaction time of 20 min (Table 1, run 10), and (D) = 1000 for a reaction time of 90 min (Table 1, run 11).

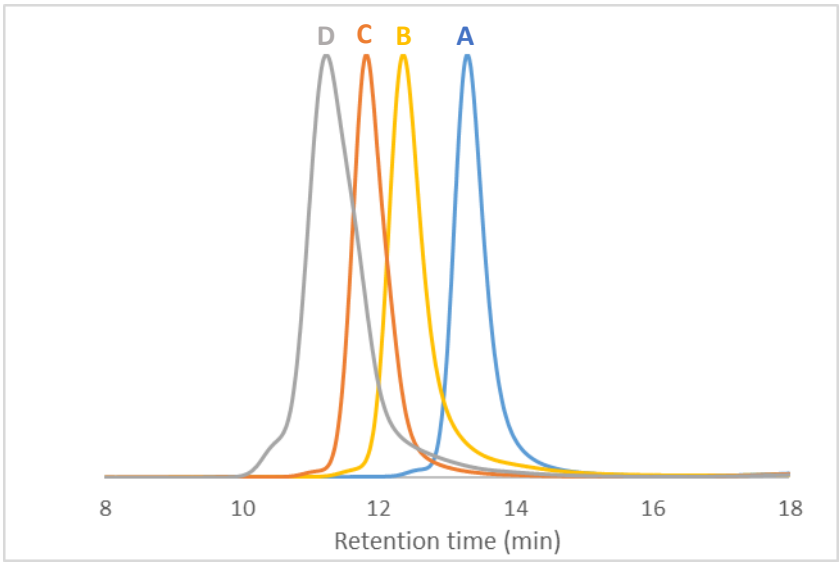

Figure S20. SEC traces of crude polymers **PM2**$_o$ obtained by ROMP of **M2**$_o$ in DCM at 25 °C using **G3'** as the initiator with [**M2**$_o$]$_0$/[**G3'**]$_0$(A) = 100 for a reaction time of 10 min (Table 1, run 12), (B) = 250 for a reaction time of 15 min (Table 1, run 13), (C) = 500 for a reaction time of 20 min (Table 1, run 14), and (D) = 1000 for a reaction time of 30 min (Table 1, run 15).

Synthesis of *exo*-5-norbornene-2,3-dicarboximido-*N*-(1,2,2,6,6-pentamethylpiperidine) (M4). *cis*-5-Norbornene-*exo*-2,3-dicarboxylic anhydride (0.7998 g; 4.9 mmoles) and 4-amino-1,2,2,6,6-pentamethylpiperidine (0.7654 g; 4.9 mmoles) were dissolved in dry toluene (15 mL) in a 25 mL round bottom flask equipped with a magnetic stirrer, a reflux condenser and a rubber septum. TEA (0.1 mL; 0.72 mmoles) was added dropwise at room temperature under argon. The resulting mixture was kept stirring for 3 days at reflux. The solvent was removed under reduced pressure. The crude product was diluted in DCM (20 mL) and then washed with a 0.1N HCl solution, deionized water and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered and the solvent was removed under reduced pressure to obtain **M4** (1.3523 g; 87.2%) as a white powder. ^{1}H NMR (400.16 MHz, $CDCl_3$), δ (ppm): 6.29 (t, *J* = 1.8 Hz, 2H, C*H*=C*H*), 4.38 (s, 1H, N-C*H*), 3.26 (s, 2H, =CH-C*H*), 2.60 (s, 2H, =CH-CH-C*H*), 2.40 (t, *J* = 12.5 Hz, 1H, N-C-C*H*H), 2.24 (s, 1H, N-CH_3), 1.48 (dd, ^3J = 9.8 Hz, ^4J = 1.5 Hz,1H, CHC*H*HCH), 1.38 (dd, ^3J = 12.4 Hz, ^2J = 3.6 Hz, 1H, N-C-CH*H*), 1.25 (dd, ^3J = 9.8 Hz, ^4J = 1.2 Hz, 1H, CHCH*H*CH), 1.16 (s, 6H, C(CH_3)CH_3), 1.07 (s, 6H, C(CH_3)CH_3) (Figure S21). FT-IR (ν cm^{-1}): 2966 (ν C-H alkane), 1692 (ν C=O imide), 731 (γ C-H alkane), 638 (γ C-H alkene). HRMS (CI-Na^+). Calcd for $C_{19}H_{28}N_2O_2$ + Na^+: 339.2043; found: 339.2042.

Poly[5-norbornene-2,3-dicarboximido-*N*-(1,2,2,6,6-pentamethylpiperidine)] (PM4). Light brown powder. [**M4**]$_0$/[**G3'**]$_0$ = 100; conversion: 100%; $\overline{M_{n,SEC}}$ = 16 900 g.mol^{-1}; *Đ* = 1.21. ^{1}H NMR (400.16 MHz, $CDCl_3$), δ (ppm): 5.80-5.40 (bs, 2H, C*H*=C*H*), 4.35 (bs, 1H, N-C*H*), 3.50-2.57 (bs, 4H, =CH-C*H*), =CH-CH-C*H*), 2.50-1.87 (bs, 4H, N-CH-C*H*H, N-CH_3), 1.83-0.75 (bs, 9H, CH-CH_2-CH, N-CH-CH*H,* C(CH_3)$_2$).

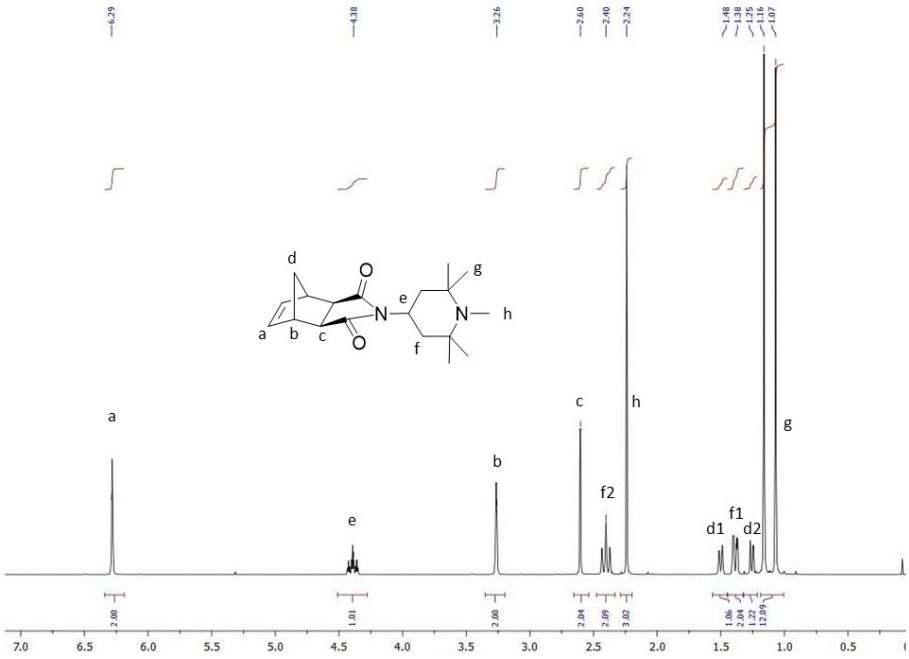

Figure S21. ^{1}H NMR spectrum of **M4** in $CDCl_3$

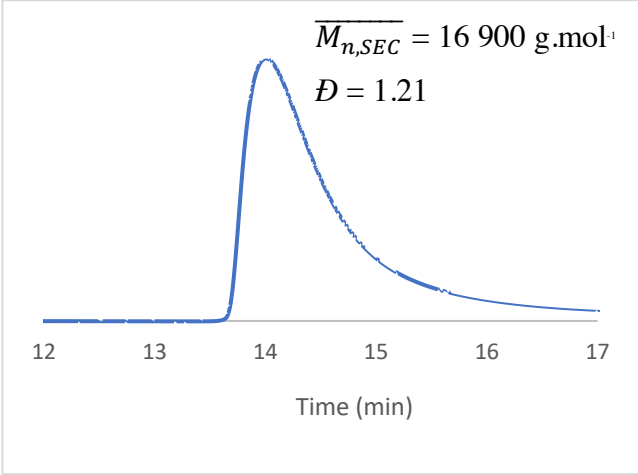

Figure S22. SEC trace of crude **PM4** obtained by ROMP of **M4** in DCM at 25 °C using **G3'** as the initiator with an initial monomer concentration of 0.05 mol.L^{-1} and an initial concentration ratio [**M4**]$_0$/[**G3'**]$_0$ = 100 for a reaction time of 15 min.

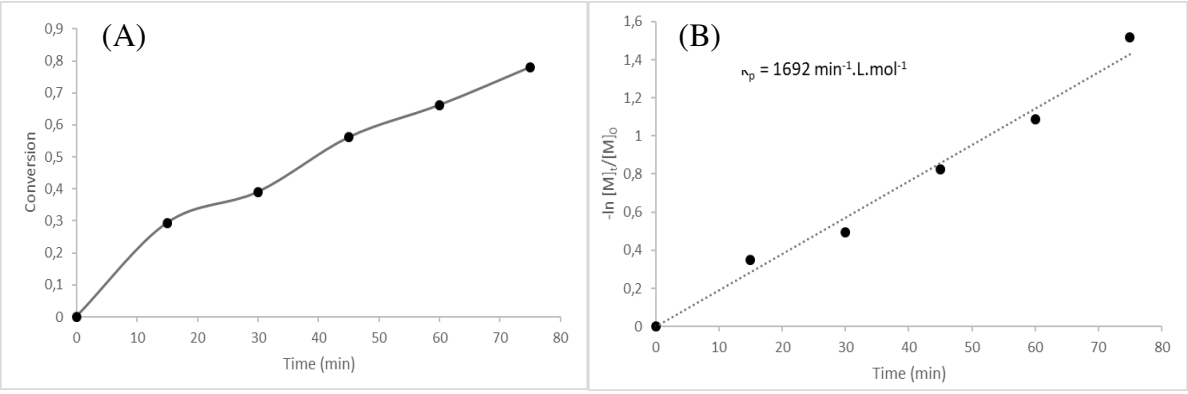

Figure S23. (A) Conversion of **M3** versus reaction time. (B) Kinetic plot - $\ln([M]_t/[M]_0)$ versus reaction time for ROMP of **M3** using **G3'** as the initiator with an initial monomer concentration of 0.05 mol.L^{-1} and a $[M]_0/[I]_0$ ratio of 100 at 25 °C in DCM.

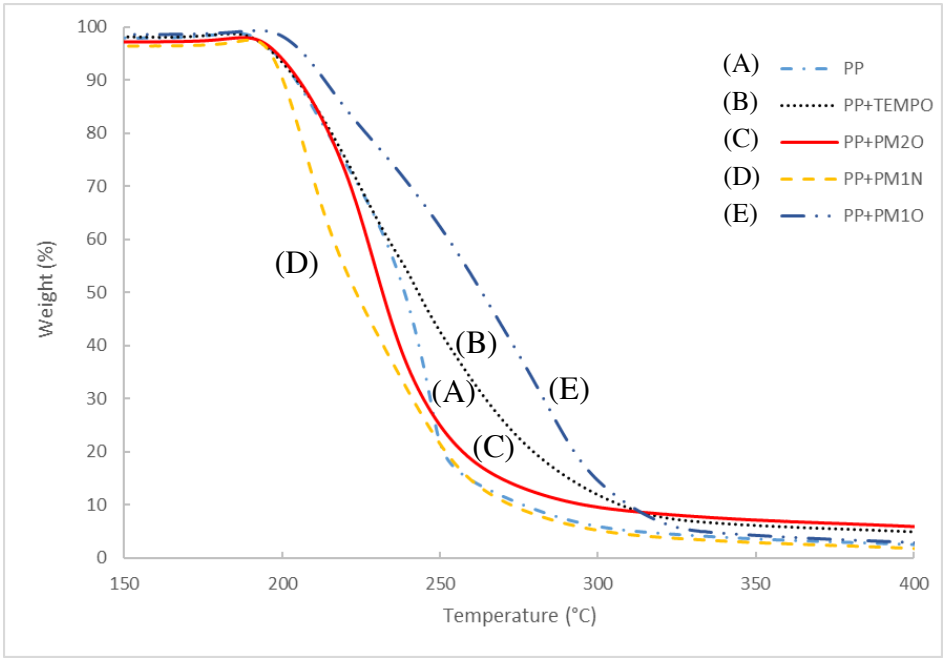

Figure S24. Thermo-Gravimetric Analyses (TGA) curves of (A) virgin PP (dotted dashed line), (B) PP/TEMPO (dotted line), (C) PP/ **PM2**$_o$ (full line), (D) PP/ **PM1**$_N$ (dashed line), and PP/ **PM1**$_o$ (double-dotted dashed line).