Synthesis of Highly Reactive Polymer Nitrile *N*-Oxides for Effective Solvent-free Grafting

Supporting Information

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Contents

1. Experimental Section

Equipments

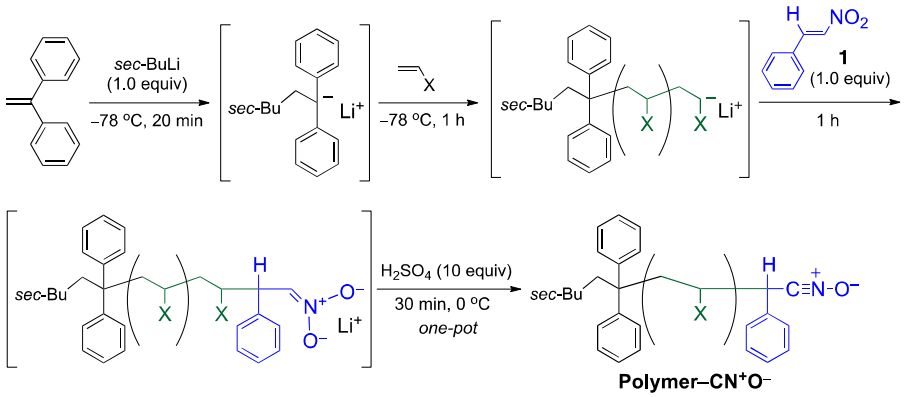
^{1}H NMR (400 MHz) and ^{13}C NMR spectra (100 MHz) were recorded on a JEOL AL-400 spectrometer using $CDCl_3$, DMSO-d_6, and acetone-d_6 as the solvents, calibrated using residual undeuterated solvents or tetramethylsilane as the internal standard. IR spectra were recorded on a JASCO FT/IR-230 spectrometer. SEC analyses using chloroform as the eluent were carried out on JASCO PU-2080 plus pump with a JASCO UV-1570 (UV detector), a JASCO RI-1530 (RI detector), and a multiangle light scattering (MALS) detector (MiniDawn TREOS, Wyatt Technology Inc.) equipped with a consecutive linear polystyrene gel columns TOSO TSK gel GMHXL and G5000HXL operating at 30 °C. TGA analyses were carried out on a Shimadzu TGA-50 instrument under N_2 atmosphere (flow rate of 50 mL/min) to determine 5% and 10% weight decomposition temperatures (T_{d5} and T_{d10}) at which 5% and 10% weight loss were observed. DSC analyses were carried out with a Shimadzu DSC-60 instrument at N_2 atmosphere (flow rate of 50 mL/min) with liquid N_2 as a refrigerant to determine a glass transition temperature (T_g). Preparative GPC were carried out using a HPLC LC-918 instrument by Japan Analysis Kogyo with a Megapak-Gel 201CP (Guard Column), a Megapak-Gel 201C, and a JAIGEL-H. MALDI-TOF MS spectra were recorded on a Shimadzu AXIMA-CFR mass spectrometer. The spectrometer was equipped with a nitrogen laser (λ = 337 nm) and with pulsed ion extraction. The operation was performed at an accelerating potential of 20 kV by a linear-positive ion mode. The sample polymer solution (1 mg/mL) was prepared in THF. The matrix (dithranol) and cationizing agent (sodium trifluoroacetate) was dissolved in THF (10 and 1 mg/mL, respectively). The polymer solution (50 μL) was then mixed with 50 μL of the matrix solution. A 1 μL portion of the final solution was deposited onto a sample target plate and allowed to dry in the air at room temperature. Mass values were calibrated by the two-point method with insulin β plus H^+ at 3497.96 and R-cyanohydroxy cinnamic acid dimer plus H^+ at 379.35. The contact angle was measured with a DM-301 contact angle meter (Kyowa Interface Science Co., Ltd.). pH value was measured with a pocket-sized waterproof pH meter KS723 (Shindengen Electric Manufacturing Co. Ltd) using pH 4.0 and 6.9 buffer solution for calibration.

Materials

Tetrahydrofuran (THF) was freshly distilled in the presence of sodium and benzophenone under argon atmosphere prior to use. *trans*-β-Nitrostyrene was purchased from Sigma-Aldrich Chemical Co. Ltd. and purified by recrystallization from isopropanol before use. Monomers were purchased from Wako Pure Chemical Industries Co. Ltd. and purified by a general distillation technique under reduced pressure to remove the polymerization inhibitor. The synthesis of poly(styrene-*co*-4-allyloxystyrene) (**PS-*co*-P4AS**) was referred to our previous work.[1] For the NMR analysis, deuterated solvents from Acros Organics were used. Other commercially available reagents and solvents were used without further purification unless otherwise noted. The basic buffer solution was prepared from sat. $NaHCO_3$ (50 mL) and adjusted to pH 10.0 by using 2 M $NaOH_{(aq.)}$ and 2 M $HCl_{(aq.)}$.

2. Chemical Synthesis

Synthesis of polymer nitrile *N*-oxides from *trans*-β-nitrostyrene



Scheme S1. Synthesis of polymer nitrile *N*-oxides from *trans*-*β*-nitrostyrene.

Synthesis of poly(methyl methacrylate) nitrile *N*-oxide (**PMMA–CN$^+$O$^–$**, **P1**)

1,1-Diphenylethylene (721 mg, 4.0 mmol) was dissolved in THF (60 mL) under argon atmosphere and the mixture was cooled to –78 °C. *s*-BuLi (1.07 M in cyclohexane, 3.74 mL, 4.0 mmol) was added into the mixture and the solution was stirred for 20 min. To the reaction mixture was added a solution of methyl methacrylate (4.00 g, 40 mmol) in THF (10 mL) and the mixture was stirred for 1 h. A solution of *trans*-*β*-nitrostyrene **1** (597 mg, 4.0 mmol) in THF (5.0 mL) was then added into the reaction mixture and the reaction mixture was warmed to –60 °C. After stirring for 1 h, concd H_2SO_4 (>95%, 3.92 g, 40 mmol) was added to the reaction mixture. After warming to 0 °C and stirring for 30 min, the reaction mixture was diluted with dichloromethane (100 mL), washed with water, dried over magnesium sulfate, filtered, and evaporated. The crude **PMMA–CN$^+$O$^–$** was dissolved in $CHCl_3$ (20 mL) and precipitated in hexane (500 mL), hexane/ethanol (500 mL, v/v = 10/1) and hexane (500 mL), repeatedly. The precipitates were collected by filtration and dried *in vacuo* to give **PMMA–CN$^+$O$^–$ P1** as a white powder.

PMMA–CN$^+$O$^–$ **P2**: To synthesize **P2**, 3.0 equiv of methyl methacrylate was used for the reaction. The reaction was performed according to the same manner as the synthesis of **P1**. Yield: 85% (2.09 g), M_n 780 (estimated by ^{1}H NMR spectrum); T_g 80 °C; T_{d5} 272 °C; T_{d10} 296 °C; ^{1}H NMR (400 MHz, 298 K, DMSO-d_6) δ 7.37–7.04 (m, –Ph-H), 3.55 (s, –COOCH_3), 1.89–1.74 (m, –CH_2C), 0.92–0.52 (m, –C–CH_3, *sec*-butyl proton) ppm; IR (KBr) υ 2297 (–C≡N$^+$–O$^–$), (C=O), 1601 (Ar, C=C), 1241 (C–O), 1149 (C–O) cm^{-1}.

PMMA–CN$^+$O$^–$ **P1**: Yield: 94% (5.16 g), M_n 1600; M_w/M_n 1.24 (estimated by SEC–MALS using $CHCl_3$ as the eluent); 96 °C; T_{d5} 294 °C; T_{d10} 308 °C.; ^{1}H NMR (400 MHz, 298 K, DMSO-d_6) δ 7.38–7.08 (M, –Ph-H), 3.55 (s, –COOCH_3), 1.89–1.75 (m, –CH_2C), 0.94–0.53 (m, –C–CH_3, *sec*-butyl proton) ppm; IR (KBr) υ 2296 (–C≡N$^+$–O$^–$), 1732 (C=O), 1599 (Ar, C=C), 1241 (C–O), 1149 (C–O) cm^{-1}.

PMMA–CN$^+$O$^–$ **S3**: To synthesize **S3**, 1.0 mmol of 1,1-diphenylethylene (180 mg), 1.0 mmol of *s*-BuLi (1.04 M in cyclohexane, 0.96 mL), 200 mmol MMA (20.24 g), and 1.0 mmol of *trans*-*β*-nitrostyrene (149 mg) were used for the reaction. The reaction was performed according to the same manner as the synthesis of **P1**. Yield: 93% (19.2 g), M_n 48000; M_w/M_n 1.28 (estimated by SEC–MALS using $CHCl_3$ as the eluent); T_g 110 °C; T_{d5} 347 °C; T_{d10} 357 °C.; ^{1}H (400 MHz, 298 K, $CHCl_3$) δ 7.27–7.23 (m, –Ph-H), 3.60 (s, –COOCH_3), 2.04–1.82 (m, –CH_2C), 1.27–0.86 (m, –C–CH_3, *sec*-butyl proton) ppm; IR (KBr) υ 2292 (–C≡N$^+$–O$^–$), 1731 (C=O), 1601 (Ar, C=C), 1242 (C–O), 1148 (C–O) cm^{-1}.

PMMA–CN$^+$O$^–$ **P3**: To synthesize **P3**, 1,1-diphenylnitroethene was used instead of *trans*-*β*-nitrostyrene. Refer to our previous work for detail.[1]

Thermal gravimetric analysis (TGA) profiles of **P1** (from *trans*-*β*-nitrostyrene) and PMMA–CN$^+$O$^–$ **P3** (from 1,1-diphenylnitroethene) were shown in Figure S1. It was noted that the decomposition of **P1** occurs at approximately 160 °C, which was lower than the starting decomposition temperature of **P3**. This result indicates the thermal instability

of **P1** at 160 °C.

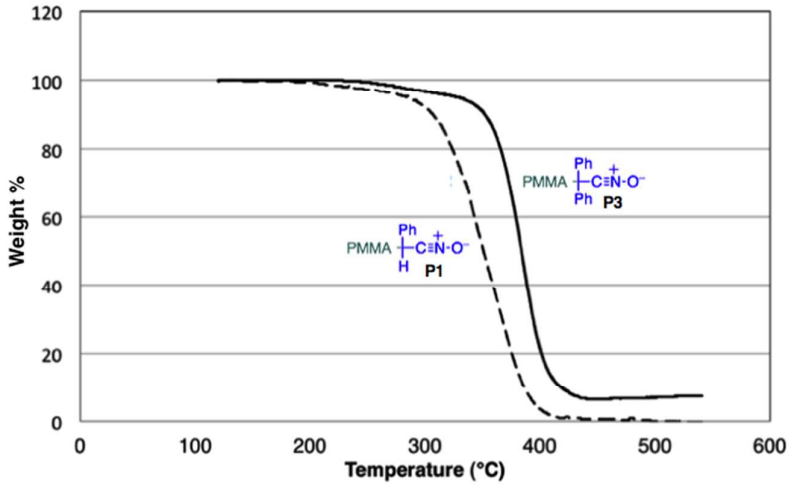


Figure S1. TGA curves of **P1** (broken line) and **P3** (thick line) (heating rate of 10 °C/min under N_2 (flow rate, 50 mL/min)).

Synthesis of poly(*tert*-butyl methacrylate) nitrile *N*-oxide (**P*t*BMA–CN$^+$O$^-$**, **P4**)

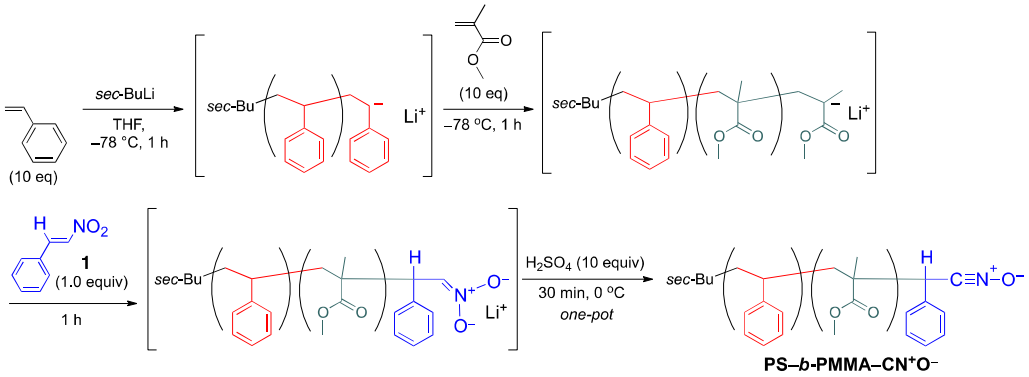
1,1-Diphenylethylene (540 mg, 3.0 mmol) was dissolved in dried THF (50 mL) under argon atmosphere and the mixture was cooled to –78 °C. *s*-BuLi (1.07 M in cyclohexane, 2.80 mL, 3.0 mmol) was added into the mixture and the mixture was stirred for 20 min. To the reaction mixture was added a solution of *tert*-butyl methacrylate (4.27 g, 30 in THF (10 mL) and the mixture was stirred for 1 h. A solution of *trans*-*β*-nitrostyrene **1** (448 mg, 3.0 mmol) in THF (5 mL) was then added into the reaction mixture and the mixture was warmed to –60 °C. After stirring for 1 h, concd (>95%, 2.94 g, 30 mmol) was added to the reaction mixture. The reaction mixture was warmed to 0 °C, stirred for 30 diluted with dichloromethane (80 mL), washed with water, dried over magnesium sulfate, filtered, and evaporated. The crude **P*t*BMA–CN$^+$O$^-$** was dissolved in $CHCl_3$ (20 mL) and precipitated in methanol/water (500 mL, v/v = 4/1) three times. The precipitates were collected by filtration and dried *in vacuo* to give **P*t*BMA–CN$^+$O$^-$ P4** in 97% yield (5.24 g) a white powder; M_n 3200; M_w/M_n 1.26 (estimated by SEC–MALS using $CHCl_3$ as the eluent); T_g 106 °C; T_d of ester decomposition 234 °C; T_{d5} 374 °C (PMAA); T_{d10} 391 °C (PMAA); ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.33–7.18 (m, Ph–H), 2.28–1.82 (m, –C$\underline{H_2}$C–), 1.41 (s, –C(C$\underline{H_3}$)$_3$), 1.12–0.47 (m, –C–C$\underline{H_3}$, *sec*-butyl proton) ppm; IR (KBr) υ 2290 (–C≡N$^+$–O$^-$), 1724 (C=O), 1598 (Ar, C=C), 1251 (C–O), 1137 (C–O) cm^{-1}.

Synthesis of poly(methyl methacrylate)-*b*-poly(*tert*-butyl methacrylate) nitrile *N*-oxide (**PMMA-*b*-P*t*MBA–CN$^+$O$^-$**)

1,1-Diphenylethylene (540 mg, 3.0 mmol) was dissolved in dried THF (80 mL) under argon atmosphere and the mixture was cooled to –78 °C. *s*-BuLi (1.07 M in cyclohexane, 2.80 mL, 3.0 mmol) was added into the mixture and the mixture was stirred for 20 min. To the reaction mixture was added a solution of methyl methacrylate (3.00 g, 30 mmol) THF (10 mL) and the mixture was stirred for 1 h. Then, a solution of *tert*-butyl methacrylate (4.27 g, 30 mmol) in THF mL) was added into the reaction and the reaction mixture was further stirred for 1 h. A solution of *trans*-*β*-nitrostyrene **1** (448 mg, 3.0 mmol) in THF (5 mL) was added into the reaction mixture and the mixture was warmed to –60 °C. After stirring for 1 h, concd H_2SO_4 (>95%, 2.94 g, 30 mmol) was added to the mixture. After warming to 0 °C and stirring for min, the reaction mixture was diluted with dichloromethane (100 mL), washed with water, dried over magnesium filtered, and evaporated. The crude **PMMA-*b*-P*t*MBA–CN$^+$O$^-$** was dissolved in $CHCl_3$ (30 mL) and precipitated in methanol/water (600 mL, v/v = 10/1), hexane/ethanol (600 mL, v/v = 10/1), and hexane (600 mL). The precipitates

collected by filtration and dried *in vacuo* to give **PMMA-*b*-P*t*MBA–CN$^+$O$^-$** in 80% yield (6.69 g) as a white powder; 5600; M_w/M_n 1.81 (estimated by SEC–MALS using $CHCl_3$ as the eluent); T_g 83 °C; T_d of ester decomposition 231 °C; 353 °C; T_{d10} 369 °C; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.30–7.14 (m, Ph–H), 3.60 (s, –COOC$\underline{H}_3$), 2.03–1.81 (m, –C$\underline{H}_2$C–), 1.41 (s, –C(C$\underline{H}_3$)$_3$), 1.21–0.57 (m, –C–C$\underline{H}_3$, *sec*-butyl proton) ppm; IR (KBr) υ 2292 (–C≡N$^+$–O$^-$), 1598 (Ar, C=C), 1251 (C–O), 1141 (C–O) cm^{-1}.

Synthesis of polystyrene-*b*-poly(methyl methacrylate) nitrile *N*-oxide (**PS-*b*-PMMA–CN$^+$O$^-$**)



Scheme S2. Synthesis of polystyrene-*b*-poly(methyl methacrylate) nitrile *N*-oxide.

A four-necked flask was placed dried THF (40 mL) under argon atmosphere and cooled to –78 °C, and then *s*-BuLi (1.07 M in cyclohexane, 1.87 mL, 2.0 mmol) was added into the THF solvent with stirring. A solution of styrene (1.04 g, 10 mmol) in THF (5 mL) was added into the reaction mixture to polymerize monomer at –78 °C. To the reaction was added a solution of methyl methacrylate (1.00 g, 10 mmol) in THF (5 mL) and the mixture was stirred for 1 h. A solution of *trans*-*β*-nitrostyrene **1** (299 mg, 2.0 mmol) in THF (5 mL) was added into the reaction mixture and the was warmed to –60 °C. After stirring for 1 h, concd H_2SO_4 (>95%, 1.96 g, 20 mmol) was added to the mixture. The mixture was warmed to 0 °C, stirred for 30 min, diluted with dichloromethane (50 mL), washed with water, dried over magnesium sulfate, filtered, and evaporated. The crude **PS-*b*-PMMA–CN$^+$O$^-$** was dissolved in $CHCl_3$ (20 mL) and precipitated in methanol/water (500 mL, v/v = 10/1) three times. The precipitates were collected by filtration and dried *vacuo* to give **PS-*b*-PMMA–CN$^+$O$^-$** in 88% yield (2.13 g) as a white powder; M_n 2400; M_w/M_n 1.45 (estimated by MALS using $CHCl_3$ as the eluent); T_g 102 °C; T_{d5} 297 °C; T_{d10} 317 °C; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.10–6.40 Ph–H), 3.60 (s, –COOC$\underline{H}_3$), 2.20 (m, –C$\underline{H}_2$CCH$_3$, –C$\underline{H}$C$_6$H$_6$), 1.42 (br, –C$\underline{H}_2$CHC$_6$H$_6$), 1.02–0.57 (m, –C–C$\underline{H}_3$, proton) ppm; IR (KBr) υ 2297 (–C≡N$^+$–O$^-$), 1732 (C=O), 1602 (Ar, C=C), 1242 (C–O), 1149 (C–O) cm^{-1}.

The stability of the polymer–CN$^+$O$^-$s was evaluated by using IR spectroscopy. The characteristic absorption bands of nitrile *N*-oxide groups in the IR spectra of **PMMA–CN$^+$O$^-$**, **P*t*BMA–CN$^+$O$^-$**, **PMMA-*b*-P*t*MBA–CN$^+$O$^-$**, and **PS-*b*-PMMA–CN$^+$O$^-$** placing at 4 °C showed little decrease for 2 months (**Figures S2**, **S3**, and **S6–S8**). In the case of **PMMA–CN$^+$O$^-$ P1**, pseudo-second-order kinetic model was applied to fit the experimental data. The half-life time of **P1** was calculated over 300 d (*ca.* 333 d), which was determined from the slope values of the time-course plots by statistical regression analysis (**Figures S4** and **S5**).

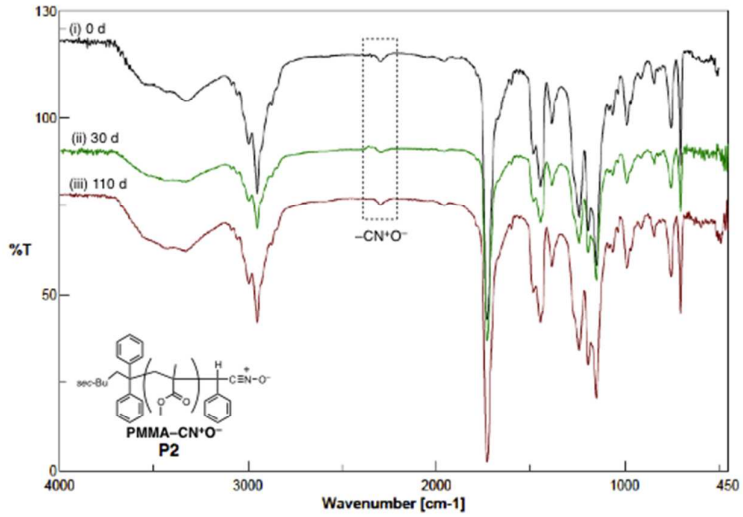


Figure S2. Time-dependent IR spectra of **PMMA–CN$^+$O$^-$ P2** (KBr).

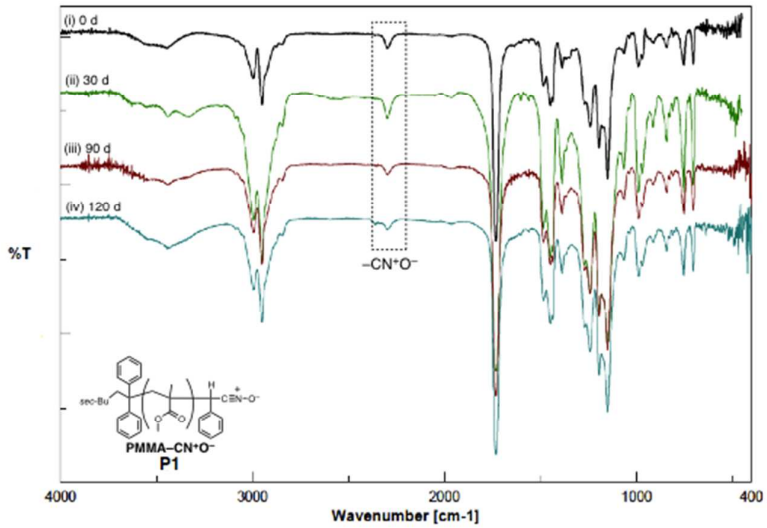


Figure S3. Time-dependent IR spectra of **PMMA–CN$^+$O$^-$ P1** (KBr).

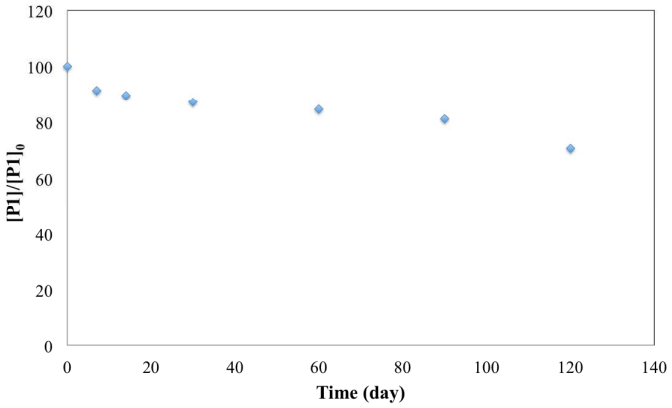


Figure S4. Time-course plots of decomposed **PMMA–CN$^+$O$^-$ P1** placing at 4 °C.

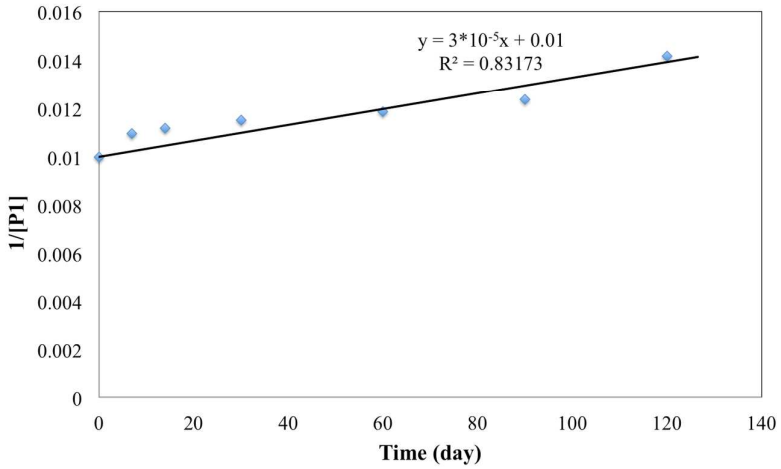


Figure S5. Second-order kinetic plots of 1/[**P1**] for the decomposition of **P1** placing at 4 °C.

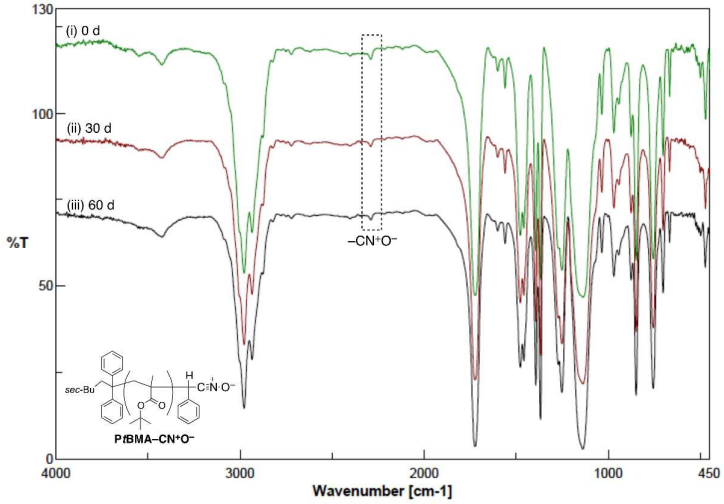


Figure S6. Time-dependent IR spectra of **P*t*BMA–CN$^+$O$^-$** (KBr).

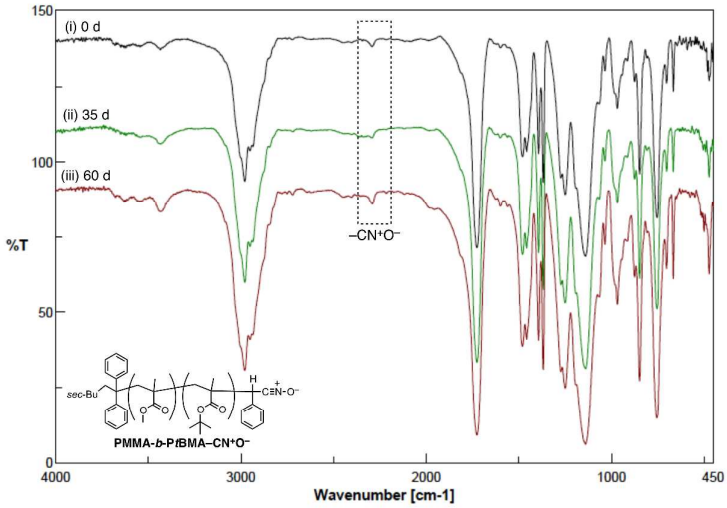


Figure S7. Time-dependent IR spectra of **PMMA-*b*-P*t*MBA–CN$^+$O$^-$** (KBr).

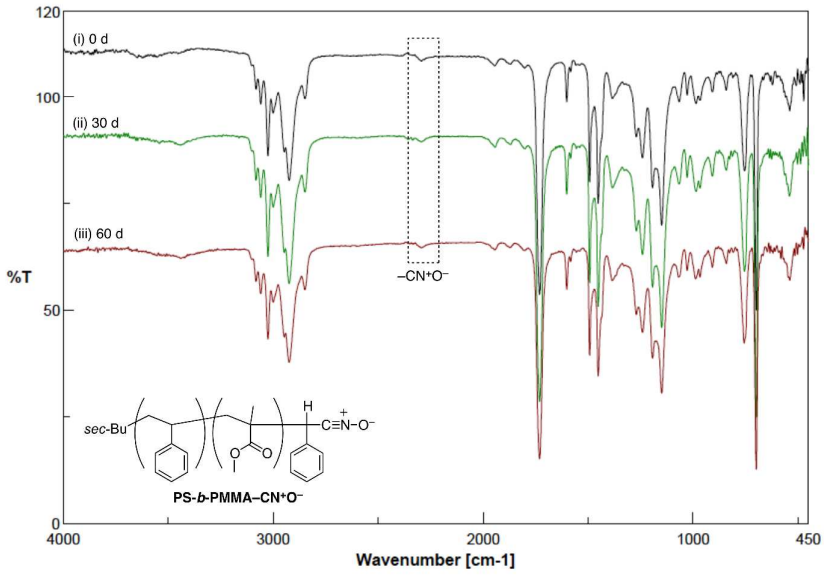
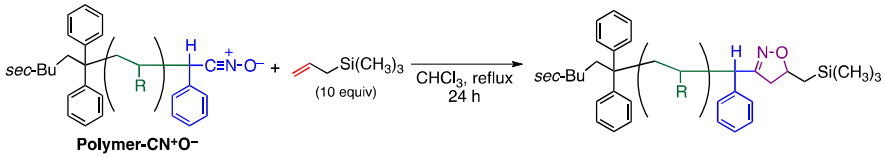


Figure S8. Time-dependent IR spectra of **PS-*b*-PMMA–CN$^+$O$^-$** (KBr).

Determination of the termination ratio of nitrile *N*-oxide group of polymer–CN$^+$O$^-$s



Scheme S3

To confirm the generation of nitrile *N*-oxide functions and determinate the termination ratios of the nitrile *N*-oxide groups, the polymer–CN$^+$O$^-$s were reacted with an excess of allyltrimethylsilane in $CHCl_3$ to obtain the isoxazolines possessing a TMS group. In comparison with the integral ratio between phenyl protons and TMS protons in the ^{1}H NMR spectra, it found that excellent contents of nitrile *N*-oxides were achieved in all of the polymer–CN$^+$O$^-$s, as shown in **Figures S9–S14**.

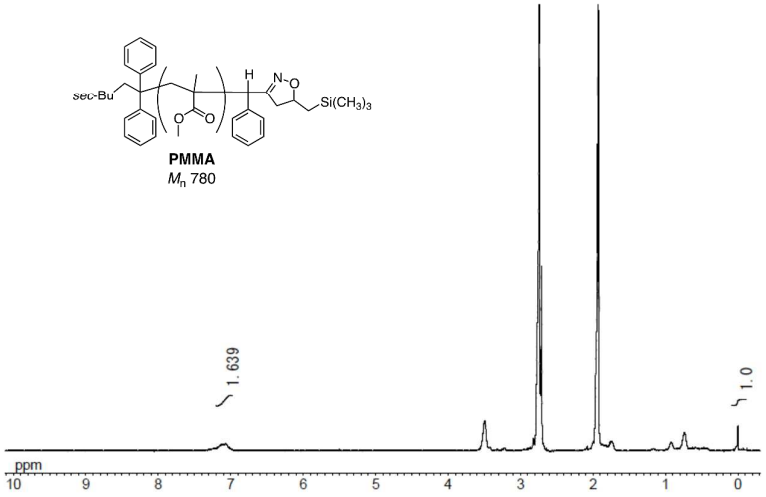


Figure S9. ^{1}H NMR spectrum of the isoxazoline from **P2** (400 MHz, 298 K, Acetone-d_6).

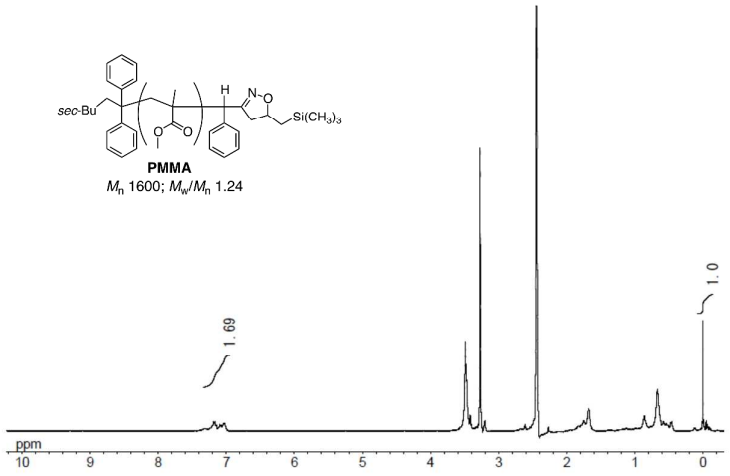


Figure S10. [1]H NMR spectrum of the isoxazoline from **P1** (400 MHz, 323 K, DMSO-d_6).

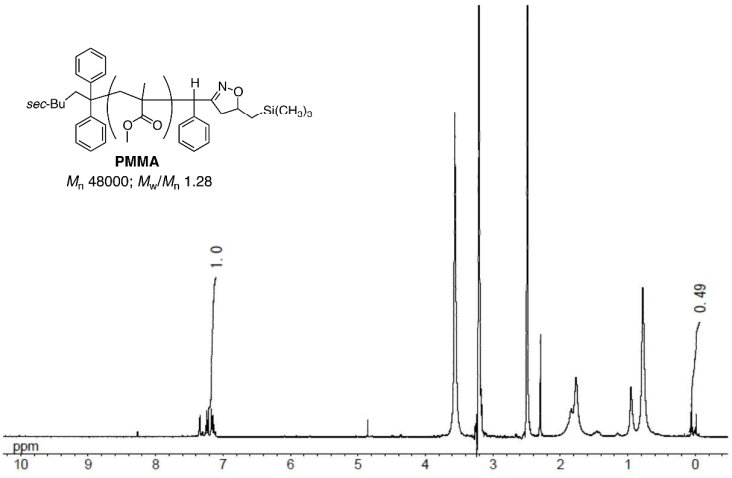


Figure S11. [1]H NMR spectrum of the isoxazoline from **S3** (400 MHz, 323 K, DMSO-d_6).

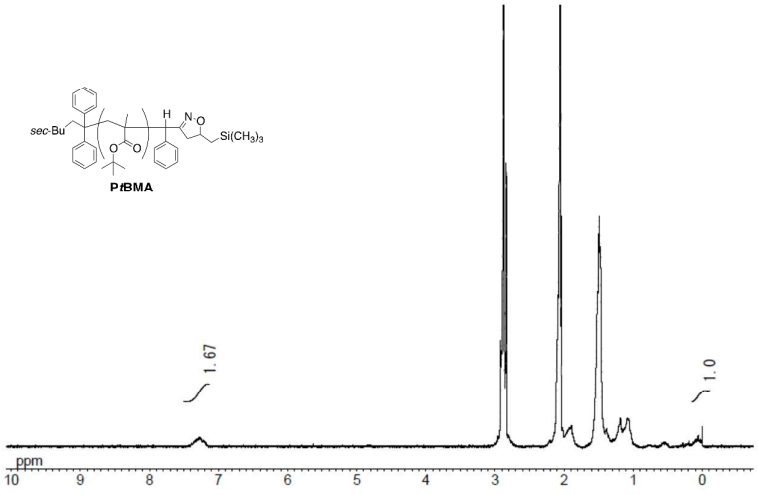


Figure S12. [1]H NMR spectrum of the isoxazoline from **P*t*BMA–CN$^+$O$^-$** (400 MHz, 298 K, Acetone-d_6).

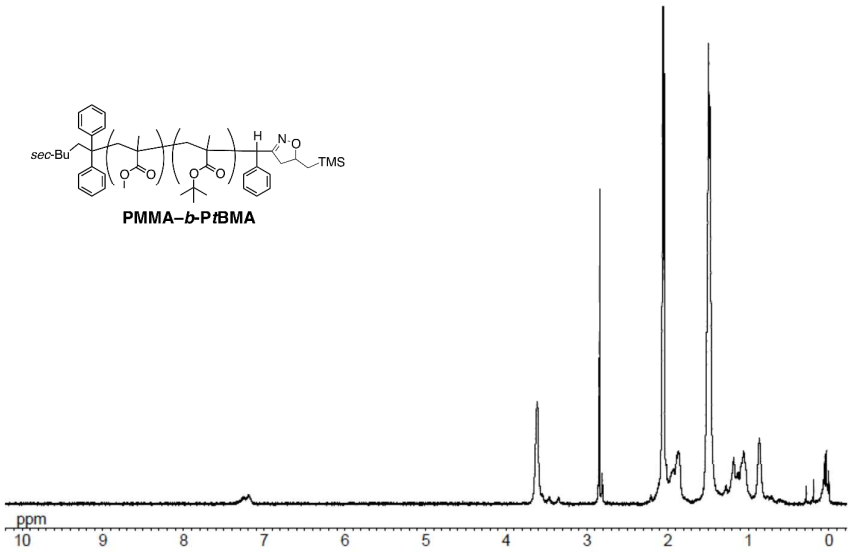


Figure S13. ^{1}H NMR spectrum of the isoxazoline from **PMMA-*b*-P*t*BMA–CN^{+}O^{-}** (400 MHz, 298 K, Acetone-d_6).

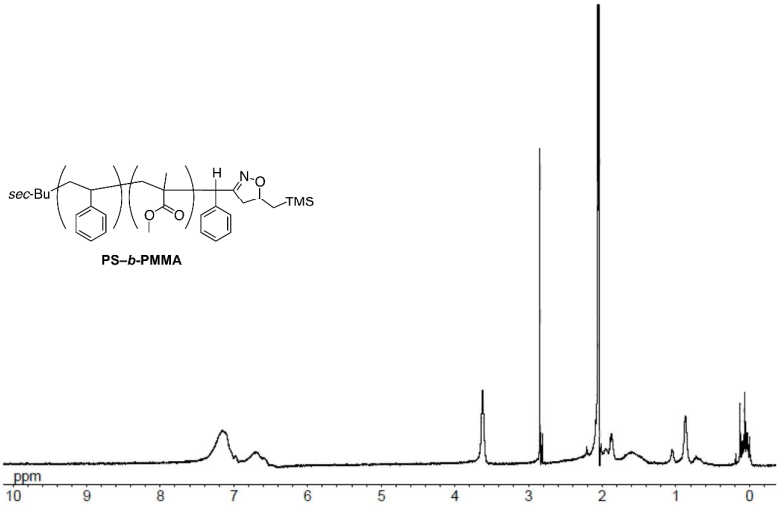
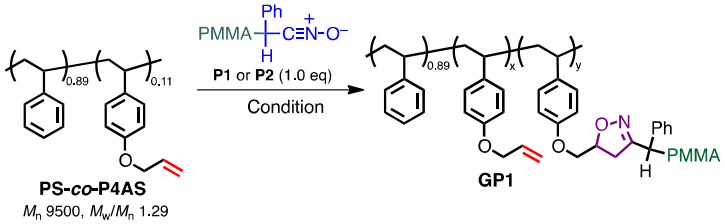


Figure S14. ^{1}H NMR spectrum of the isoxazoline from **PS-*b*-MMA–CN^{+}O^{-}** (400 MHz, 298 K, Acetone-d_6).

Typical procedure for the grafting reaction of **PMMA–CN^{+}O^{-}** onto poly(styrene-*co*-4-allyloxystyrene) (**PS-*co*-P4AS)**



Scheme S4

PS-*co*-P4AS (100 mg, 10.5 μmol) was mixed with **PMMA–CN^{+}O^{-}** (M_n 1600, M_w/M_n 1.24, 157 mg, 0.10 mmol) on a mortar and warmed to the arbitrary temperature. After grinding for the arbitrary reaction time, the mixture was

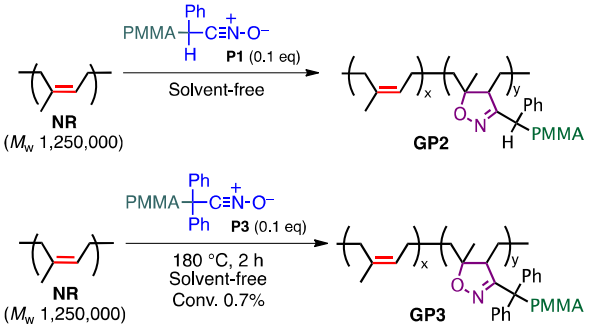
dissolved in $CHCl_3$ (3.0 mL) and precipitated from methanol (100 mL) to give the products. The products were collected by filtration and dried *in vacuo* to give the graft polymers **GP1** as yellow or brown solids. The conversions were calculated through a comparison of the integral ratio in the ^{1}H NMR spectra between the phenyl proton signals from **PS-*co*-P4AS** and **PMMA–CN$^+$O$^-$** (*ca.* 7.38–6.56 ppm) and the remaining olefin proton signals from **PS-*co*-P4AS** (6.01, 5.37, and 5.21 ppm).

Table S1. Results for the grafting reaction of **PS-*co*-P4AS** with PMMA–CN$^+$O$^-$.

Entry	PMMA–CN$^+$O$^-$	M_n	Temp. (°C)	Time (h)	Conv. (%)[a]	Yield (%)	**GP1**
1	**P3**	2000	130	2	0[b]	95	–
2	**P1**	1600	100	2	21	98	**GP1a**
3	**P1**	1600	130	2	67	90	**GP1b**
4	**P1**	1600	130	6	86	93	**GP1c**
5	**P1**	1600	160	2	39	96	**GP1d**
6	**P2**	780	100	2	38	81	**GP1e**
7	**P2**	780	130	2	54	100	**GP1f**

[a] Determined from the ratio of ^{1}H NMR integrals. [b] No reaction.

Typical procedures for the grafting reaction of **PMMA–CN$^+$O$^-$** onto nature rubber (NR).



Scheme S5

(Entries 1 and 4, Table S2): NR (50 mg, 0.734 mmol of the monomeric unit) was directly mixed with **PMMA–CN$^+$O$^-$** (11.8 mg, 0.0734 mmol, 10 mol% of internal alkene) on a mortar at arbitrary temperature. After grinding for the arbitrary reaction time, the mixture was cooled to room temperature, dissolved in $CHCl_3$ (5 mL), and precipitated into methanol (100 mL). The resulting solids were collected by filtration, washed with acetone for several times to remove free **PMMA–CN$^+$O$^-$** and dried *in vacuo* to give the graft NR as a brown solid. The conversions were calculated through a comparison of the integral ratio in ^{1}H NMR spectra between the remaining olefin proton signals at δ 5.12 ppm and the PMMA methoxy proton signals at δ 3.60 ppm.

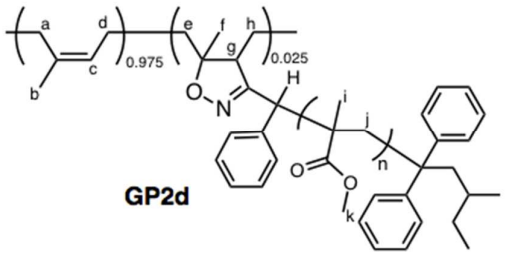
(Entries of 2, 4, and 5): NR (50 mg, 0.734 mmol of the monomeric unit) was put on a mortar and warmed at 160 °C to melt the NR. After preheating for 1 h, the mixture was cooled to the reaction temperature and mixed with **PMMA–CN$^+$O$^-$** (11.8 mg, 0.0734 mmol). After grinding for the arbitrary reaction time, the mixture was cooled to room temperature, dissolved in $CHCl_3$ (5 mL), and precipitated into methanol (100 mL). The resulting solids were collected by filtration, washed with acetone for several times to remove free **PMMA–CN$^+$O$^-$**, and dried *in vacuo* to give the graft NR as a brown solid. The conversions were calculated through a comparison of the integral ratio in the ^{1}H NMR spectra between the remaining olefin proton signals at δ 5.12 ppm and the PMMA methoxy proton signals at δ 3.60

ppm.

Table S2. Results for the grafting reaction of NR with PMMA–CN^+O^-.

Entry	PMMA–CN^+O^-	Temp. (°C)	Time (h)	Conv. (%)[a,b]	Yield(%)[c]	Graft polymer
1	**P3**[d]	180	2	0.7	97	**GP3**
2[f]	**P1**[e]	130	6	11.4	100	**GP2a**
3	**P1**[e]	140	6	8.7	100	**GP2b**
4[f]	**P1**[e]	140	2	15.1	98	**GP2c**
5[f]	**P1**[e]	140	6	24.9	49[g]	**GP2d**

[a] Determined from the ratio of ^{1}H NMR integrals. [b] Based on the mole of nitrile *N*-oxide. [c] Based on weight of NR and grafted PMMA. [d] M_n 2000, PDI 1.36. [e] M_n 1600, PDI 1.24. [f] Preheating at 160 °C for 1 h and then cooling to reaction temperature in 15 min. [g] Partly dissolved in acetone.



GP2d

GP2d: No T_g was observed; T_{d5} 175 °C; T_{d10} 199 °C; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.31–7.16 (m, –Ph–H), 5.12 (s, –C=CH, c), 3.60 (br, –COOCH_3, k), 2.68 (br, –CH–, g), 2.17 (s, –C(CH_3), f), 2.05 (s, –C(CH_3), b), 1.82–1.68 (m, –CH_2C–, j), 1,68 (s, –CH_2–, a, d, e, h) 1.25–0.46 (m, –C–CH_3, i, *sec*-butyl proton) ppm; IR (KBr) υ 1716 (C=O), 1642 (C=C) cm^{-1}.

Preparation of a glass plate bearing allyl-functional groups on the surface (**Allyl-GS**)

Glass plates (2.7x2.7 cm) were immersed in Piranha solution (concd H_2SO_4: H_2O_2 = 3: 1 (v/v)) overnight. After washed with water 3 times and dried at room temperature, 10 plates of the glass were set into a vessel coloration. $CHCl_3$ (22 mL) was added into the vessel coloration, followed by allyltrichlorosilane (2 drops by using a glass pipet, *ca.* 0.1 mL). The glass plates were placed in the reaction solvent to proceed silane coupling reaction for 12 h, and the prepared **Allyl-GS** were washed with $CHCl_3$ for several times, dried in air, and kept in MeOH for usage.

Preparation of a glass plate bearing poly(*tert*-butyl methacrylate) grafting on the surface (**P*t*BMA-GS**)

P*t*BMA–CN^+O^- (200 mg, 0.06 mmol) was coated on a prepared **Allyl-GS** and heated at 130 °C. After 2 h, the glass plate was washed with $CHCl_3$ repeatedly to remove free P*t*BMA–CN^+O^- and dried in air to obtain a P*t*BMA-modified glass surface (**P*t*BMA-GS**).

Preparation of a glass plate bearing poly(methylacrylic acid) grafting on the surface (**PMAA-GS**)

The prepared **P*t*BMA-GS** was placed on a hot plate and heated at 240 °C for 15 min to achieve the ester decomposition of P*t*BMA moieties. After cooling to room temperature, the glass plate was washed with $CHCl_3$ and dried in air to obtain a PMAA-modified glass surface (**PMAA-GS**).

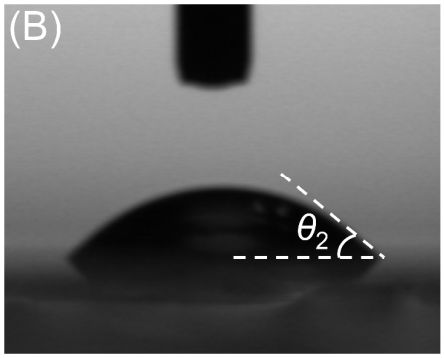


Figure S14. Water contact angle of **P*t*BMA-GS** (B, θ_2 = 43.8°). The angle was calculated by averaging the values for three different measurements.

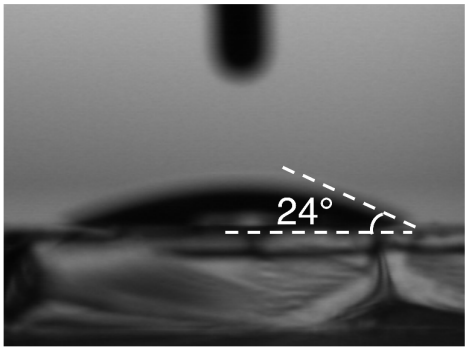


Figure S15. Water contact angle of **PMAA-GS** using a basic buffer solution (pH = 10). The angle was calculated by averaging the values for three different measurements.

3. Thermal decomposition of P*t*BMA–CN^+O^-

Thermal gravimetric analysis (TGA) was used to investigate the decomposition behavior of **P*t*BMA–CN^+O^-** (**P4**, M_n 3200, PDI 1.26). The thermal decomposition curve of **P4** shows a three-step decomposition behavior (**Figure S16**). According to the literature reported by Grant and Grassie,[2] the weight-loss at around 235 °C can be attributed to ester decomposition and was approximately 37%, which coincided with the weight fraction of the butyl group moiety in P*t*BMA–CN^+O^-, indicating that the ester decomposition temperature was around 235 °C. **P4** was further heated at 240 °C for 2 h to examine the ester decomposition behavior. It was found that the ester decomposition of **P4** performed rapidly at 240 °C and completed in 10 min, as shown in **Figure S17**. In addition, no further weight loss was observed even maintaining at 240 °C for 2 h, suggesting that the generated PMAA had no further decomposition at 240 °C.

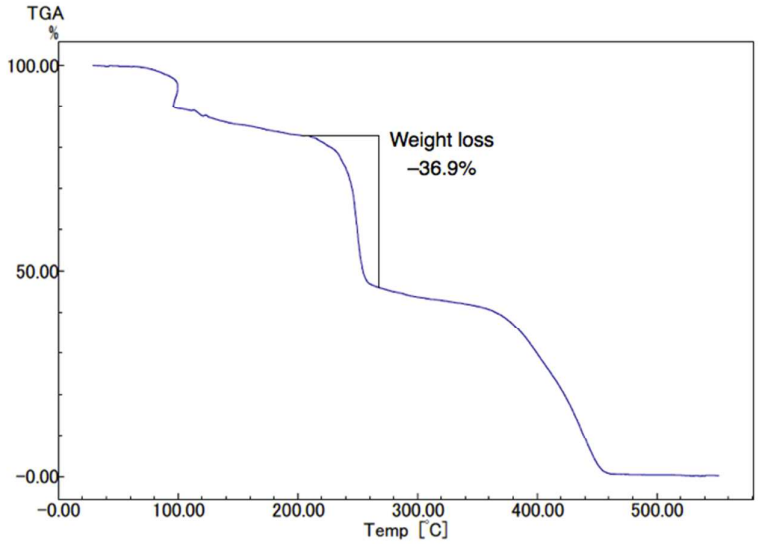


Figure S16. TGA curve of P*t*BMA–$CN^{+}O^{-}$ **P4** (heating rate of 10 °C/min under N_2 (flow rate, 50 mL/min)).

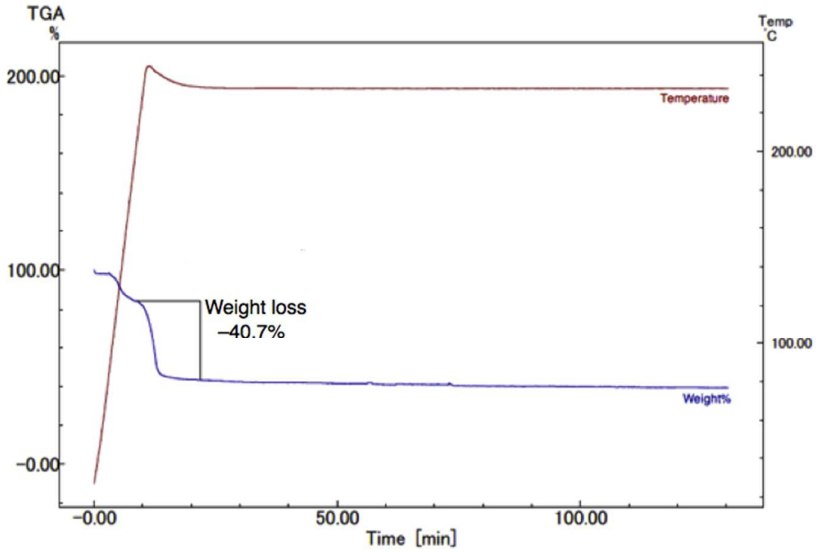


Figure S17. TGA curve of P*t*BMA–$CN^{+}O^{-}$ **P4** at 240 °C under N_2 (flow rate, 50 mL/min).

4. Spectral Data

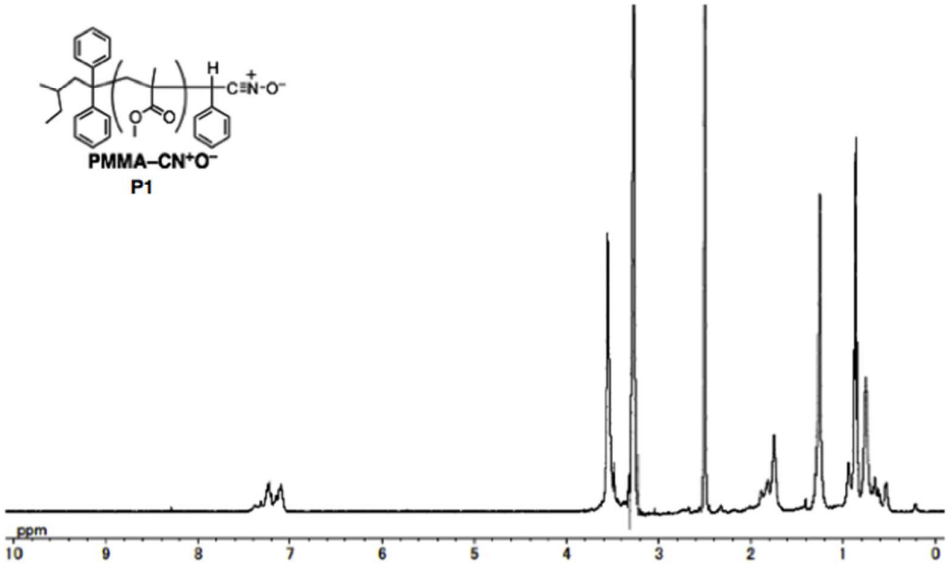


Figure S18. ^{1}H NMR spectrum of **PMMA–CN^{+}O^{-} P1** (400 MHz, 298 K, DMSO-d_6).

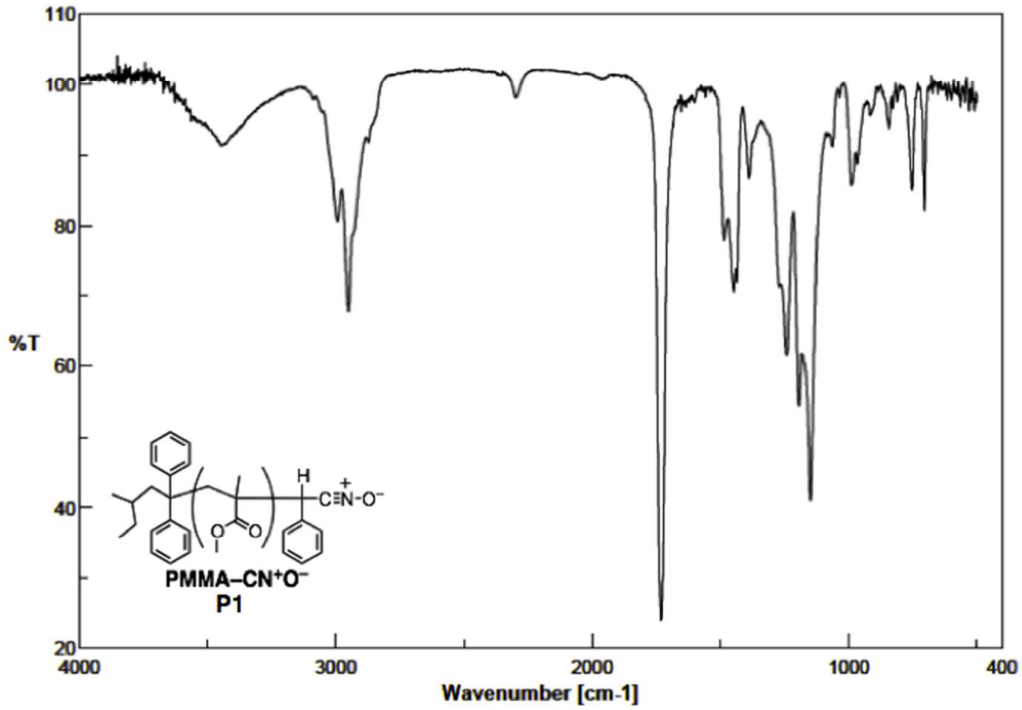


Figure S19. IR spectrum of **PMMA–CN^{+}O^{-} P1** (KBr).

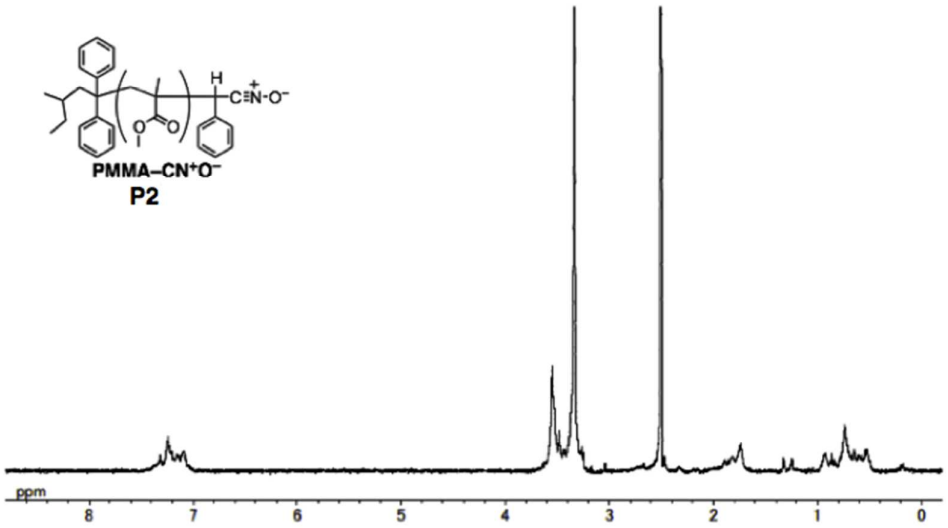


Figure S20. ^{1}H NMR spectrum of **PMMA–CN^{+}O^{-} P2** (400 MHz, 298 K, DMSO-d_6).

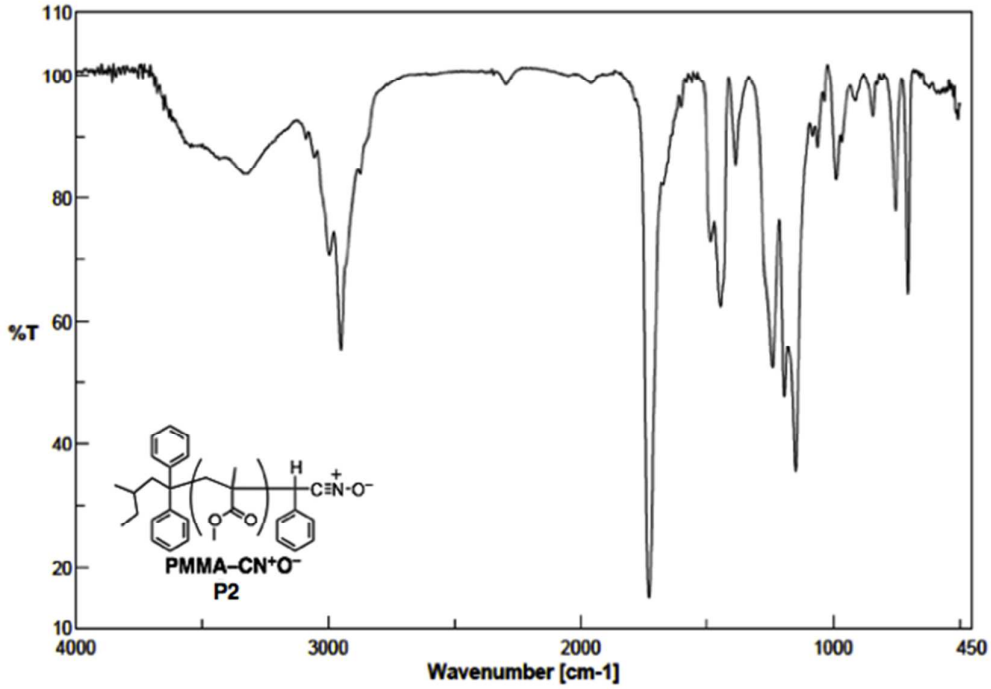


Figure S21. IR spectrum of **PMMA–CN^{+}O^{-} P2** (KBr).

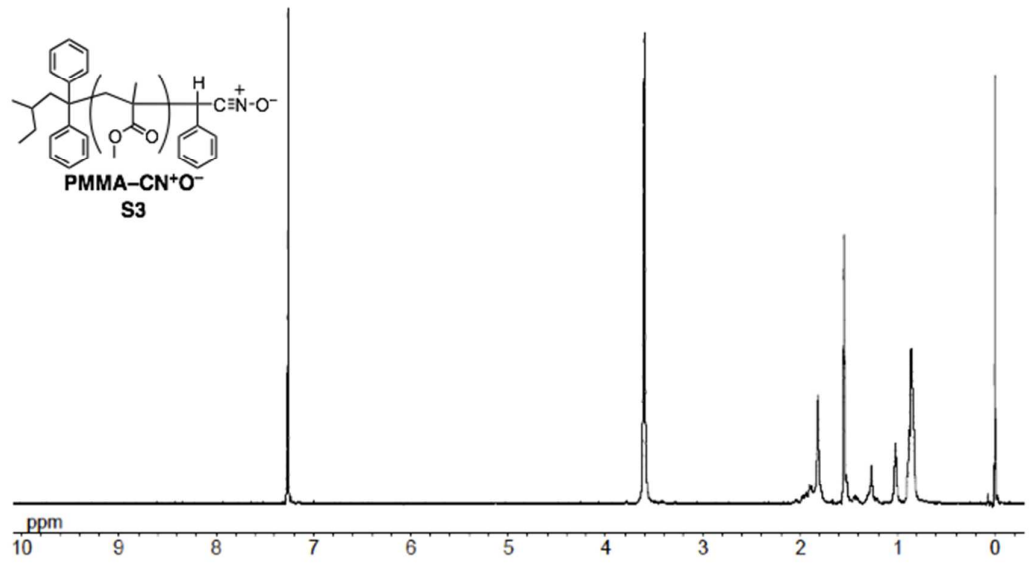


Figure S22. ^{1}H NMR spectrum of **PMMA–CN^{+}O^{-} S3** (400 MHz, 298 K, $CDCl_3$).

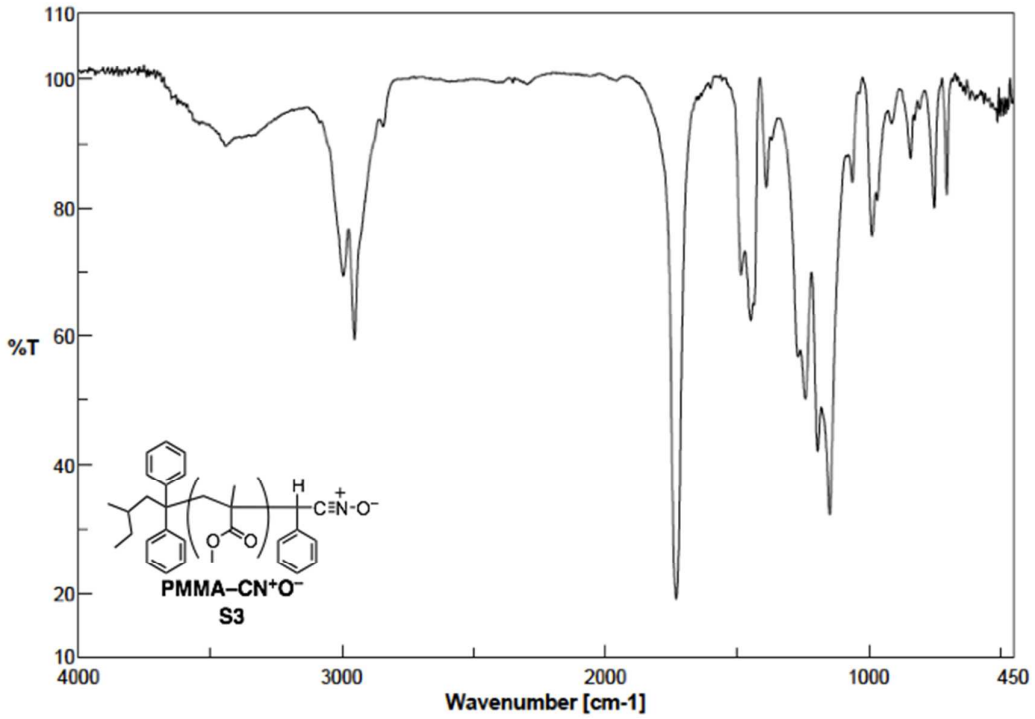


Figure S23. IR spectrum of **PMMA–CN^{+}O^{-} S3** (KBr).

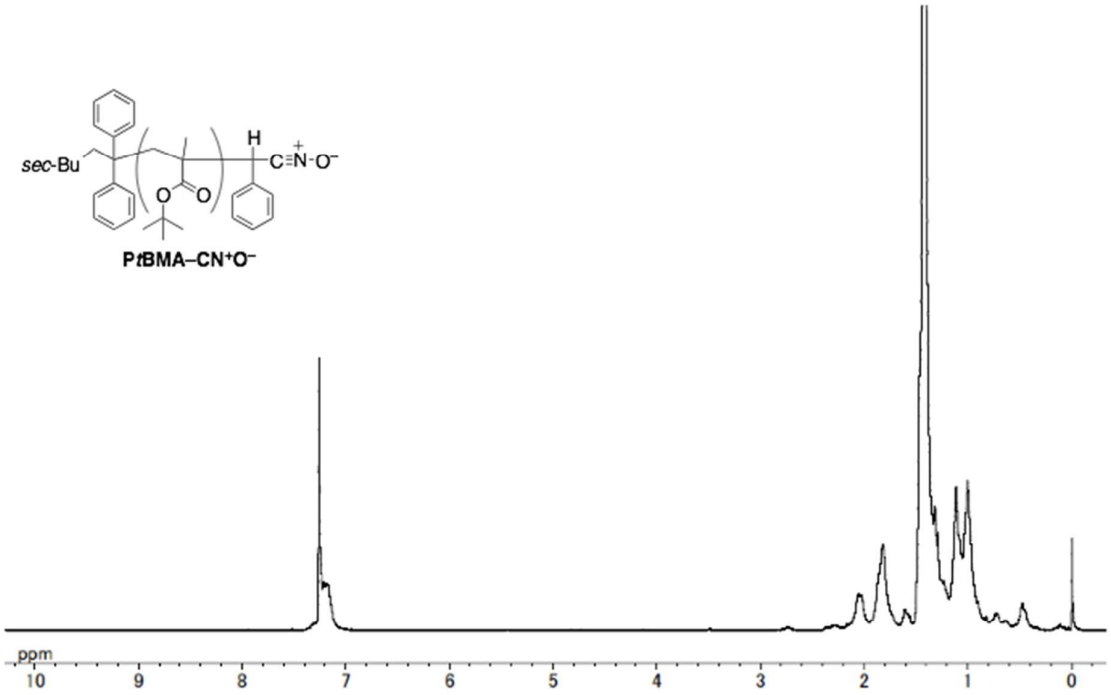


Figure S24. ^{1}H NMR spectrum of **P*t*BMA–CN^{+}O^{-}** (400 MHz, 298 K, $CDCl_3$).

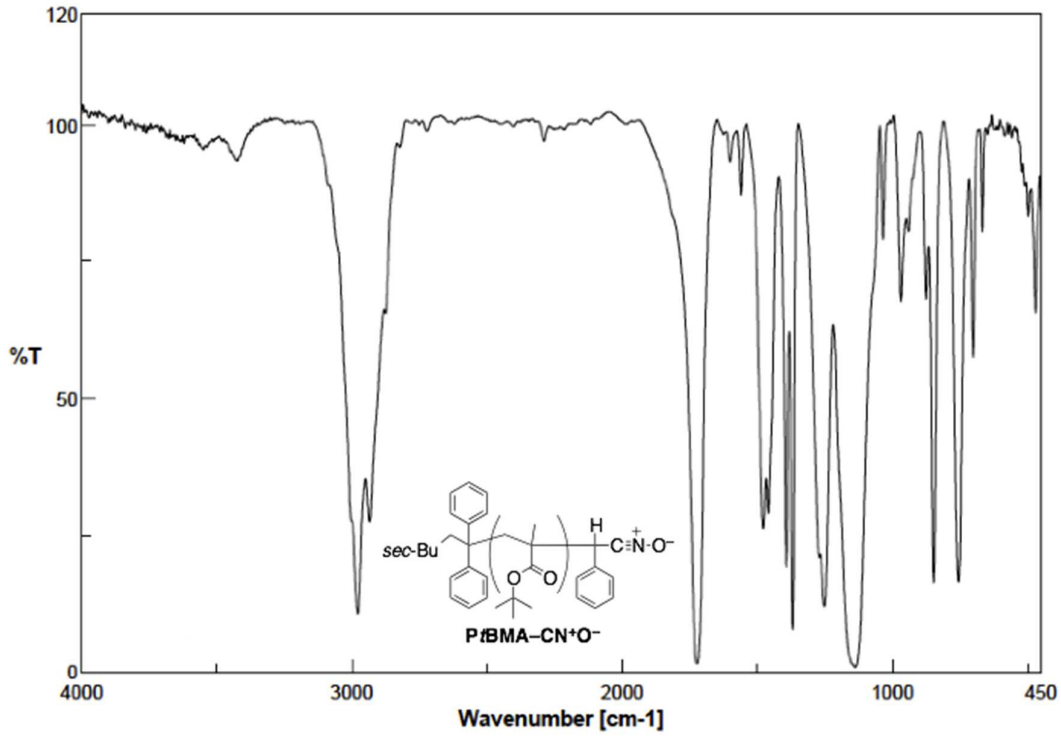


Figure S25. IR spectrum of **P*t*BMA–CN^{+}O^{-}** (KBr).

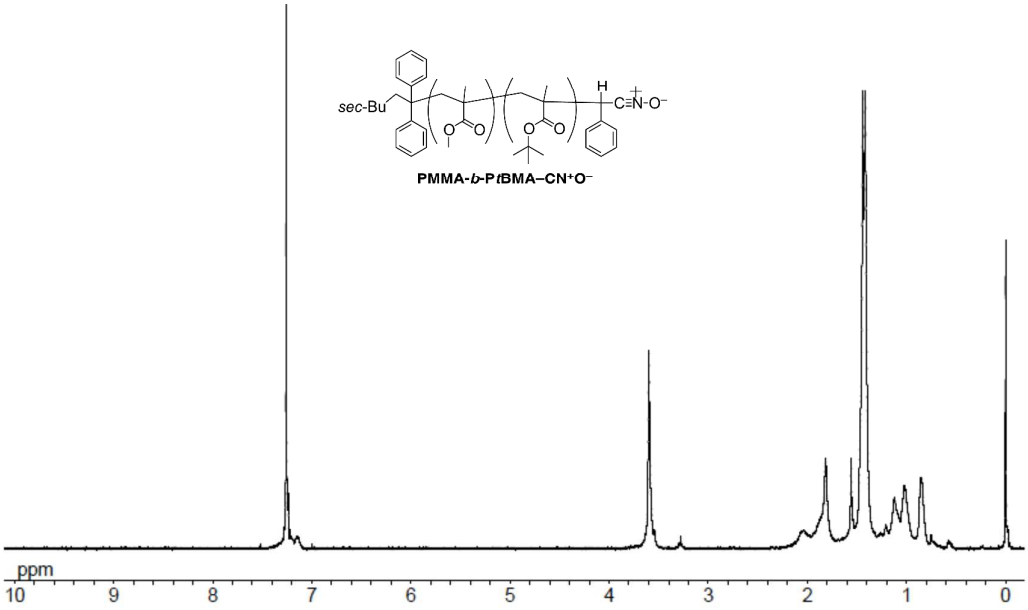


Figure S26. ^{1}H NMR spectrum of **PMMA-*b*-P*t*BMA–CN^{+}O^{-}** (400 MHz, 298 K, $CDCl_3$).

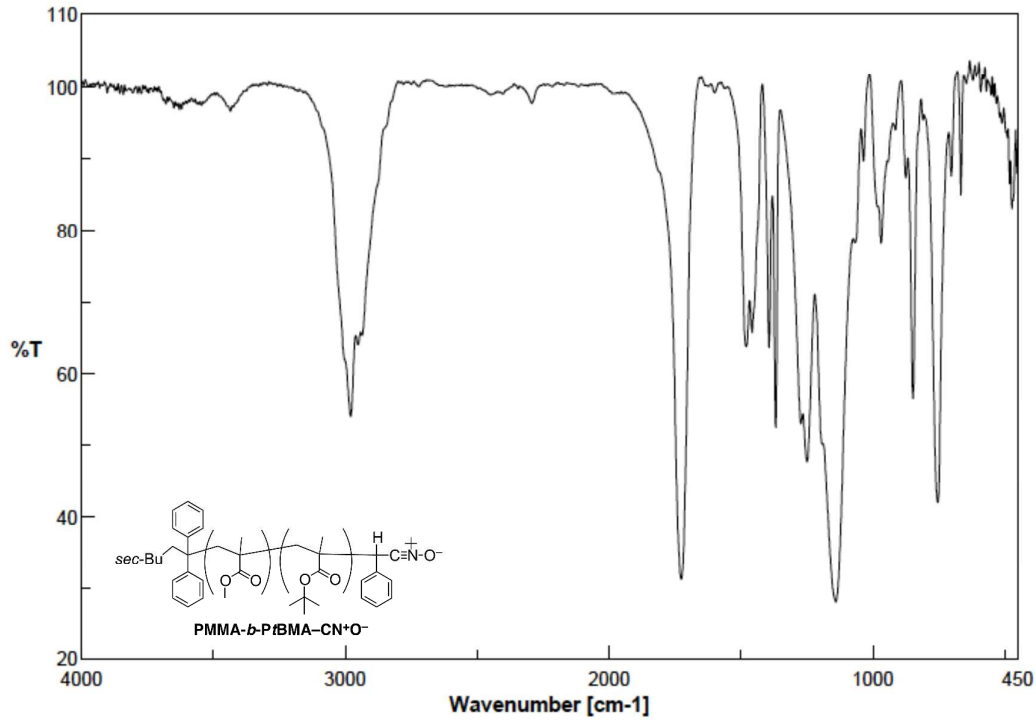


Figure S27. IR spectrum of **PMMA-*b*-P*t*BMA–CN^{+}O^{-}** (KBr).

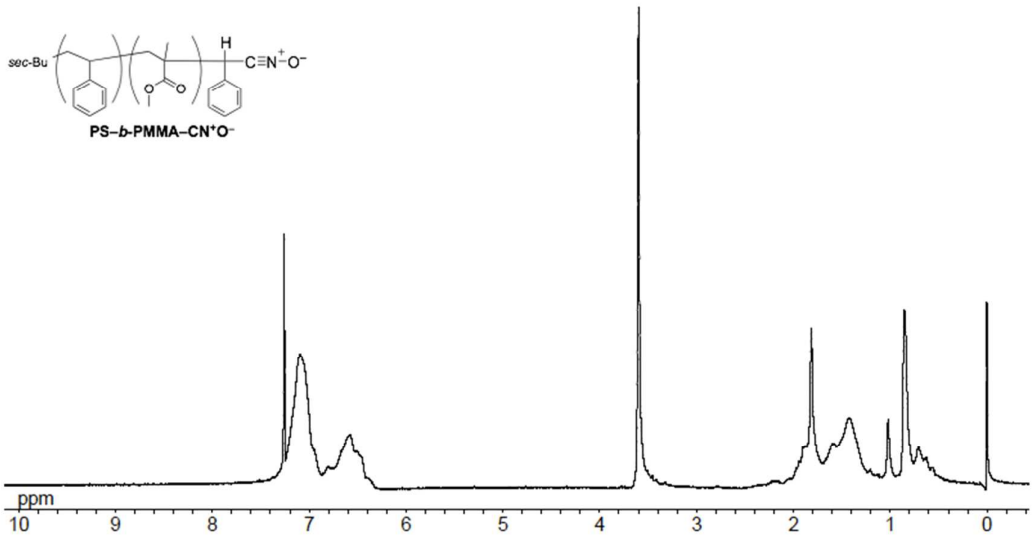


Figure S28. ^{1}H NMR spectrum of **PS-*b*-PMMA–CN^{+}O^{-}** (400 MHz, 298 K, $CDCl_3$).

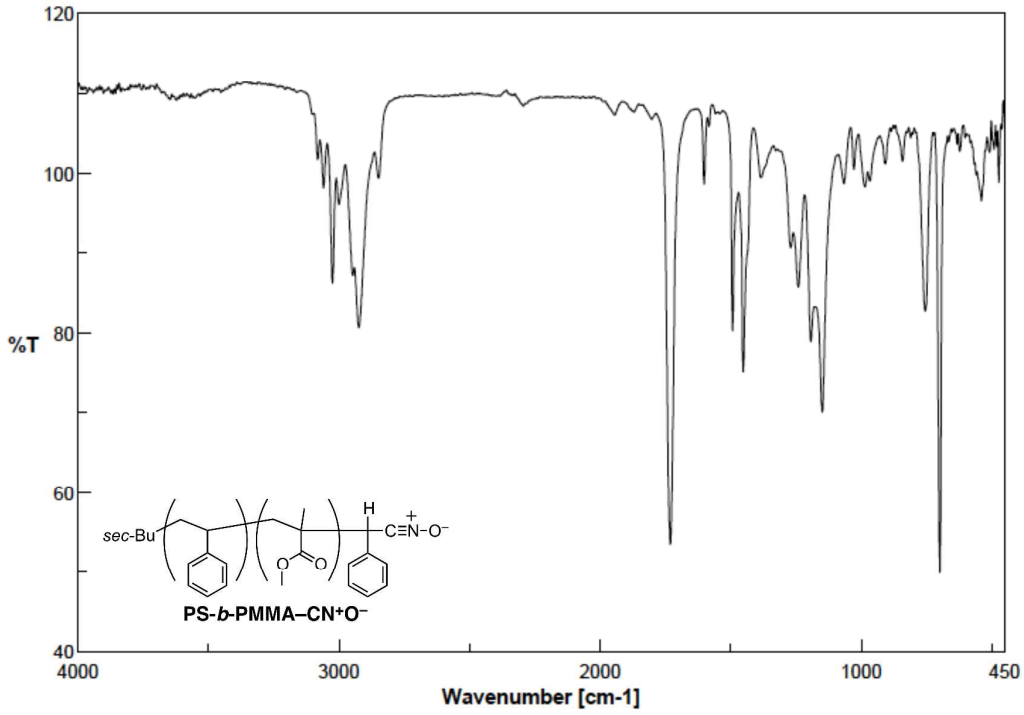


Figure S29. IR spectrum of **PS-*b*-PMMA–CN^{+}O^{-}** (KBr).

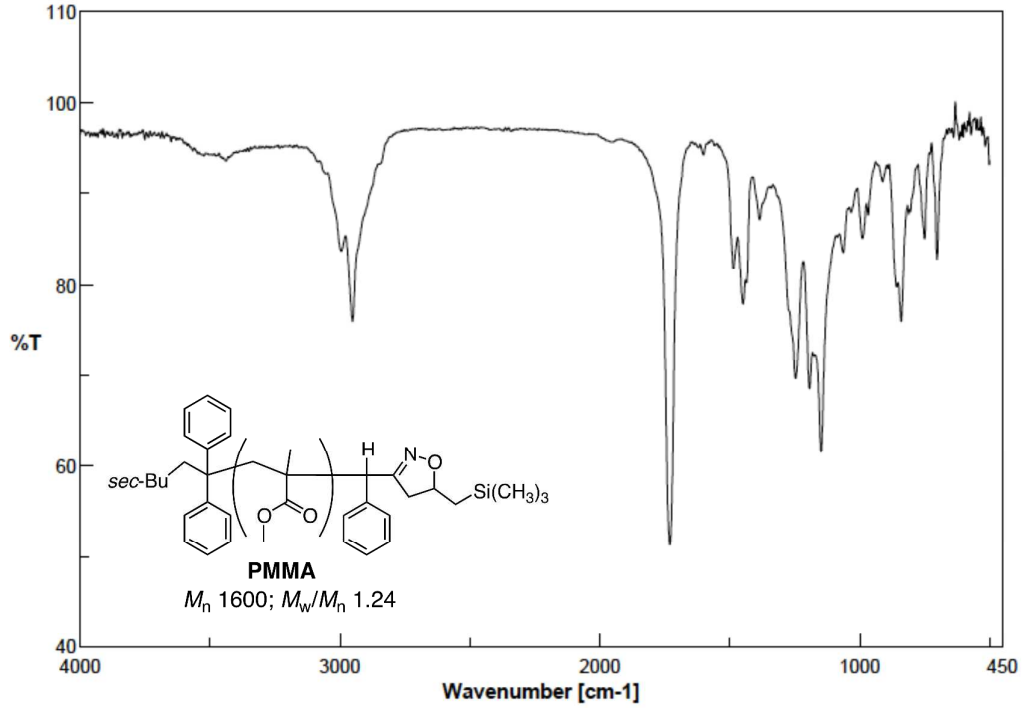


Figure S30. IR spectrum of the isoxazoline from **P1** (KBr).

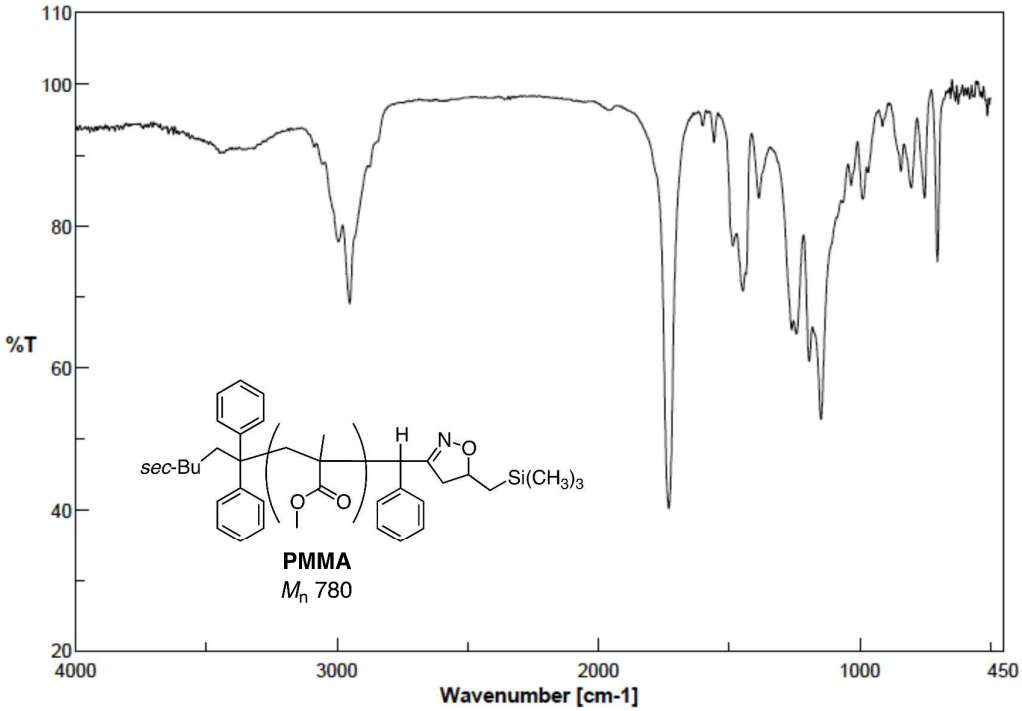


Figure S31. IR spectrum of the isoxazoline from **P2** (KBr).

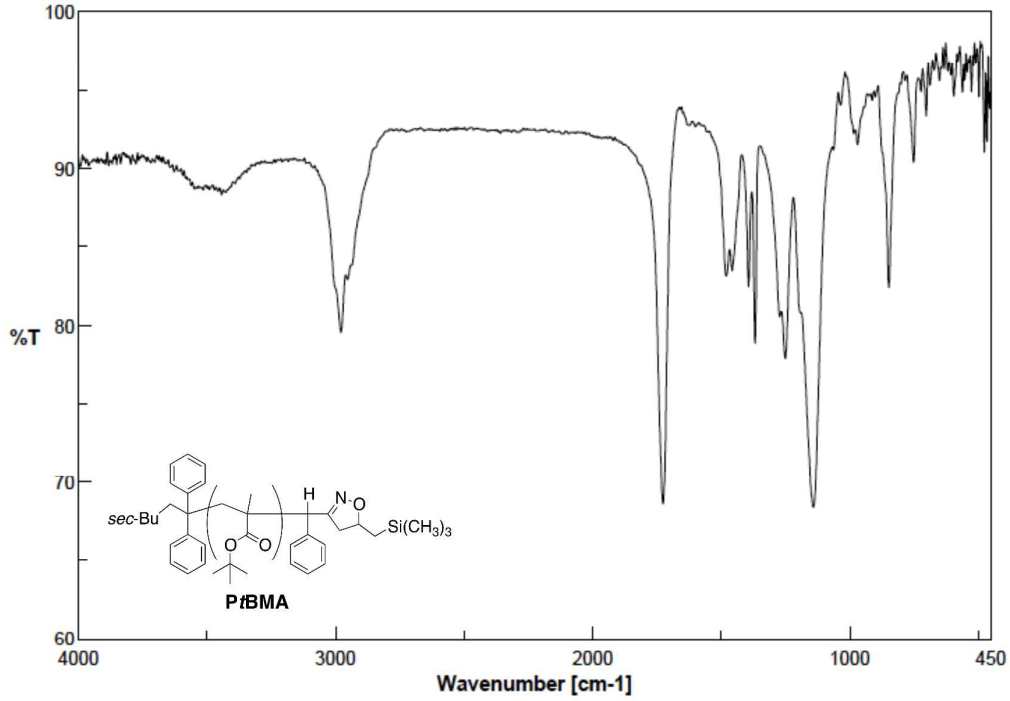


Figure S32. IR spectrum of the isoxazoline from **P*t*BMA–CN^{+}O^{-}** (KBr).

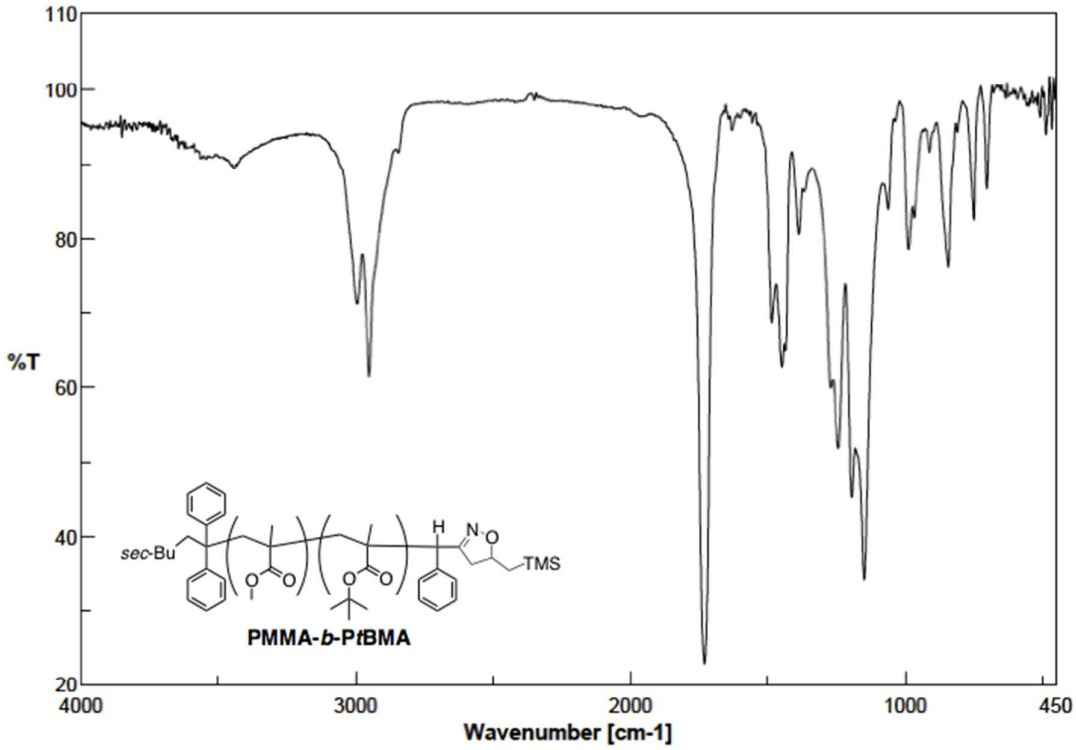


Figure S33. IR spectrum of the isoxazoline from **PMMA-*b*-P*t*BMA–CN^{+}O^{-}** (KBr).

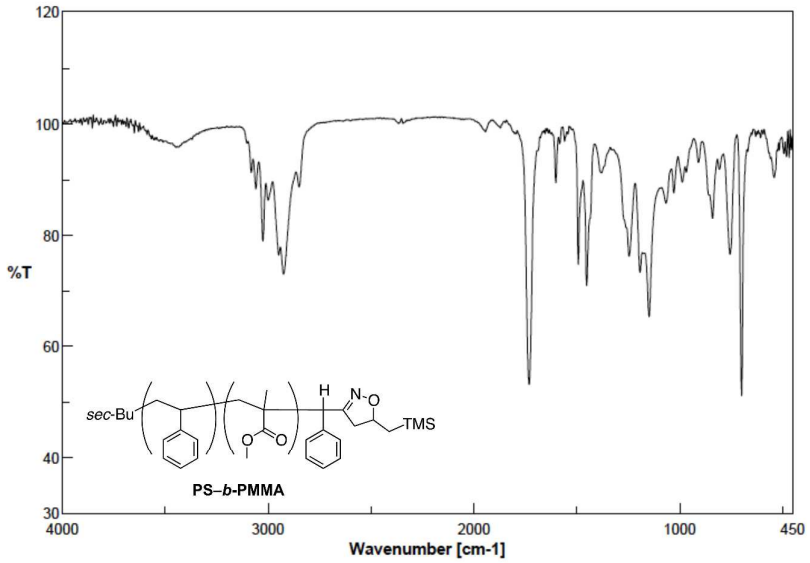
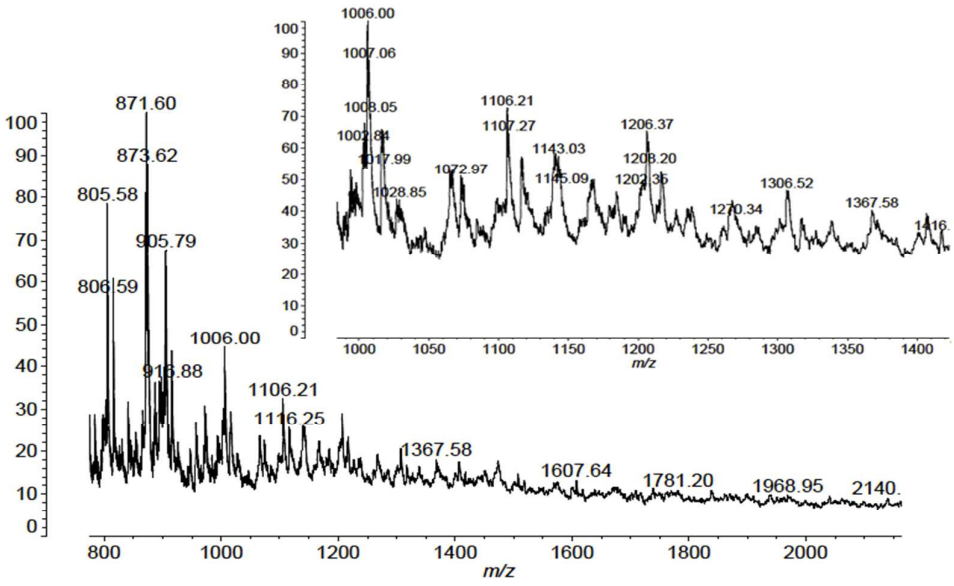
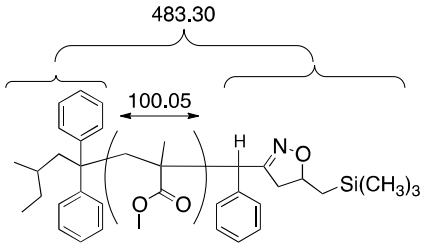


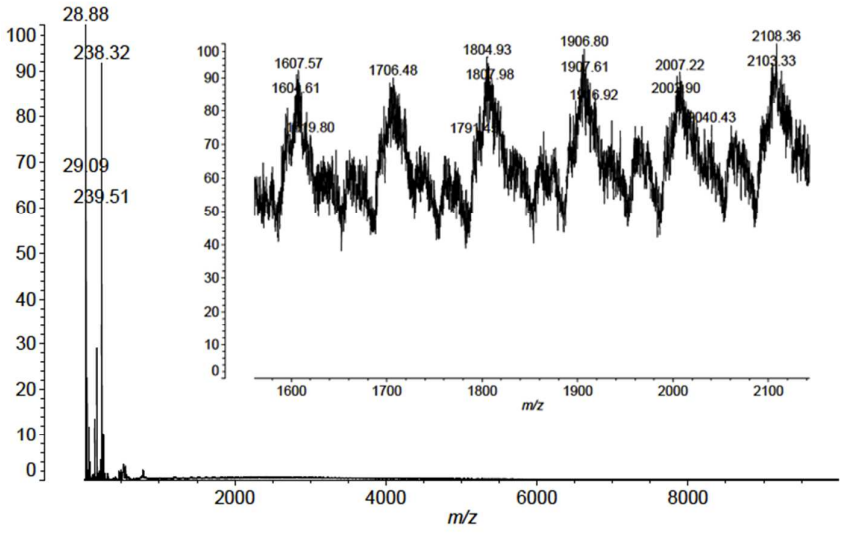
Figure S34. IR spectrum of the isoxazoline from **PS-*b*-PMMA–CN^{+}O^{-}** (KBr).

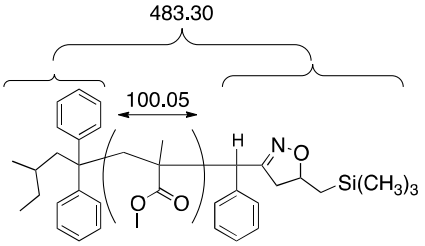




n	Theoretical values (M+Na^{+})
11	1606.84
12	1706.89
13	1806.94
14	1906.99
15	2007.04
16	2107.09

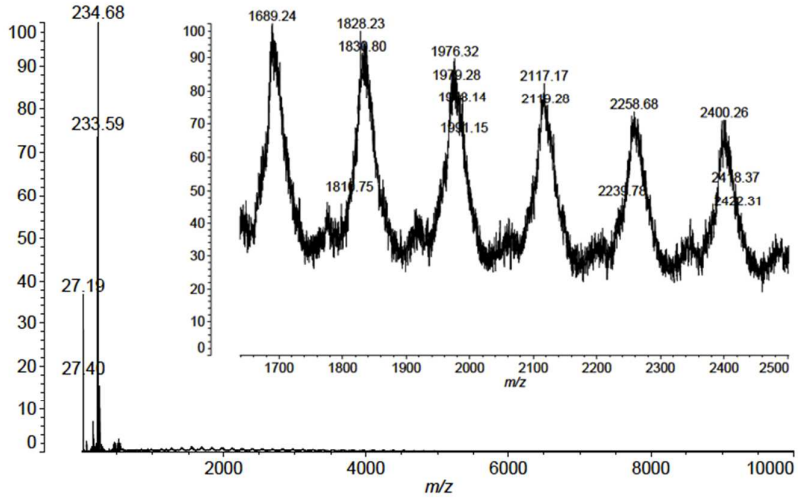
Figure S35. MALDI-TOF MS spectrum of the adduct of PMMA–CN^{+}O^{-} **P2** to allyltrimethylsilane (matrix: dithranol).





n	Theoretical values (M+Na$^+$)
5	1006.54
6	1106.59
7	1206.64
8	1306.69

Figure S36. MALDI-TOF MS spectrum of the adduct of PMMA–CN$^+$O$^-$ **P1** to allyltrimethylsilane (matrix: dithranol).



n	Theoretical values	
	M	M – $OC(CH_3)_3$
9	1762.20	1689.14
10	1904.30	1831.24
11	2046.40	1973.34
12	2188.50	2115.44
13	2330.60	2257.54
14	2472.70	2399.64

Figure S37. MALDI-TOF MS spectrum of the adduct of **P*t*BMA–CN^+O^-** to allyltrimethylsilane (matrix: dithranol).

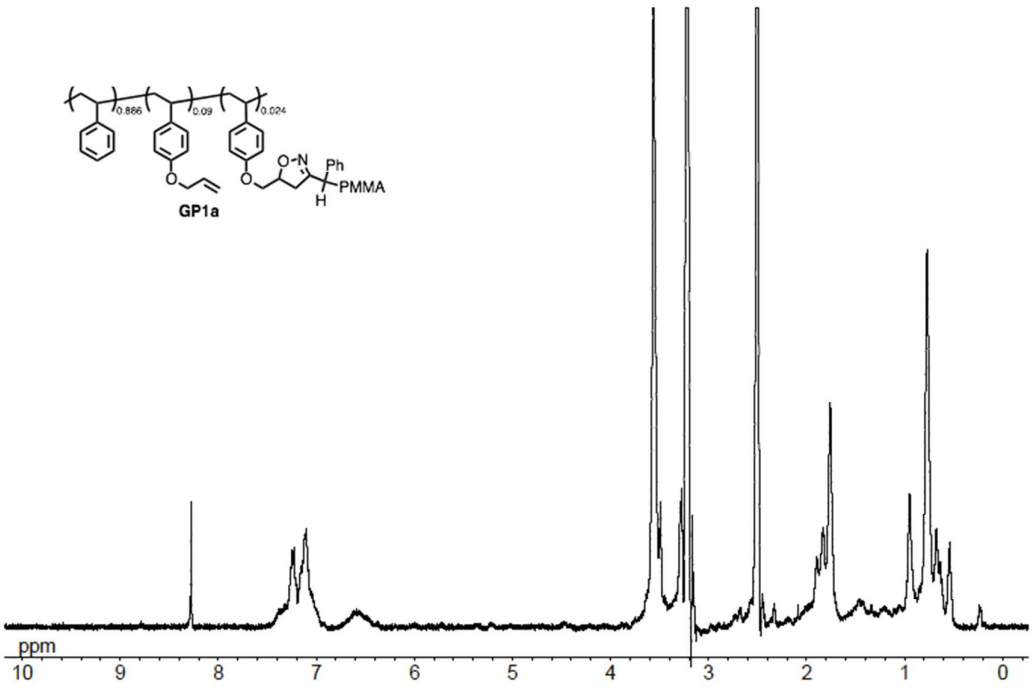


Figure S38. ^{1}H NMR spectrum of **GP1a** (400 MHz, 298 K, DMSO-d_6).

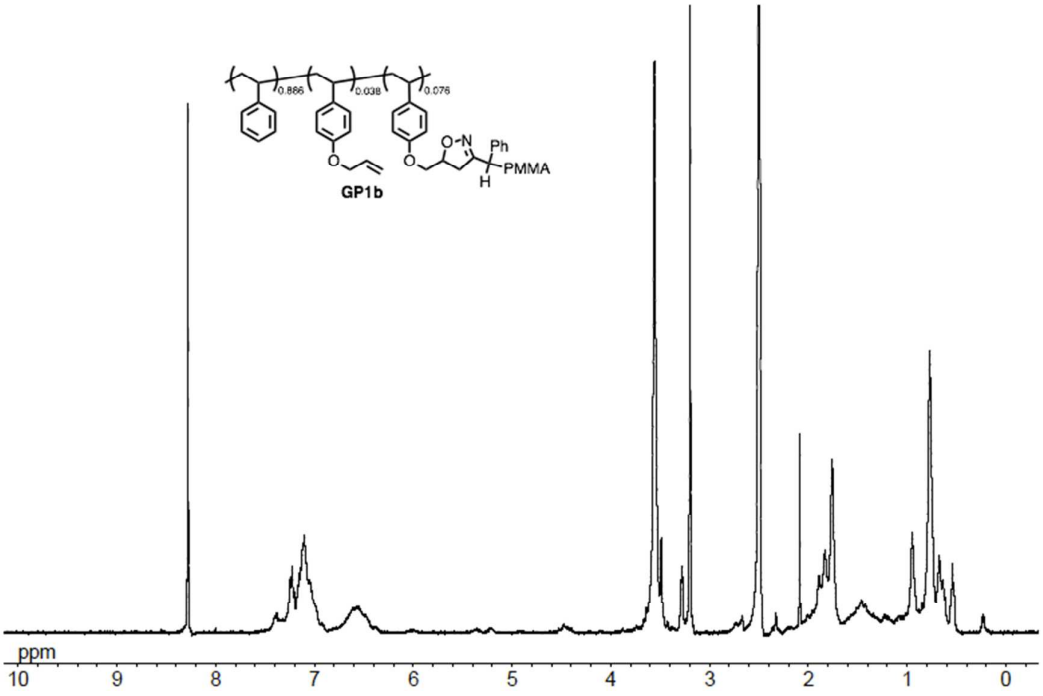


Figure S39. ^{1}H NMR spectrum of **GP1b** (400 MHz, 298 K, DMSO-d_6).

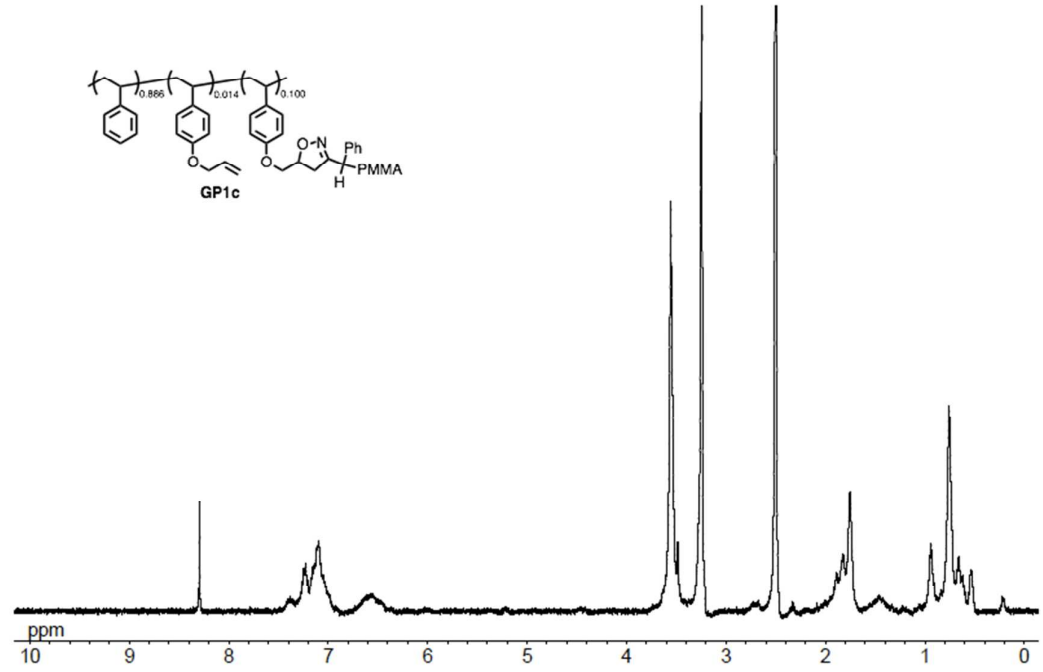


Figure S40. ^{1}H NMR spectrum of **GP1c** (400 MHz, 298 K, DMSO-d_6).

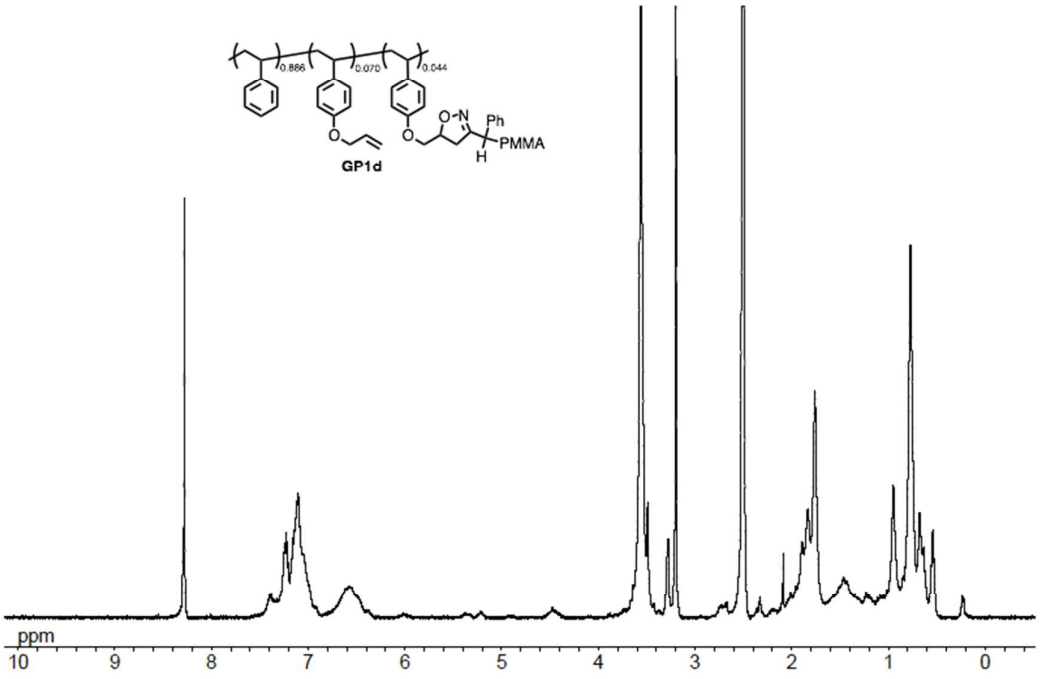


Figure S41. ^{1}H NMR spectrum of **GP1d** (400 MHz, 298 K, DMSO-d_6).

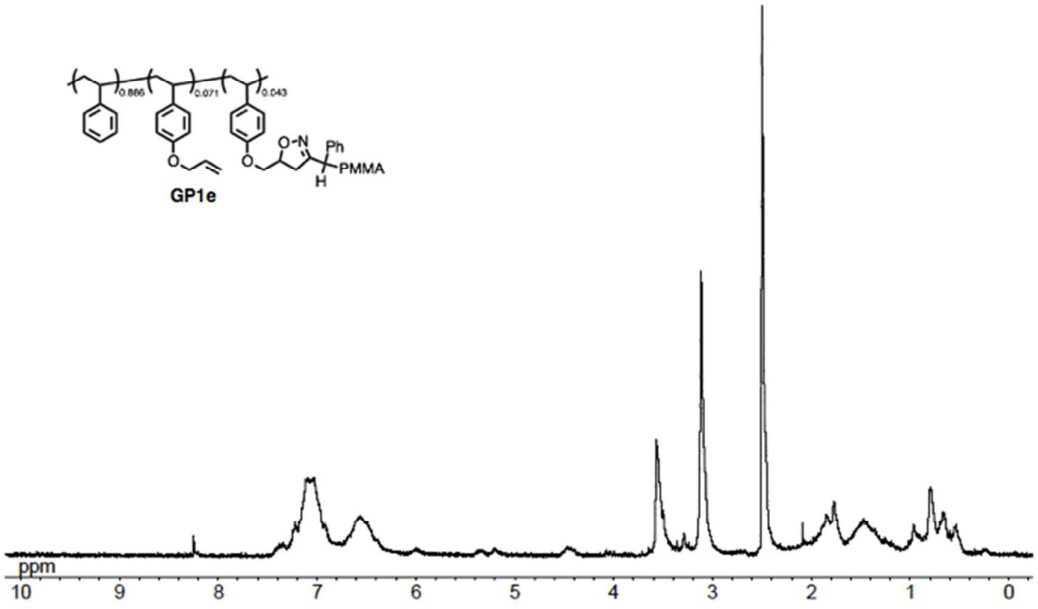


Figure S42. ^{1}H NMR spectrum of **GP1e** (400 MHz, 298 K, DMSO-d_6).

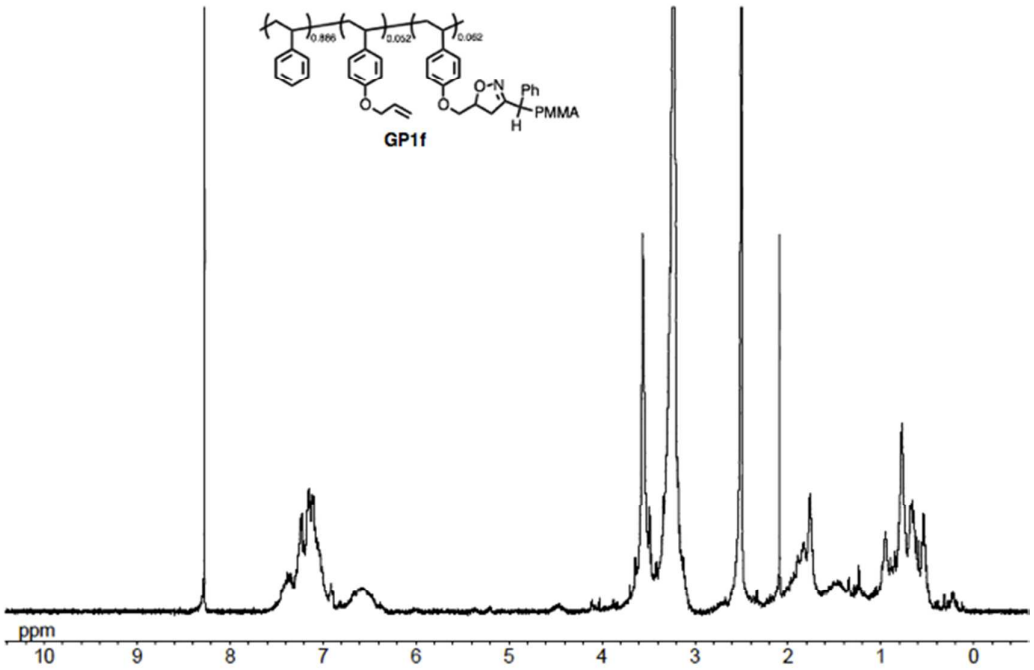


Figure S43. ^{1}H NMR spectrum of **GP1f** (400 MHz, 298 K, DMSO-d_6).

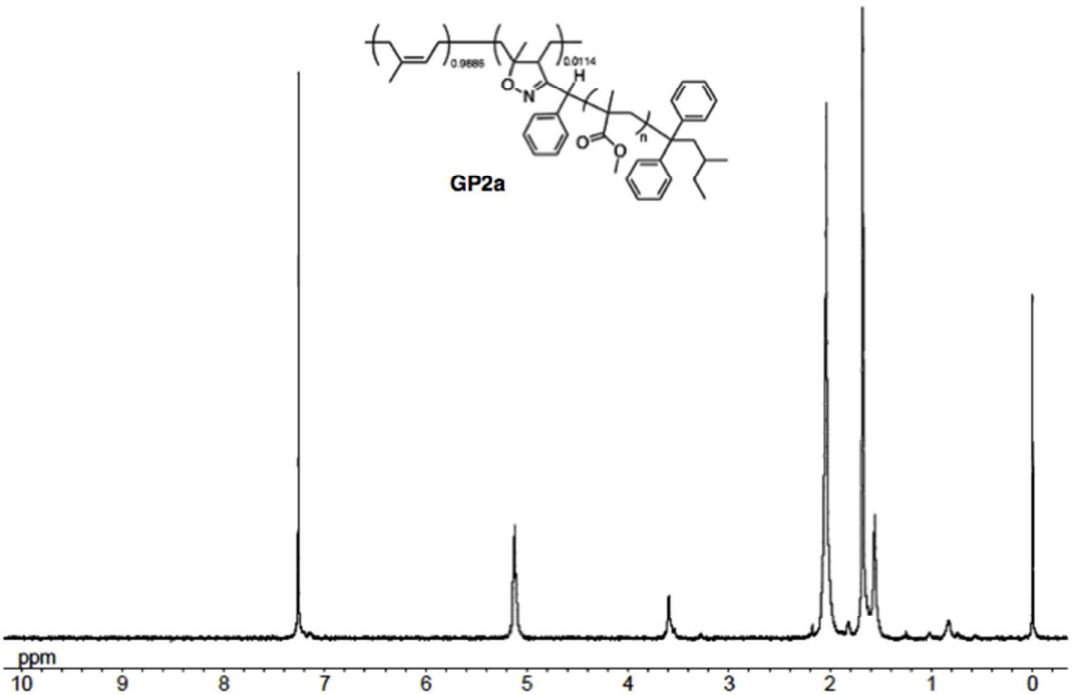


Figure S44. ^{1}H NMR spectrum of **GP2a** (400 MHz, 298 K, $CDCl_3$).

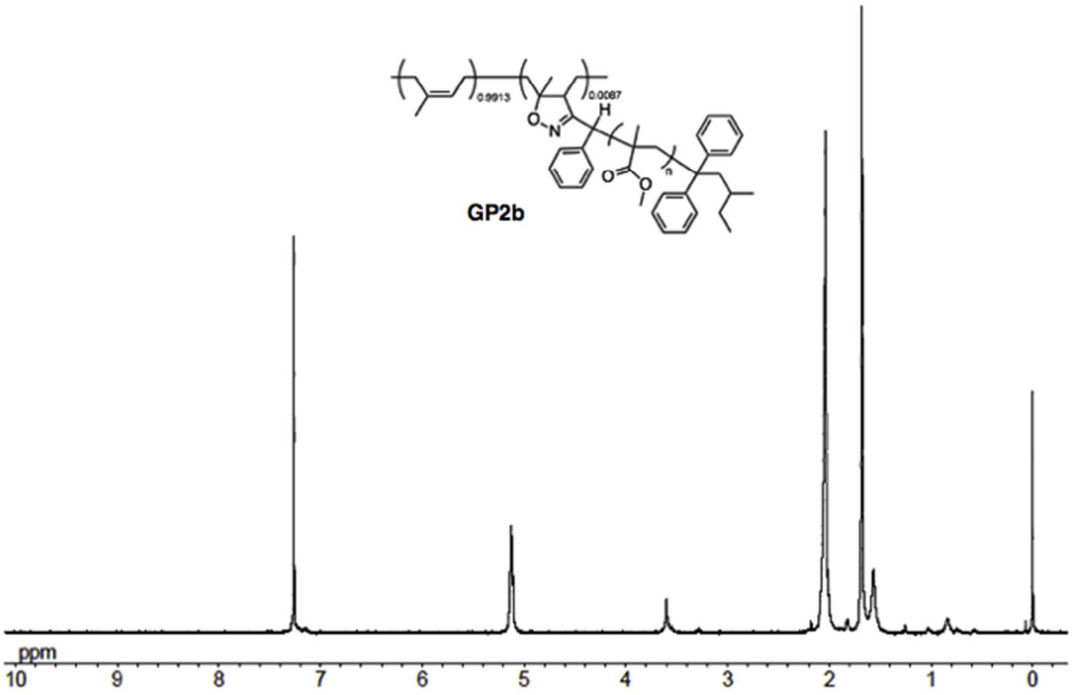


Figure S45. ^{1}H NMR spectrum of **GP2b** (400 MHz, 298 K, $CDCl_3$).

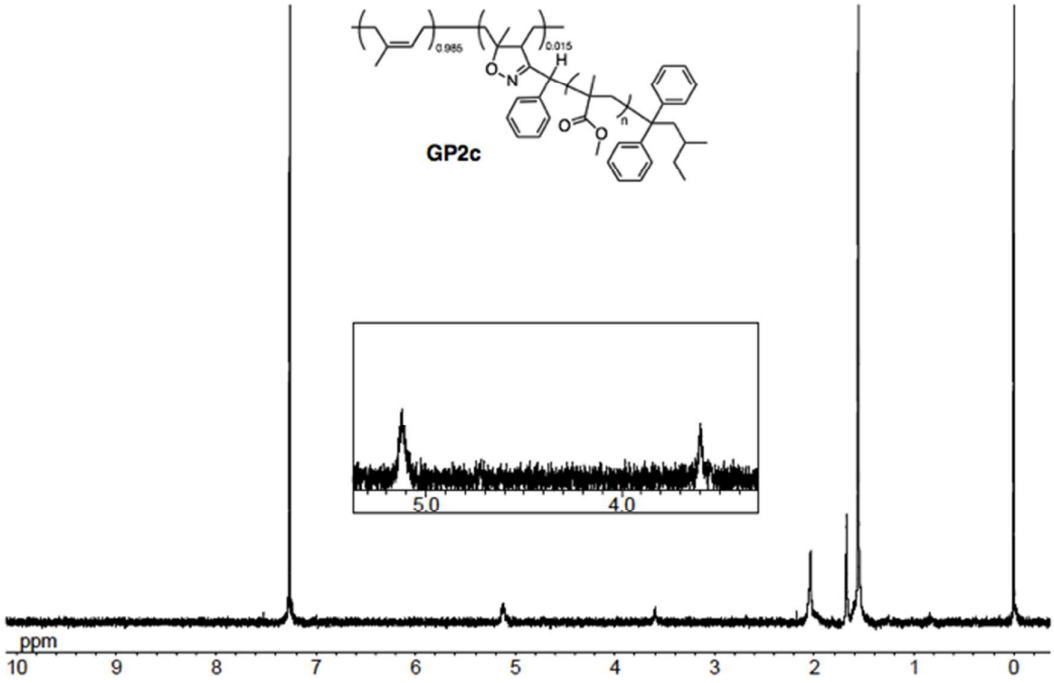


Figure S46. ^{1}H NMR spectrum of **GP2c** (400 MHz, 298 K, $CDCl_3$).

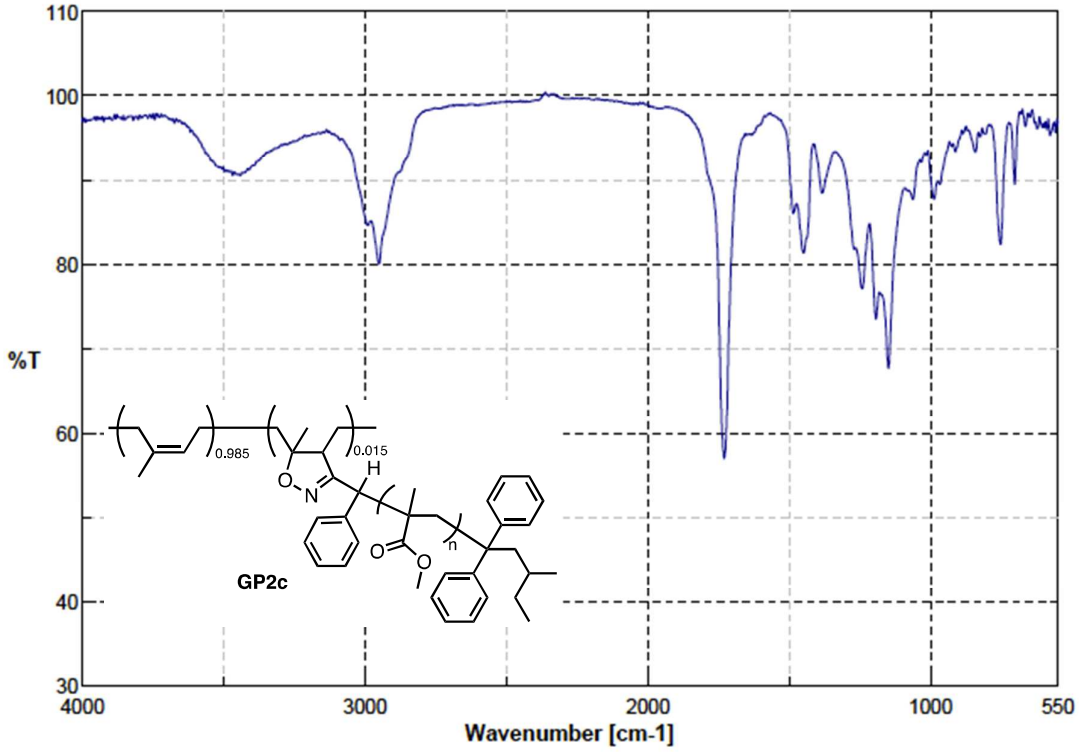


Figure S47. IR spectrum of **GP2c** (KBr).

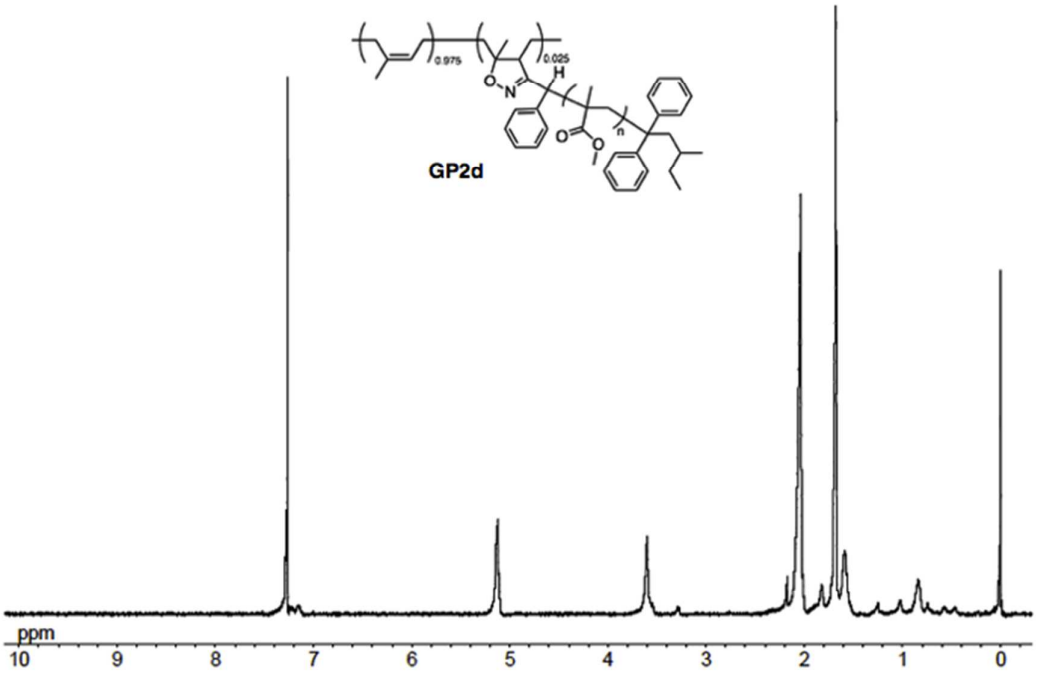


Figure S48. ^{1}H NMR spectrum of **GP2d** (400 MHz, 298 K, $CDCl_3$).

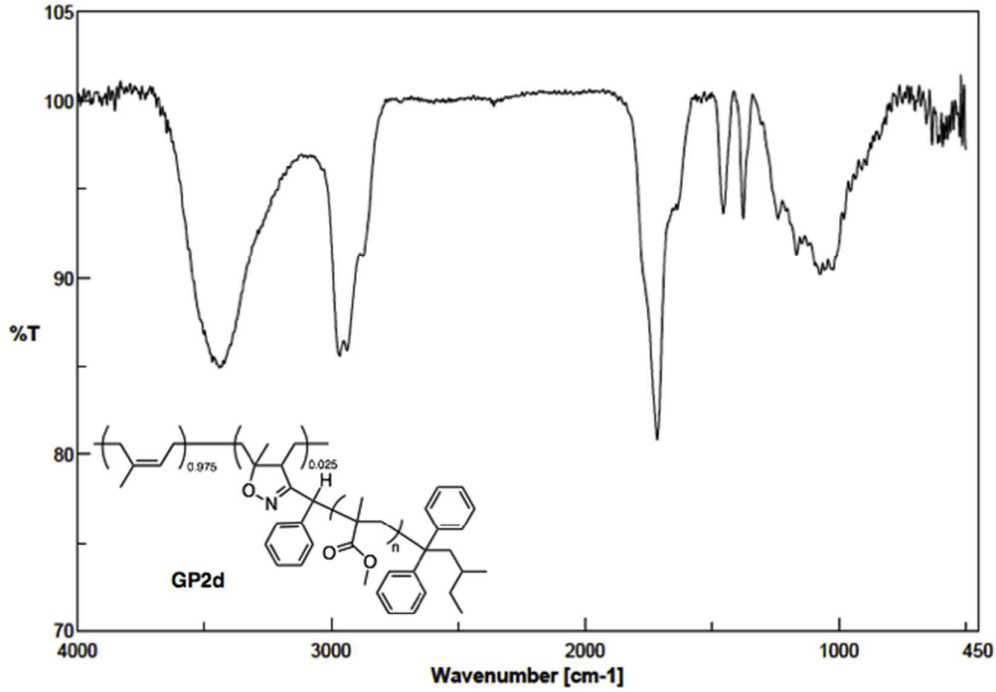


Figure S49. IR spectrum of **GP2d** (KBr).

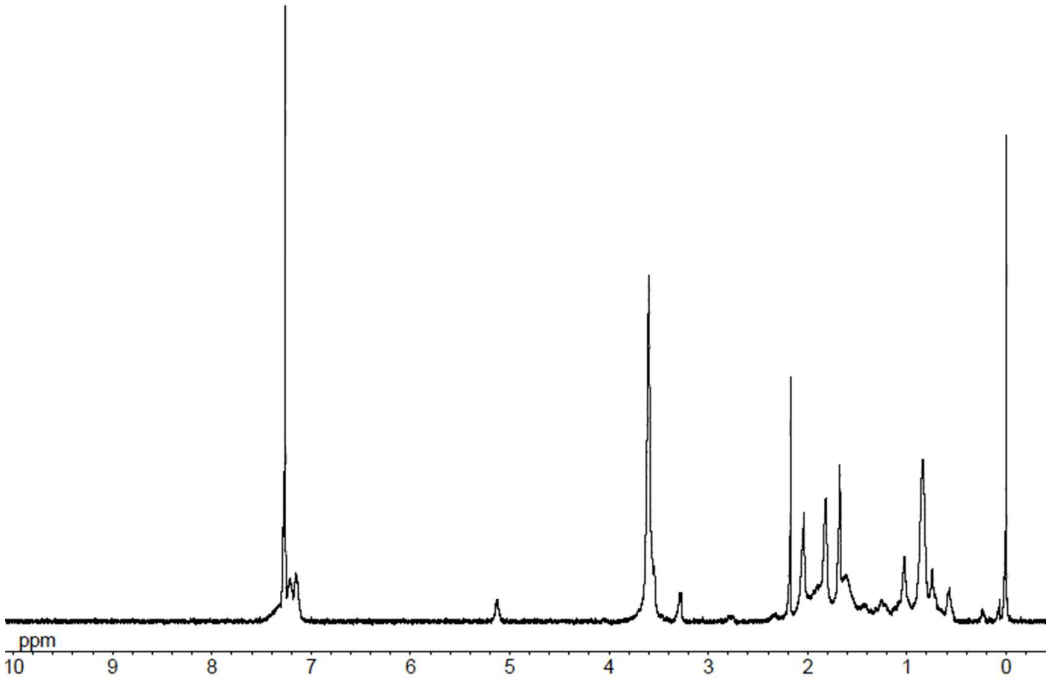


Figure S50. ^{1}H NMR spectrum of the product dissolving in acetone from crude **GP2d** (400 MHz, 298 K, $CDCl_3$).

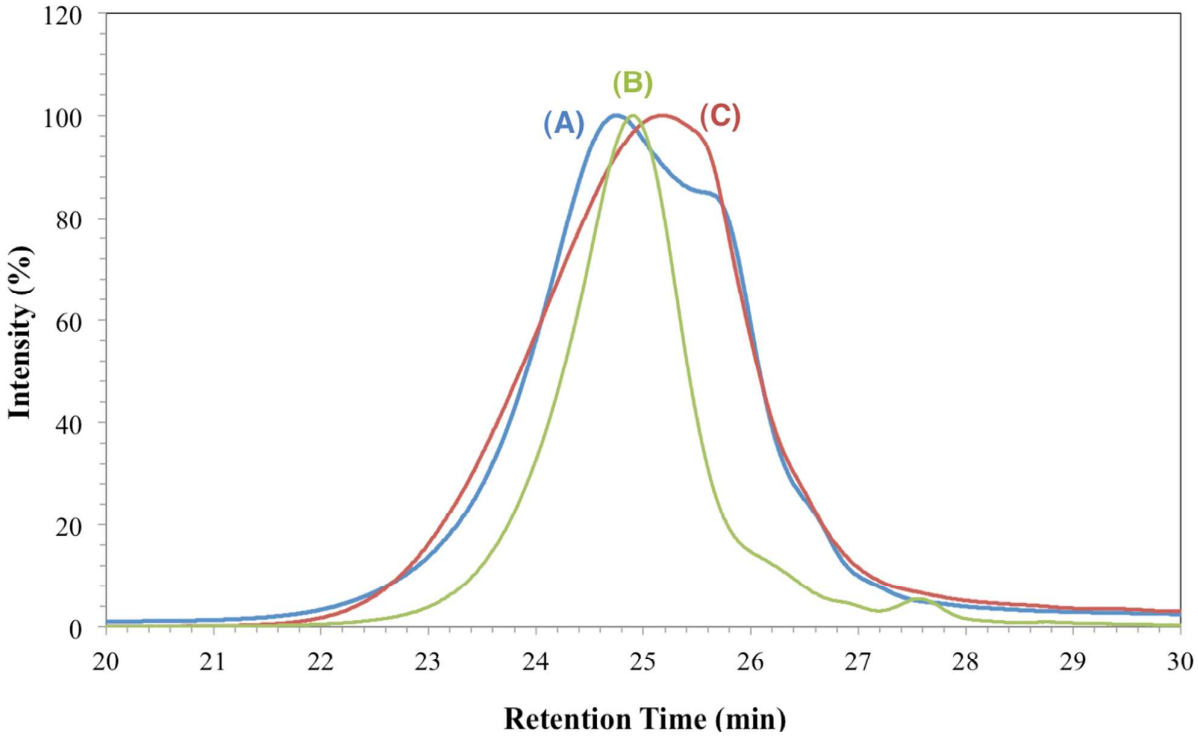


Figure S51. SEC profiles of (A) a co-injected mixture of PMMA–CN^+O^- **P1** and graft copolymer **GP2d**, (B) PMMA–CN^+O^- **P1**, and (C) graft copolymer **GP2d** (eluent: $CHCl_3$).

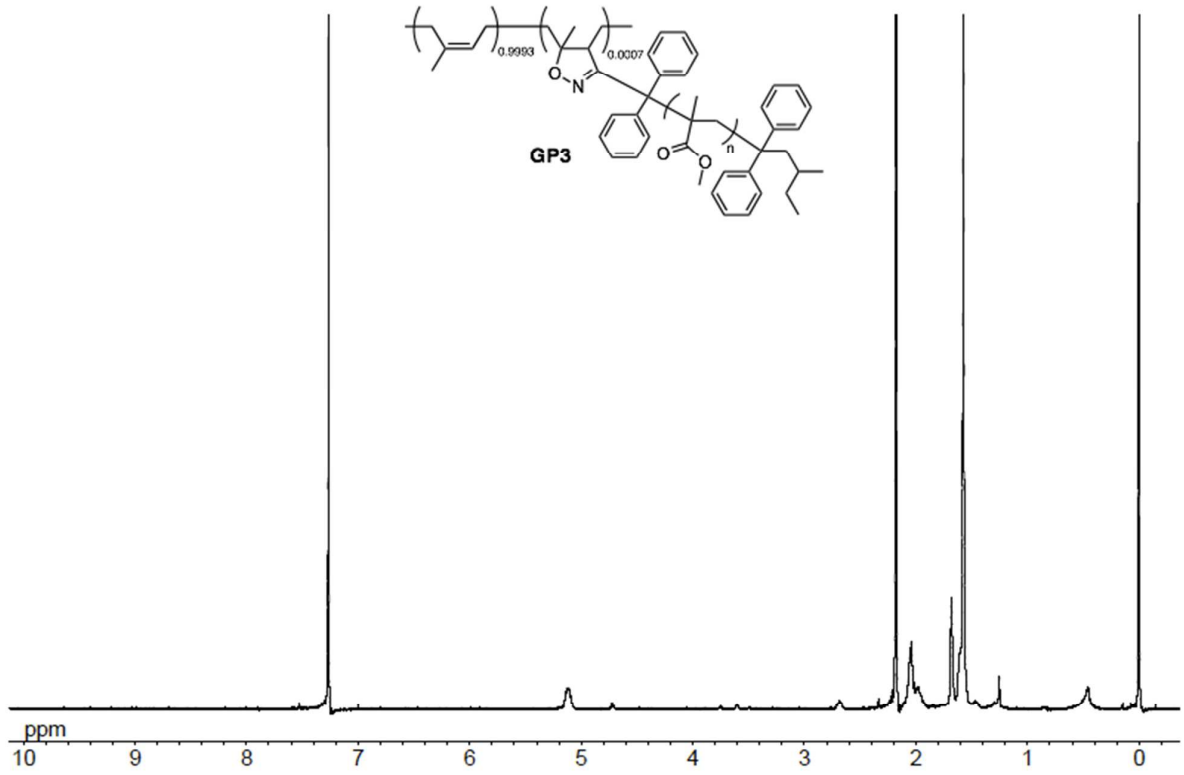


Figure S52. ^{1}H NMR spectrum of **GP3** (400 MHz, 298 K, $CDCl_3$).

References

[1] Wang, C.-G.; Koyama, Y.; Yonekawa, M.; Uchida, S.; Takata, T. *Chem. Commun.* **2013**, *49*, 7723–7725.

[2] Grant, D. H.; Grassie, N. *Polymer*, **1960**, *1*, 445–455.