

Electronic Supplementary Information (ESI)

Synthesis of Vinyl Iodide Chain-end Polymers *via* Organocatalyzed Chain-end Transformation

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1. Experimental

Materials. Butyl acrylate (BA) (>99.8%, Tokyo Chemical Industry (TCI), Japan), 2-methoxyethyl acrylate (MEA) (>98%, TCI), methyl methacrylate (MMA) (>99.8%, TCI), 2-iodo-2-methylpropionitrile (CP-I) (>95%, TCI), phenylacetylene (PA) (98%, Aldrich, USA), 4-ethynylbenzyl alcohol (EBA) (97%, Aldrich), 4-ethynyltrifluorotoluene (TFT) (97%, Aldrich), 4-ethynylbiphenyl (EBP) (97%, Aldrich), poly(ethylene glycol) methyl ether thiol (average molecular weight = 800) (Aldrich), 2-phenylethanethiol (98%, Aldrich), 3,6-dioxa-1,8-octanedithiol (>97%, TCI), dodecanethiol (\geq 98%, Aldrich), 2-mercaptoethanol (>98%, TCI), triphenylphosphine (>95%, TCI), copper iodide (\geq 99.5%, Aldrich), 1,10-phenanthroline (\geq 99%, Aldrich), potassium phosphate tribasic (\geq 98%, Aldrich), multi-walled carbon nanotubes (CNT) (>90% carbon basis, 110-170 nm diameter, 5-9 μ m length, Aldrich), diethylene glycol dimethyl ether (diglyme) (>99.0%, TCI), tetrahydrofuran (THF) (>99.5%, Kanto Chemical, Japan), methanol (\geq 99.8%, VWR, USA), chloroform (>99%, VWR), hexane (>99%, International Scientific, Singapore), toluene (99.5%, J.T. Baker, USA), tetrabutylammonium iodide

(BNI) (>98%, TCI), sodium trifluoroacetate (NaTFA) (>98%, TCI), and *trans*-2-[3-(4-*t*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (>99%, Aldrich) were used as received. 3-(Polyethylene glycol monomethyl ether)-prop-1-yne (PEG-alkyne) (average molecular weight = 400) was synthesized according to the literature.¹

Analytical GPC. The gel permeation chromatography (GPC) analysis was performed on a Shimadzu LC-2030C Plus liquid chromatograph (Kyoto, Japan). The Shimadzu LC-2030C Plus GPC was equipped with a Shodex (Japan) KF-804L mixed gel column (300 × 8.0 mm; bead size = 7 μm; pore size = 1500 Å) and a Shodex LF-804 mixed gel column (300 × 8.0 mm; bead size = 6 μm; pore size = 3000 Å). The eluent was THF at a flow rate of 0.7 mL/min (40 °C). Sample detection and quantification were conducted using a Shimadzu differential refractometer RID-20A. The column system was calibrated with standard poly(methyl methacrylate)s (PMMA)s.

Preparative GPC. Polymers were purified with a preparative GPC (LC-9204, Japan Analytical Industry, Tokyo) equipped with JAIGEL 1H and 2H polystyrene gel columns (600×40 mm; bead size = 16 μm; pore size = 20-30 (1H) and 40-50 (2H) Å). Chloroform was used as eluent at a flow rate of 14 mL/min (room temperature).

NMR. The NMR spectra were recorded on a Bruker (Germany) BBFO spectrometer (400 MHz) at ambient temperature. Acetonitrile-*d*₃ or CDCl₃ (Cambridge Isotope Laboratories, USA) was used as a solvent, and the chemical shift was calibrated using the residual undeuterated solvent or tetramethylsilane (TMS) as the internal standard.

MALDI-TOF-MS. The matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) spectra were recorded on a JMS-S3000 SpiralTOF (JEOL, Japan) at an accelerating potential of 20 kV in the positive spiral mode. We prepared a polymer solution (polymer sample: 10 g/L in THF), a matrix solution (DCTB: 60 g/L in THF), and a cationization agent solution (NaTFA: 10 g/L in THF). The polymer solution, the DCTB solution, and the cationization agent solution were mixed in a

ratio of 1/2/1 (v/v/v). Then, 5 μL of the mixed solution was deposited on the target plate spot and dried in the air at room temperature.

Sonication. The sonication of CNT samples was performed in a SK8300GT ultrasonic cleaner (KUDOS, China) at a frequency of 35 kHz and an ultrasonic power of 600W.

CNT Dispersion Size Analysis. The CNT dispersion size analysis was performed on a Mastersizer 3000 laser diffraction particle size analyzer (Malvern Panalytical, UK) at a stirring speed of 1000 rpm.

Synthesis of PBA-I. A mixture of BA (20.0 g, 156 mmol), CP-I (304 mg, 1.56 mmol), and BNI (2.31 g, 6.24 mmol) was heated in a Schlenk flask at 110 °C under argon atmosphere with magnetic stirring. After 6 h, the mixture was cooled to room temperature and diluted with THF (10 mL). The polymer was reprecipitated from methanol/water (7/3 v/v) (200 mL) twice to completely remove the monomer and catalyst and dried in vacuo to give a PBA-I (monomer conversion = 26%, $M_n = 4000$ and $D = 1.19$ after purification).

Synthesis of PMEAI-I. A mixture of MEA (3.0 g, 23 mmol), CP-I (45 mg, 0.23 mmol), and BNI (341 mg, 0.92 mmol) was heated in a Schlenk flask at 110 °C under argon atmosphere with magnetic stirring. After 6 h, the mixture was cooled to room temperature and diluted with CHCl_3 (10 mL). The polymer was purified using a preparative GPC and reprecipitated into hexane to completely remove the monomer and catalyst and dried in vacuo to give a PMEAI-I (monomer conversion = 31%, $M_n = 6200$ and $D = 1.25$ after purification).

Synthesis of PMMA-I. A mixture of MMA (4.0 g, 40 mmol), CP-I (78 mg, 0.40 mmol), and BNI (148 mg, 0.40 mmol) was heated in a Schlenk flask at 70 °C under argon atmosphere with magnetic stirring. After 40 min, the mixture was cooled to room temperature and diluted with CHCl_3 (10 mL). The polymer was purified using a preparative GPC and reprecipitated into hexane to completely remove the monomer and catalyst and dried in vacuo to give a PMMA-I (monomer conversion = 37%, $M_n = 4200$ and $D = 1.19$ after purification).

Synthesis of Vinyl Iodide Chain-End Polymers. In a typical run, a mixture of alkyne, Polymer-I (PBA-I, PMEAI or PMMA-I), BNI, and diglyme (solvent) was heated in a Schlenk flask at 110 °C under argon atmosphere with magnetic stirring for a prescribed time. After the reaction, the mixture was cooled to room temperature and dissolved in CHCl₃. The polymer was purified using a preparative GPC to remove small molecules, and the purified polymer was analyzed with MALDI-TOF-MS.

Cross-Coupling of Vinyl Iodide Chain-End Polymers with Thiols. A vinyl iodide chain-end polymer PBA-PA_m-I listed in Table 1 (entry 2) (140 mg, 0.035 mmol), dodecanethiol (71 mg, 0.35 mmol), 1,10-phenanthroline (7.6 mg, 0.042 mmol), and triphenylphosphine (22 mg, 0.084 mmol) in toluene (1 mL) were added to a Schlenk flask and the solution was degassed *via* three freeze-pump-thaw cycles. Potassium phosphate tribasic (15 mg, 0.070 mmol) and copper iodide (6.7 mg, 0.035 mmol) were then added to the solution under argon atmosphere. The mixture was heated at 100 °C under magnetic stirring for 24 h. After the reaction, the polymer was purified using a preparative GPC to remove small molecules. The purified polymer was analyzed with MALDI-TOF-MS. The reactions with mercaptoethanol, 2-phenylethanethiol, 3,6-dioxa-1,8-octanedithiol, and poly(ethylene glycol) methyl ether thiol were conducted similarly.

Dispersion of Carbon Nanotube. A mixture of 1 mg of multi-walled CNT (110–170 nm diameter, 5–9 μm length) and 200 mg of polymer (PBA-PA_m-I or PBA-I) in 8 mL of toluene was sonicated for 30 min and subsequently stood for 30 min (Fig. 2). A 1 mL sample was taken using a syringe, further diluted with 7 mL of toluene, and was analyzed using a dispersion size analyzer.

2. ^1H NMR Analysis of Polymer-Iodides.

Fig. S1 shows the ^1H NMR spectrum of the purified PBA-I. The OCH_2 protons (d) of the monomer units appeared at 3.9–4.2 ppm. The downfield shifted signal at 4.3–4.4 ppm was assigned to the ω -terminal chain-end CH unit (c') bearing iodine. From the peak areas of c' and d , as well as the M_n value (= 4000) determined with GPC, the fraction of the iodine chain end was calculated to be 98% (93–100% with experimental error). The M_n value (= 4000) is not an absolute molecular weight but a PMMA-calibrated GPC value, and thus the calculated iodide-chain-end fidelity is viewed as an estimate.

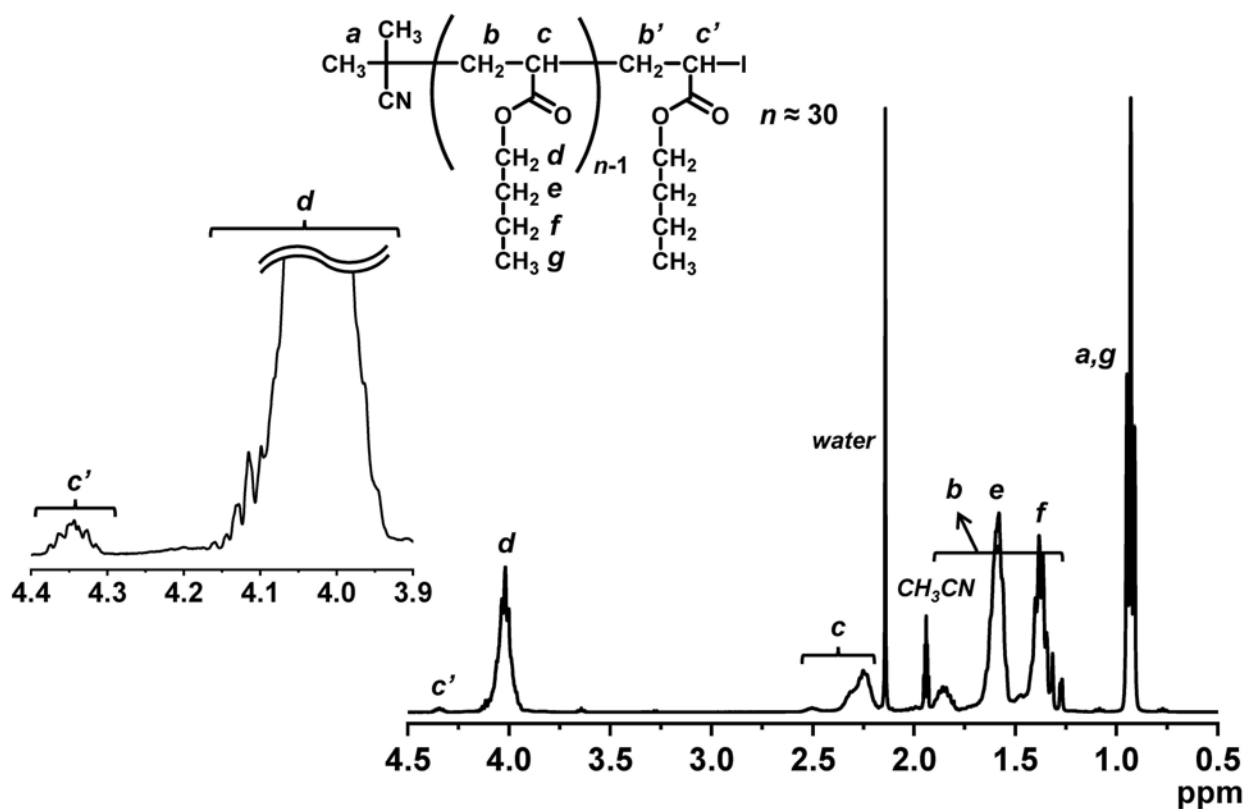


Fig. S1. ^1H NMR spectrum (CD_3CN) of PBA-I.

Fig. S2 shows the ^1H NMR spectrum of the purified PMEAI. The ester OCH_2 protons of the side chains (c) appeared at 4.0–4.4 ppm. The downfield shifted signal at 4.4–4.5 ppm was assigned to the ω -terminal chain-end CH unit (b'). From the peak areas of b' and c , as well as the M_n value (= 6200) determined with GPC, the fraction of the iodine chain end was calculated to be 88% (83–93% with experimental error). The M_n value (= 6200) is not an absolute molecular weight but a PMMA-calibrated GPC value, and thus the calculated iodide-chain-end fidelity is viewed as an estimate.

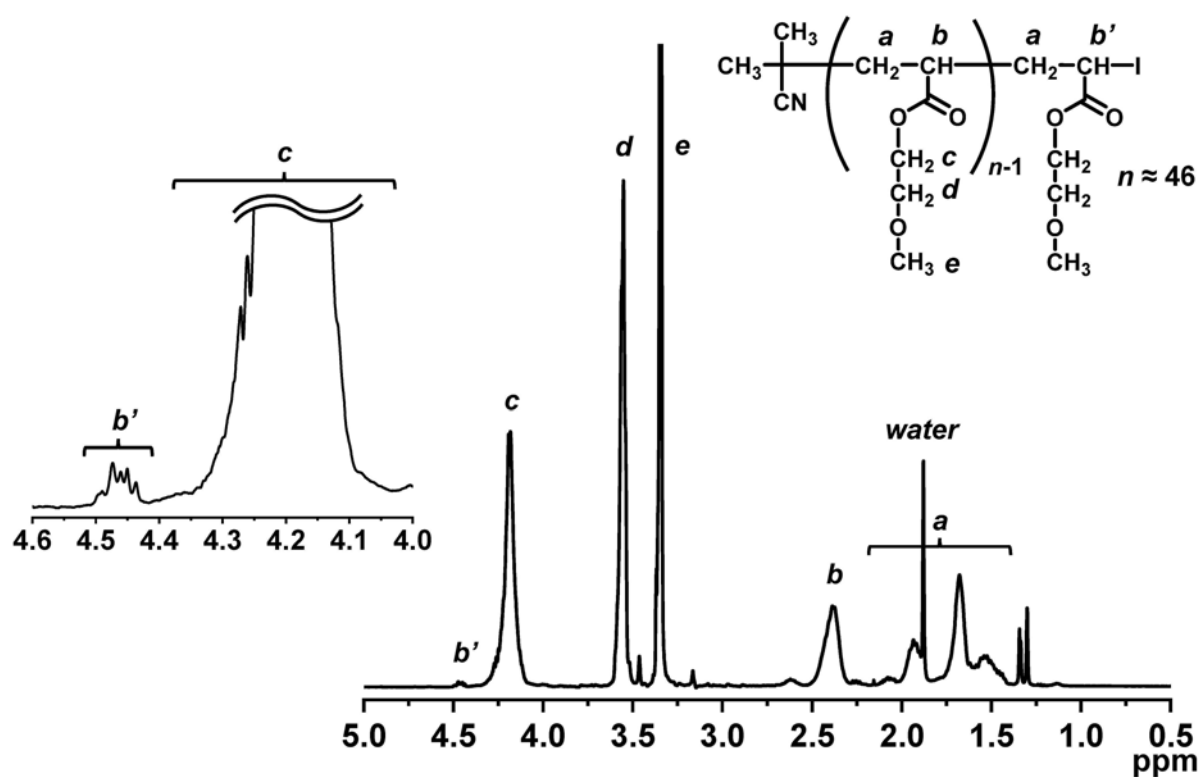


Fig. S2. ^1H NMR spectrum (CDCl_3) of PMEAI.

Fig. S3 shows the ^1H NMR spectrum of the purified PMMA-I. The ester OCH_3 protons of the side chains (a) appear at 3.5–3.7 ppm. The ω -terminal chain-end OCH_3 unit (a') appears at 3.72–3.76 ppm. From the peak area of a and a' , as well as the M_n value (= 4200) determined with GPC, the fraction of the iodine chain end was calculated to be 87% (82–92% with experimental error).

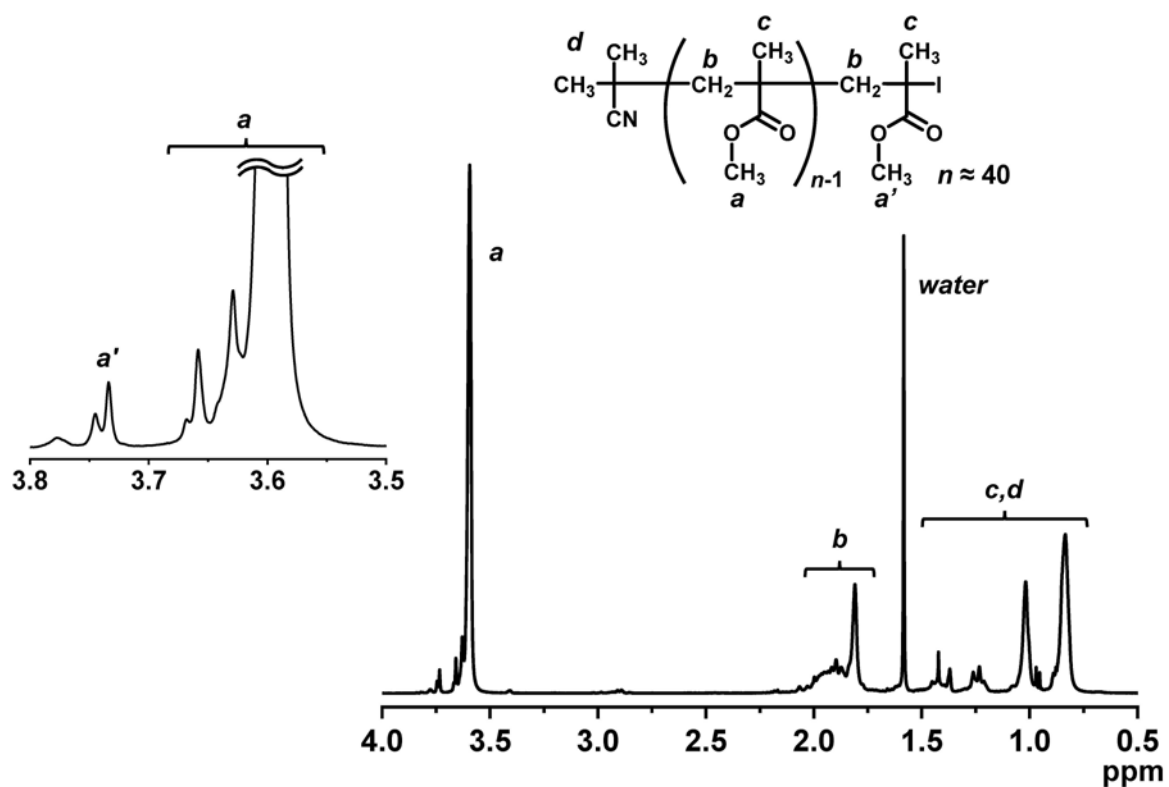


Fig. S3. ^1H NMR spectrum (CDCl_3) of PMMA-I.

3. MALDI-TOF-MS analysis of Polymer-I.

The obtained PBA-I, PMEAI, and PMMA-I were analyzed with MALDI-TOF-MS. The theoretical masses of the polymers are calculated as follows:

$$68.05 + 128.0838 \times n + Y + 22.99 \text{ (for PBA-I)} \quad (1)$$

$$68.05 + 130.0625 \times n + Y + 22.99 \text{ (for PMEAI)} \quad (2)$$

$$68.05 + 100.0524 \times n + Y + 22.99 \text{ (for PMMA-I)} \quad (3)$$

where 68.05 is the mass of the initiating CP chain end, 128.0838 is the mass of the repeating unit of BA monomer, 130.0625 is the mass of the repeating unit of MEA monomer, 100.0524 is the mass of the repeating unit of MMA, 22.99 is the mass of the additive cation Na^+ , n is the degree of polymerization, and Y is the mass of the terminal chain end. The theoretical masses and experimental masses given in the figures are those without ^{13}C atoms (containing only ^{12}C atoms).

Figs. S4a and S4b show the MALDI-TOF-MS spectrum of PBA-I. A main series of peaks were observed at 2523.58, for example, with regular intervals of 128.09 (BA unit) (Fig. S4a). The experimental isotope distribution well matches the theoretical distribution of PBA-I (Fig. S4b). Three series of minor peaks were also observed at 2537.85, 2541.82 and 2595.81. These species were generated during the polymerization or during the MALDI-TOF-MS analysis. These species are assigned to PBA with an unsaturated chain end (PBA-ene) (theoretical mass = 2537.64), PBA with a hydroxyl chain end (PBA-OH) (theoretical mass = 2541.63), and PBA with a lactone ring chain end (PBA-Lac) (theoretical mass = 2595.64). No radical-radical termination product was observed (theoretical mass = 2592.61). Because of the radical nature of the polymerization, termination did occur. The result suggests that the amount of the terminated polymer was negligibly small in this particular case.

The MALDI-TOF-MS spectrum of PMEAI is shown in Fig. S4c. A main series of peaks at 4250.23 with regular intervals of 130.06 (MEA unit) were observed and corresponds to PMEAI (theoretical mass = 4249.90). Four series of minor peaks were also observed at 4266.40, 4270.47, 4288.41 and 4324.43. They are assigned to PMEAI macromonomer (PMEAI-ene) (theoretical mass = 4266.06), PMEAI with a hydroxyl chain end (PMEAI-OH) (theoretical mass = 4270.06), and PMEAI with a lactone ring chain end (PMEAI-Lac) (theoretical mass = 4324.07). The species experimentally observed at 4288.41 remains unclear.

Fig. S4d shows the MALDI-TOF-MS spectrum of PMMA-I. PMMA-I was not observed directly. Instead, two polymer species generated from PMMA-I were observed with regular intervals of 100.06 (MMA unit). These species correspond to PMMA-Lac (theoretical mass = 4478.32) and PMMA-ene (theoretical mass = 4492.34), which were generated during the MALDI-TOS-MS analysis.^{2,3}

4. MALDI-TOF-MS Analysis for the Reaction of PBA-I and 10 Equiv. of PA for 14 h.

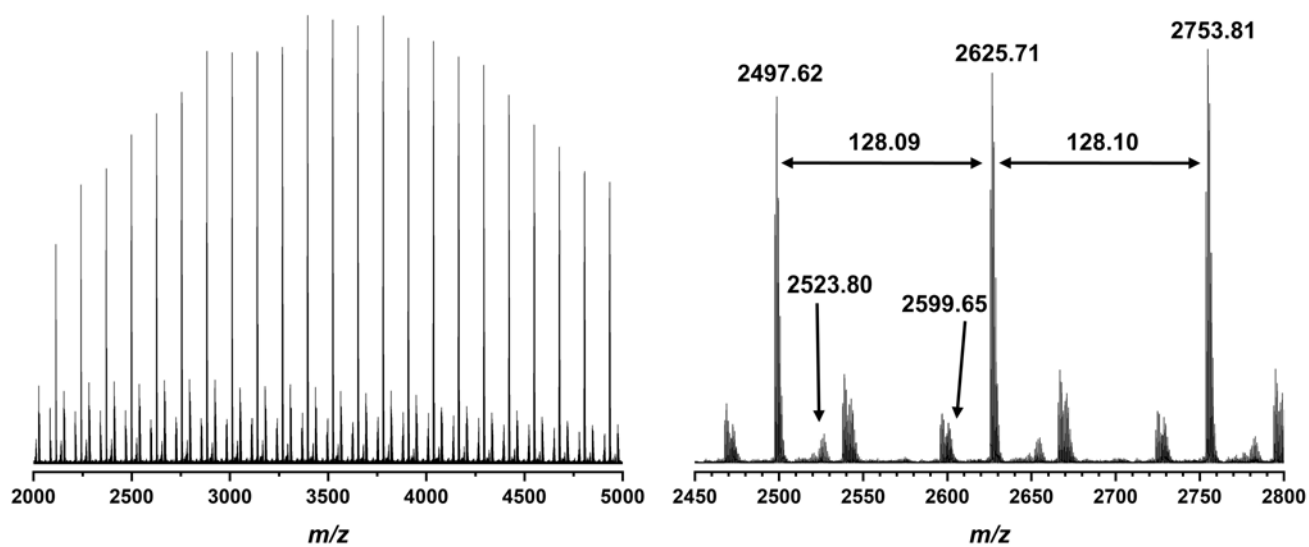


Fig. S5. MALDI-TOF-MS spectrum for the reaction of PBA-I and 10 equivalent of PA for 14 h (Table 1, entry 2).

5. MALDI-TOF-MS Analysis for the Reaction of PBA-I and 30 Equiv. of PA.

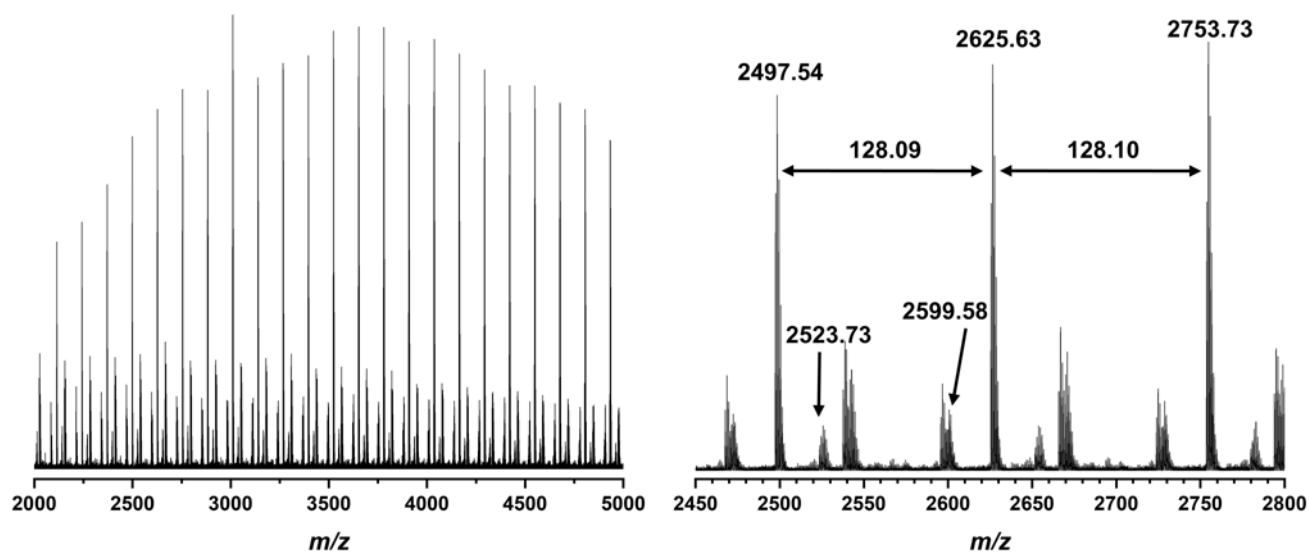


Fig. S6. MALDI-TOF-MS spectrum for the reaction of PBA-I and 30 equivalent of PA (Table 1, entry 3).

6. MALDI-TOF-MS Analysis for the Reaction of PBA-I and 60 Equiv. of PA.

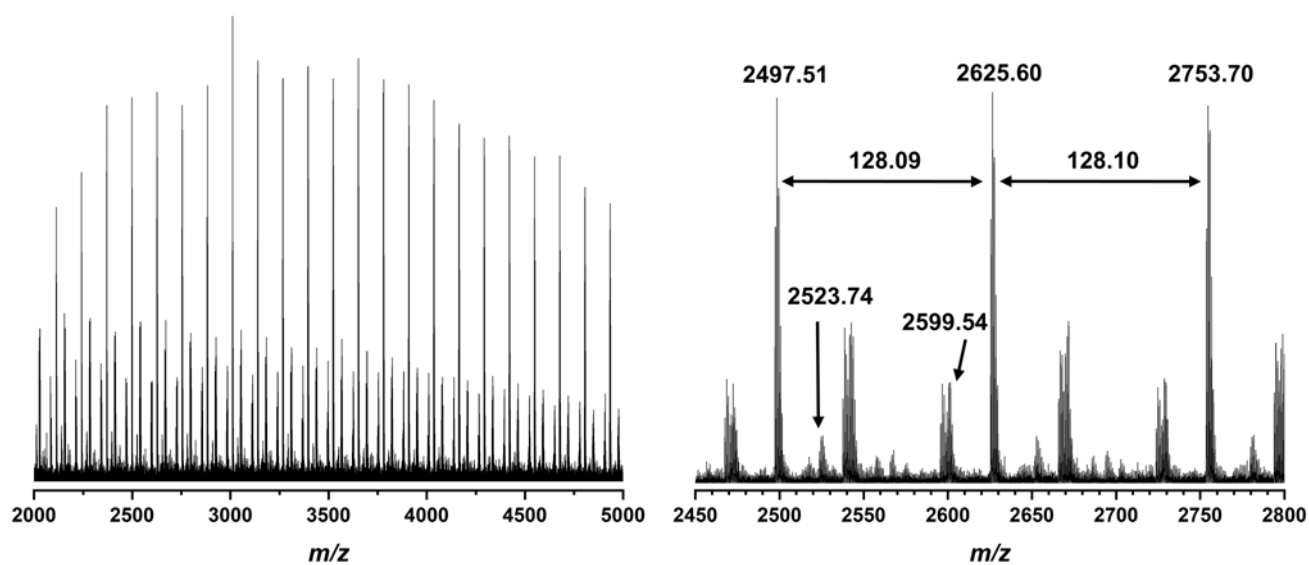


Fig. S7. MALDI-TOF-MS spectrum for the reaction of PBA-I and 60 equivalent of PA (Table 1, entry 4).

7. MALDI-TOF-MS Analysis for the Reaction of PBA-I and 100 Equiv. of PA.

Fig. S8 shows the MALDI-TOF-MS spectrum for the reaction of PBA-I with 100 equivalent of PA without solvent (Table 1, entry 5). We observed three additional series at 2573.59, 2547.63 and 2521.62 belonging to PBA-PA₃-I, PBA-PA₄-I, and PBA-PA₅-I, respectively (theoretical mass = 2573.42, 2547.39, and 2521.35, respectively).

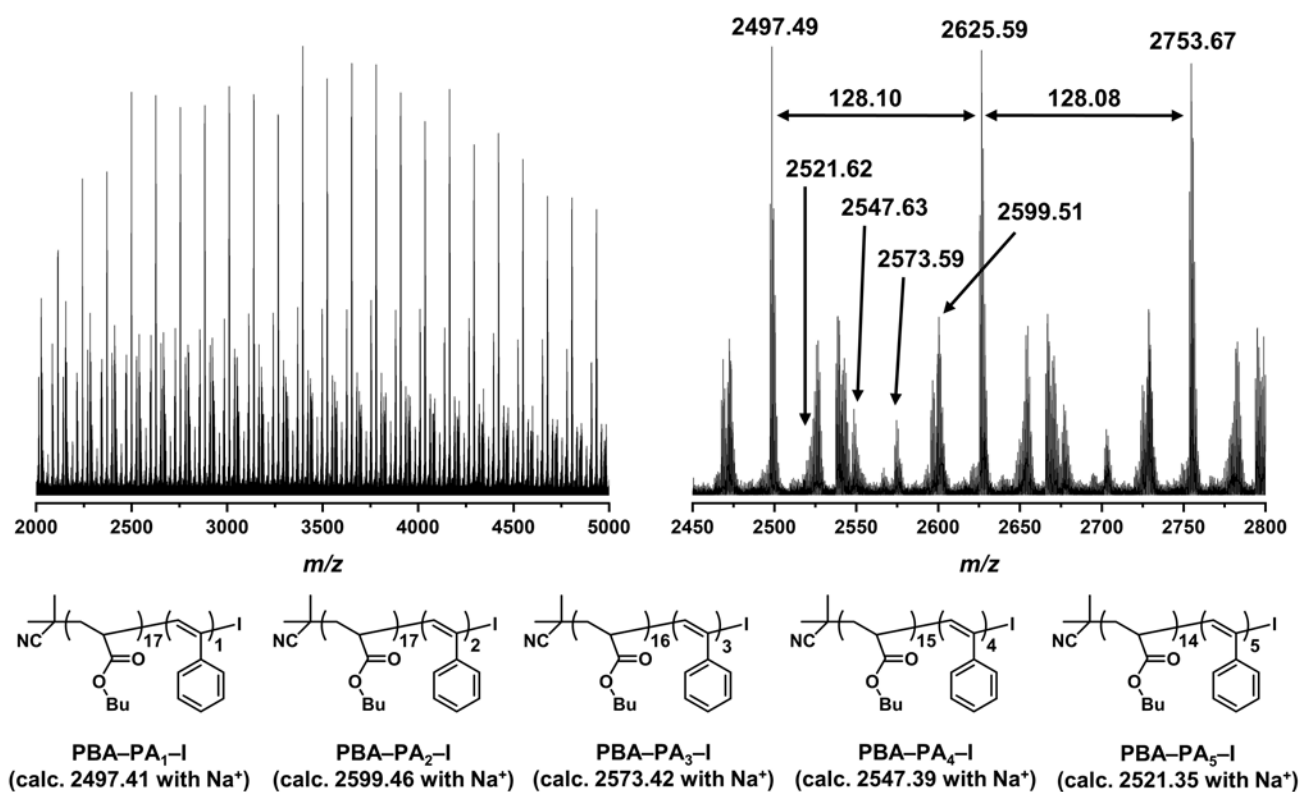


Fig. S8. MALDI-TOF-MS spectrum for the reaction of PBA-I and 100 equivalent of PA without solvent (Table 1, entry 5).

8. MALDI-TOF-MS Analysis for the Reaction of PBA-I and 100 Equiv. of PA.

Fig. S9 shows the MALDI-TOF-MS spectrum for the reaction of PBA-I with 100 equivalent of PA in 50% diglyme (solvent) (Table 1, entry 6).

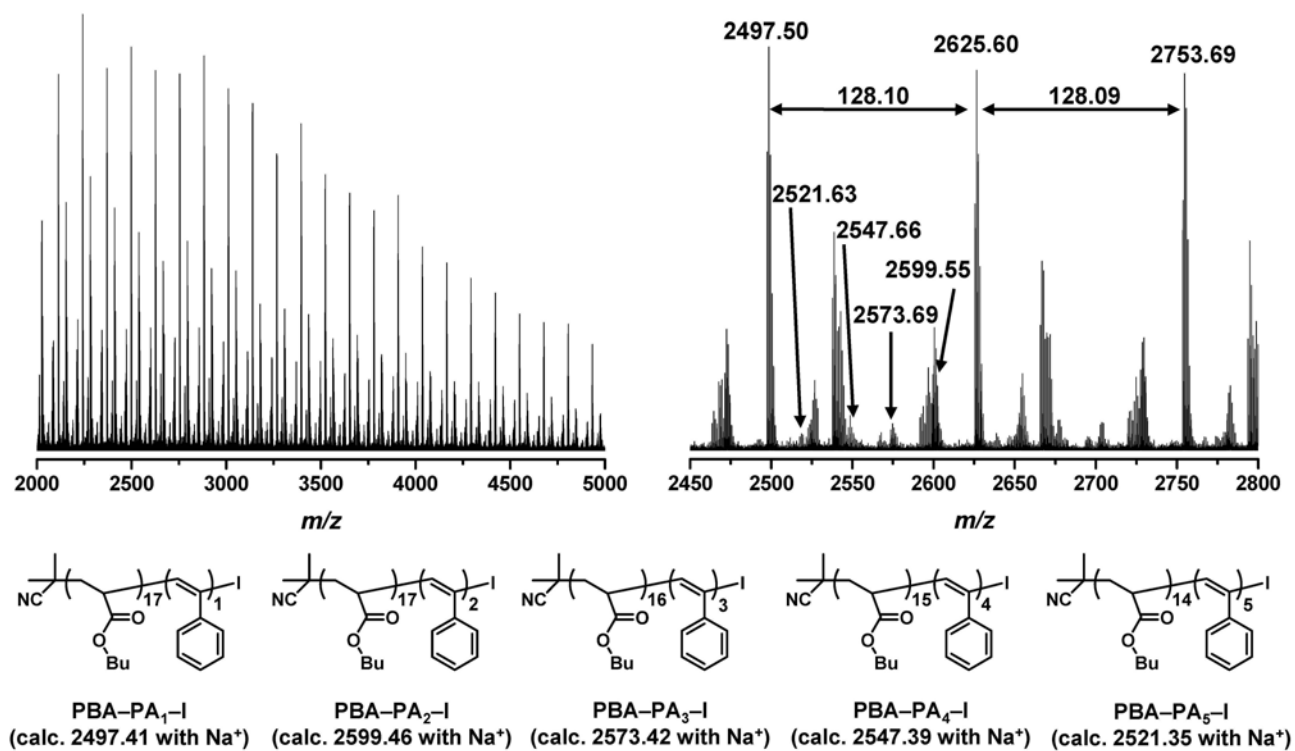


Fig. S9. MALDI-TOF-MS spectrum for the reaction of PBA-I and 100 equivalent of PA in 50% diglyme (solvent) (Table 1, entry 6).

9. MALDI-TOF-MS Analysis for the Reaction of PBA-I and 300 Equiv. of PA.

Fig. S10 shows the MALDI-TOF-MS spectrum for the reaction of PBA-I with 300 equivalent of PA, (Table 1, entry 7). We observed an additional series at 2495.37 belonging to PBA-PA₆-I (theoretical mass = 2495.31).

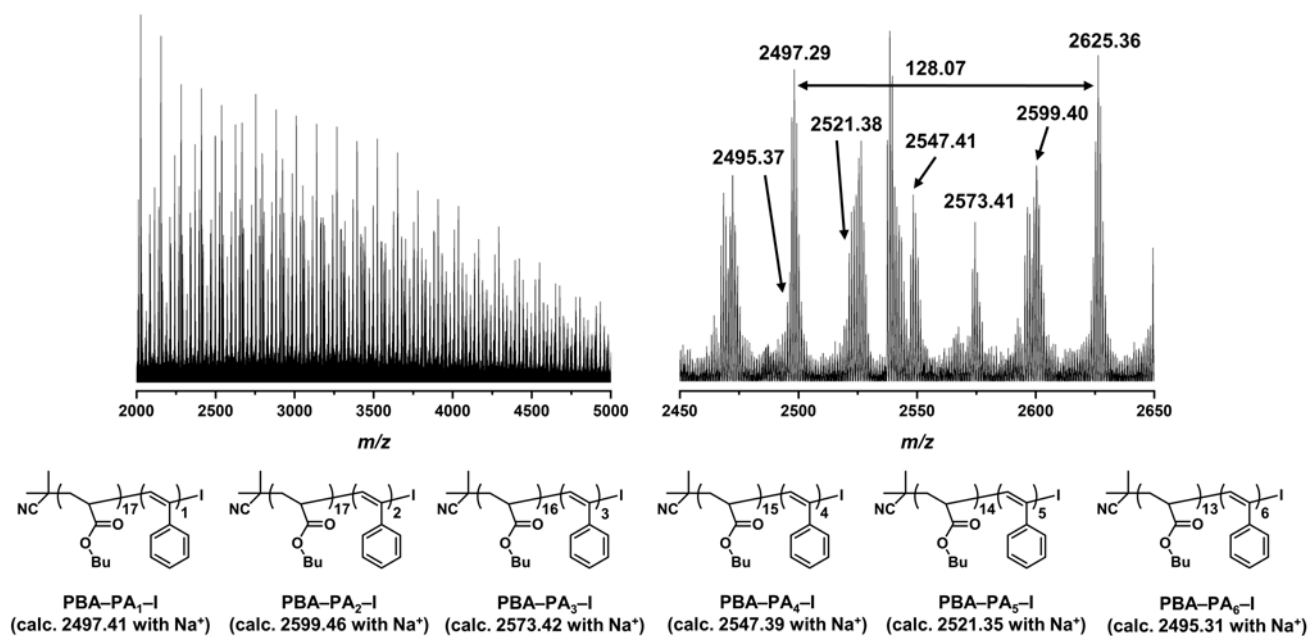


Fig. S10. MALDI-TOF-MS spectrum for the reaction of PBA-I and 300 equivalent of PA (Table 1, entry 7).

10. MALDI-TOF-MS Analysis for the Reaction of PMEAI and PA.

Fig. S11 shows the MALDI-TOF-MS spectrum for the reaction of PMEAI with PA (Table 1, entry 8). No PMEAI remained, and we observed only one series of major peaks at 4352.16, corresponding to PMEAI-PA₁-I (theoretical mass = 4351.94). Based on the peak intensity ratios, 90% of PMEAI was converted to the desired PMEAI-PA₁-I. The rest (10%) was an unidentified species at 4253.26. The peaks observed at 4270.29 and 4324.30 correspond to PMEAI-OH and PMEAI-Lac, respectively, which were observed in the original PMEAI sample (Fig. S4c) and are excluded from the calculation.

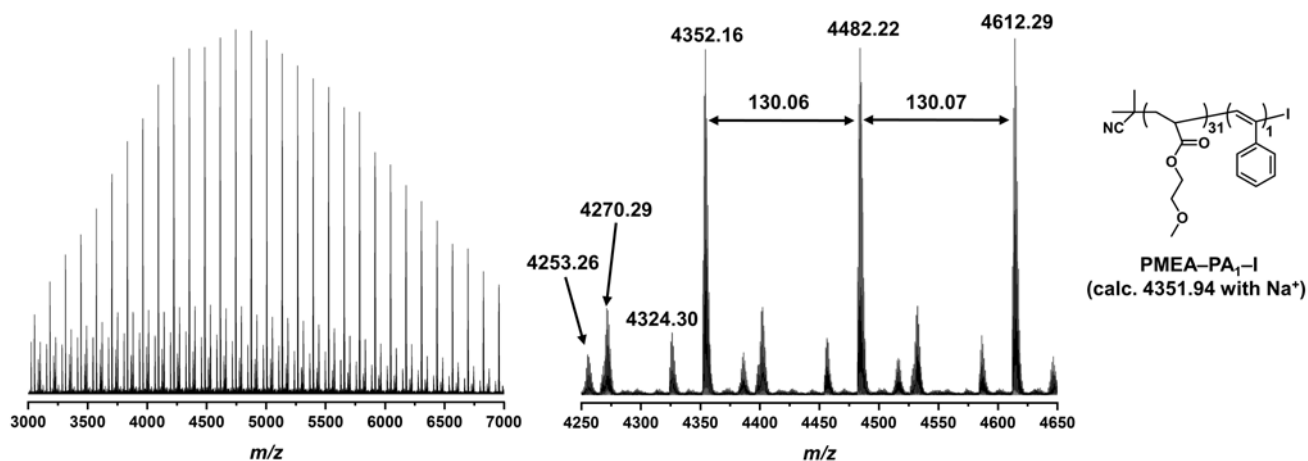
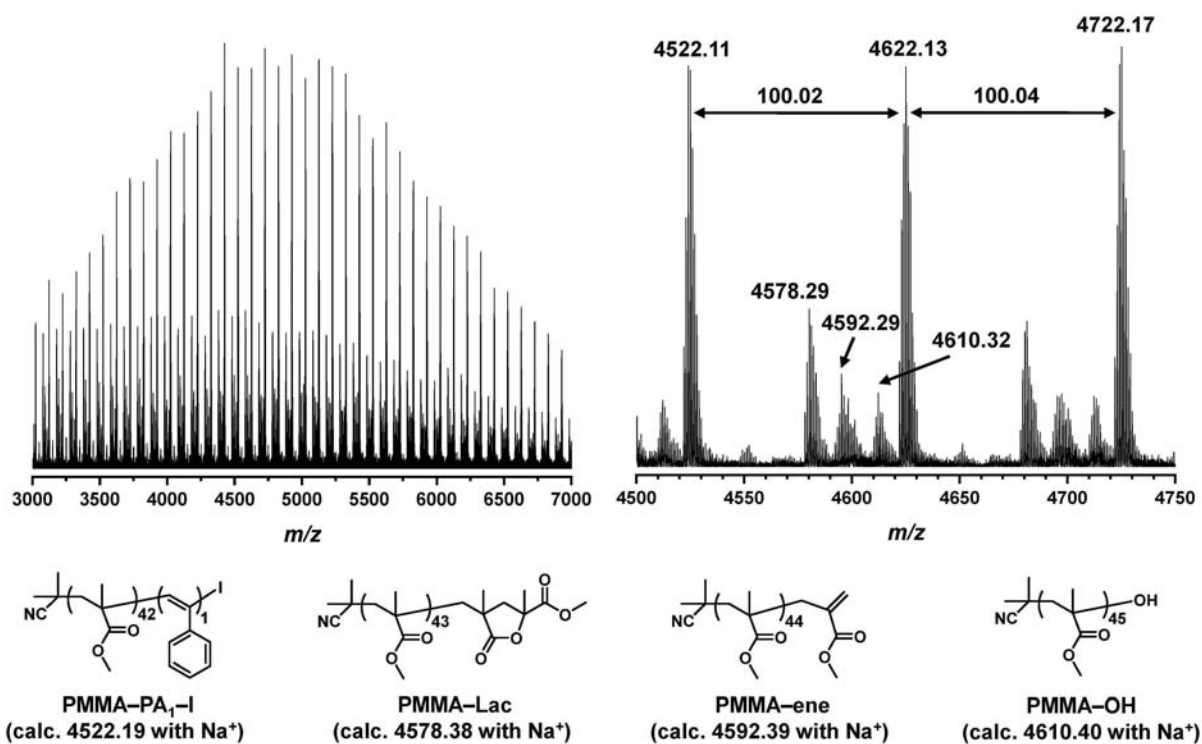


Fig. S11. MALDI-TOF-MS spectrum after the reaction of PMEAI and PA (Table 1, entry 8).

11. MALDI-TOF-MS Analysis for the Reaction of PMMA-I and PA.

Fig. S12 shows the MALDI-TOF-MS spectrum for the reaction of PMMA-I with PA. 41% of PMMA-I remained. As Fig. S4d shows, PMMA-I was converted to PMMA-Lac (theoretical mass = 4578.38) and PMMA-ene (theoretical mass = 4592.39) during the MALDI-TOS-MS analysis. Thus, the sum (41%) of PMMA-Lac and PMMA-ene observed in Fig. S12a is the fraction of the remaining PMMA-I. The isotope distribution (Fig. S12b) indicates a mixture of PMMA-PA₁-I and PMMA-PA₂-I at a ratio of 82:18, although PMMA-PA_{*m*}-I with more PA units ($m \geq 3$) might also be generated as a possibility. The values (41% for PMMA-I, 50% for PMMA-PA₁-I, and 9% for PMMA-PA₂-I) given in Table 1 (entry 9) assume no generation of PMMA-PA_{*m*}-I with $m \geq 3$.

(a) Reaction of PMMA-I with 100 equiv. PA (70 °C, 14 h) (Table 1, entry 9)



(b) Isotope distributions

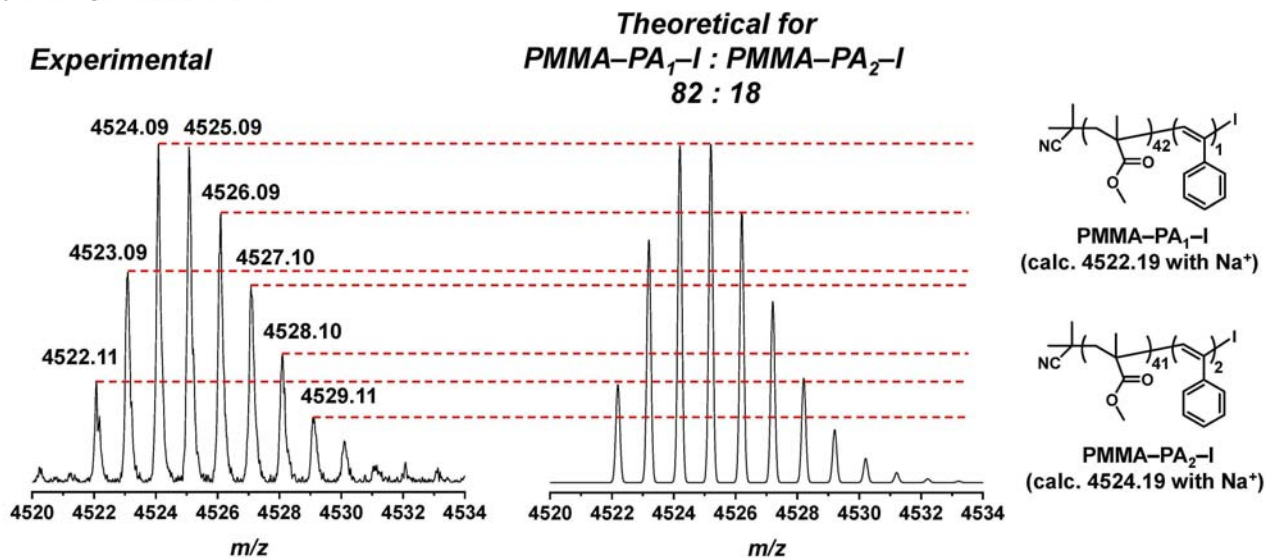
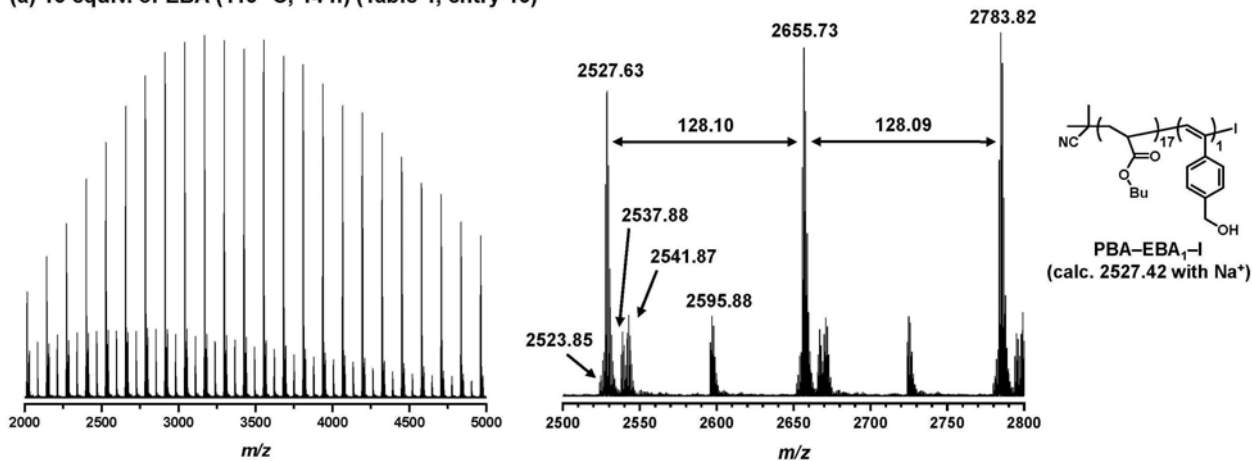


Fig. S12. (a) MALDI-TOF-MS spectrum of the polymer after the reaction of PMMA-I and PA (Table 1, entry 9) and (b) isotope distribution of the polymer experimentally obtained and theoretical isotope distribution for a mixture of PMMA-PA₁-I and PMMA-PA₂-I (82:18).

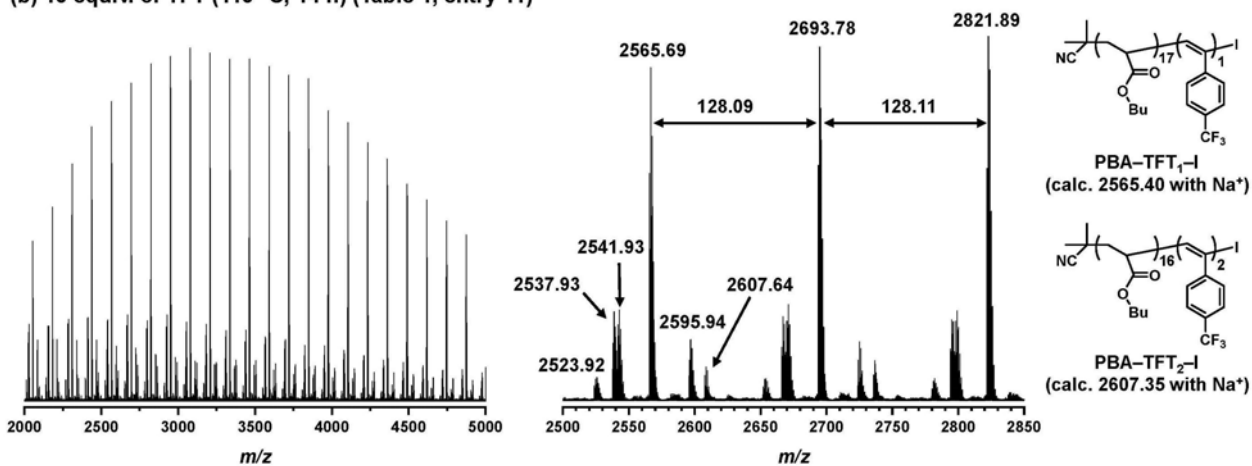
12. MALDI-TOF-MS Analysis for the Reactions of PBA-I with EBA, TFT, and EBP.

Fig. S13a shows the MALDI-TOF-MS spectrum for the reaction of PBA-I with EBA (Table 1, entry 10). The peak at 2527.63 corresponds to PBA-EBA₁-I (theoretical mass = 2527.42). 92% of PBA-I was converted to the desired PBA-EBA₁-I, and 8% of PBA-I remained. The peaks at 2537.88, 2541.87 and 2595.88 correspond to PBA-ene, PBA-OH, and PBA-Lac, respectively, which were observed in the original PBA-I (Fig. S4a) and are excluded from the calculation. Fig. S13b shows the MALDI-TOF-MS spectrum for the reaction of PBA-I with TFT (Table 1, entry 11). The peak at 2565.69 corresponds to PBA-TFT₁-I (theoretical mass = 2565.40). PBA-I was converted to the desired PBA-TFT₁-I (84%) as well as PBA-TFT₂-I (9%), and 7% of PBA-I remained. The peaks at 2537.93, 2541.93 and 2595.94 were excluded from the calculation for the same reason as above. Fig. S13c shows the MALDI-TOF-MS spectrum for the reaction of PBA-I with EBP (Table 1, entry 12). The peak at 2573.46 corresponds to PBA-EBP₁-I (theoretical mass = 2573.45). PBA-I was converted to the desired PBA-EBP₁-I (79%) as well as PBA-EBP₂-I (11%), and 10% of PBA-I remained. The peaks at 2537.66, 2541.55 and 2595.66 were excluded from the calculation for the same reason as above.

(a) 10 equiv. of EBA (110 °C, 14 h) (Table 1, entry 10)



(b) 10 equiv. of TFT (110 °C, 14 h) (Table 1, entry 11)



(c) 10 equiv. of EBP (110 °C, 14 h) (Table 1, entry 12)

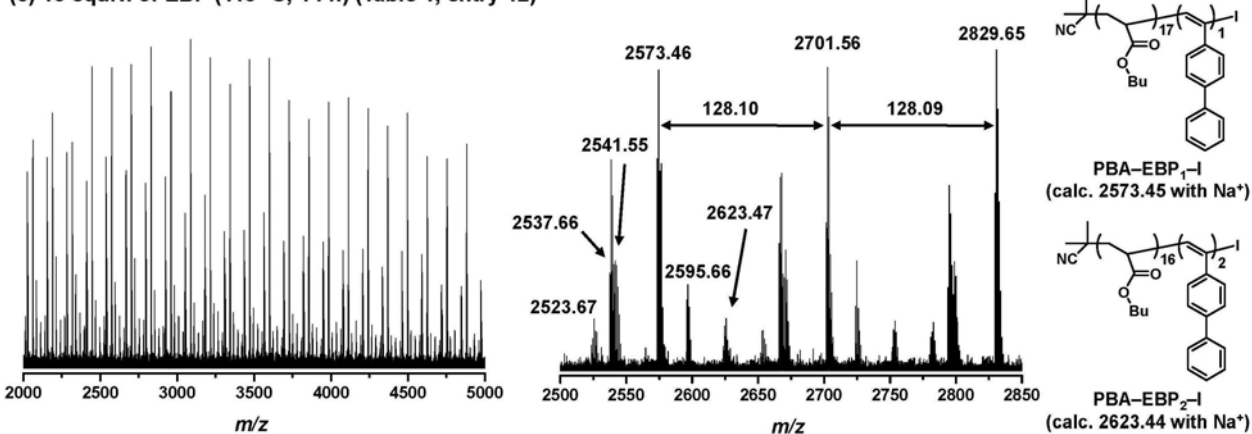


Fig. S13. MALDI-TOF-MS spectra after the reactions of PBA-I with (a) EBA (Table 1, entry 10), (b) TFT (Table 1, entry 11), and (c) EBP (Table 1, entry 12).

13. ^1H NMR Analysis of PBA-(PEG-alkyne) $_m$ -I.

Fig. S14 shows the ^1H NMR spectrum of the purified PBA-(PEG-alkyne) $_m$ -I (Table 1, entry 13). The average n value of the BA monomer units was approximately 30, as discussed above (Fig. S1). The average m value was determined to be approximately 2.1 from the peak areas of OCH_2 protons (a) of the BA monomer units (3.95–4.17 ppm) and $=\text{CCH}_2$ protons (b) of the PEG-alkyne units (4.18–4.23 ppm).

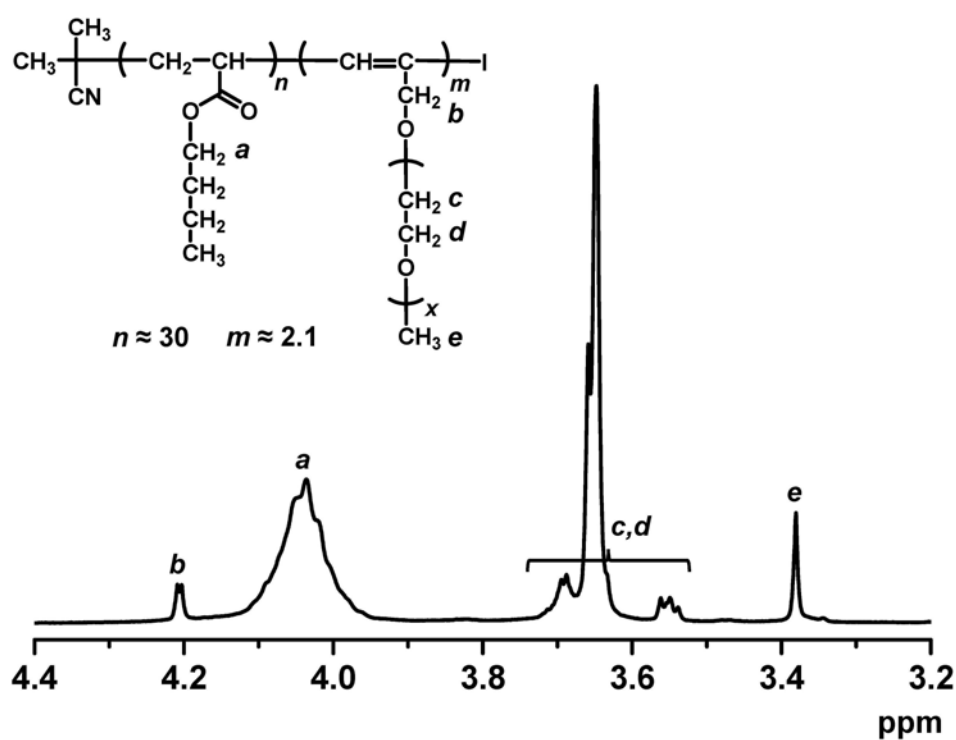


Fig. S14. ^1H NMR spectrum (CDCl_3) of PBA-(PEG-alkyne) $_m$ -I (Table 1, entry 13).

14. MALDI-TOF-MS Analysis for Cross-coupling Reactions of PBA-PA_m-I with Dodecanethiol, Mercaptoethanol, 2-Phenylethanethiol, and 3,6-Dioxa-1,8-octanedithiol.

Fig. S15 shows the MALDI-TOF-MS spectrum for the cross-coupling of PBA-PA_m-I (with $m = 0$ (5%), $m = 1$ (86%), and $m = 2$ (9%) (Table 1, entry 2)) with dodecanethiol (Table 2, entry 1). The peak at 2571.63 corresponds to PBA-PA₁-SC₁₂H₂₅ (theoretical mass = 2571.68) and the peak at 2545.60 corresponds to PBA-PA₂-SC₁₂H₂₅ (theoretical mass = 2545.64). Based on the peak intensities, PBA-PA_m-SC₁₂H₂₅ ($m = 1$ and 2) was generated (85%), a small amount of PBA-PA₁-I ($m = 1$) remained unreacted (10%) (theoretical mass = 2497.41), and PBA-I ($m = 0$) was converted to identified species (5%). The peaks at 2537.61 and 2595.60 belong to PBA-ene and PBA-Lac, which were observed in the original PBA-I (Fig. S4a) and are excluded from the calculations.

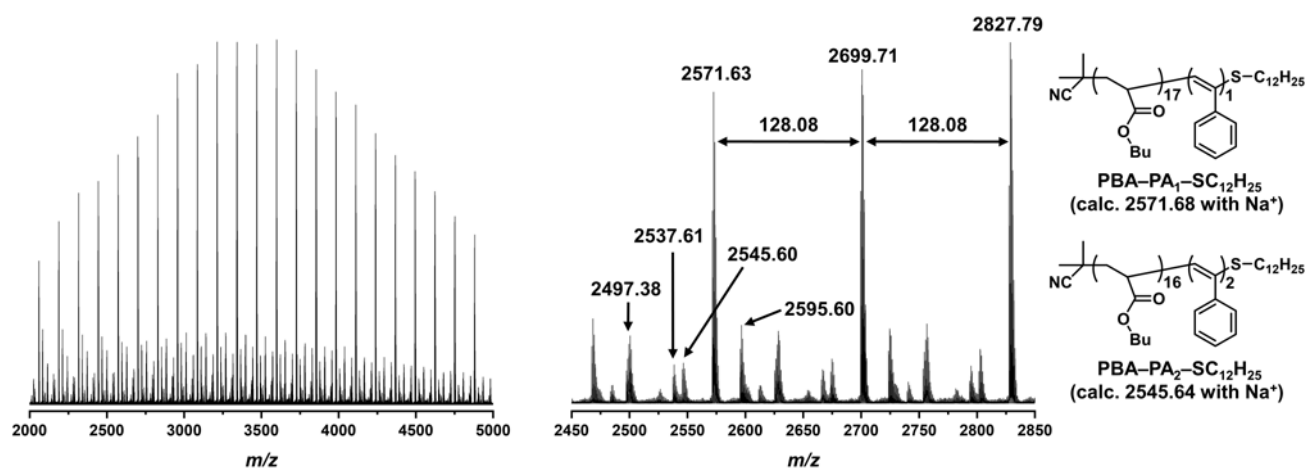


Fig. S15. MALDI-TOF-MS spectrum after the cross-coupling reaction of PBA-PA_m-I with dodecanethiol (Table 2, entry 1).

Fig. S16 shows the MALDI-TOF-MS spectrum for the cross-coupling of PBA-PA_m-I (with $m = 0$ (5%), $m = 1$ (86%), and $m = 2$ (9%) (Table 1, entry 2)) with mercaptoethanol (Table 2, entry 2). The peak at 2447.07 corresponds to PBA-PA₁-SC₂H₄OH (theoretical mass = 2447.52) and the peak at 2549.10 corresponds to PBA-PA₂-SCH₂H₄OH (theoretical mass = 2549.56). Based on the peak intensities, PBA-PA_m-SC₂H₄OH ($m = 1$ and 2) was generated (46%), and some amount of PBA-PA₁-I ($m = 1$) remained unreacted (22%) (theoretical mass = 2497.41). The peaks at 2499.14, 2507.07, 2525.17, 2561.11, and 2615.19 are unidentified side products (totally 32%). The peaks at 2537.19 and 2595.17 belong to PBA-ene and PBA-Lac, respectively, which were observed in the original PBA-I (Fig. S4a) and are excluded from the calculations.

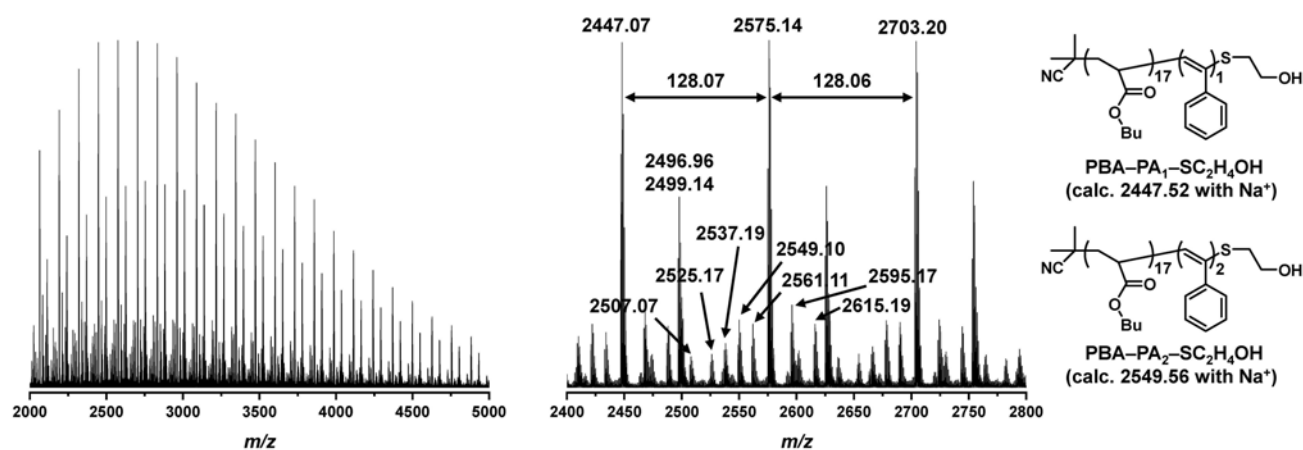


Fig. S16. MALDI-TOF-MS spectrum after the cross-coupling reaction of PBA-PA_m-I with mercaptoethanol (Table 2, entry 2).

Fig. S17 shows the MALDI-TOF-MS spectrum for the cross-coupling of PBA-PA_m-I (with $m = 0$ (5%), $m = 1$ (86%), and $m = 2$ (9%) (Table 1, entry 2)) with 2-phenylethanethiol. The peak at 2507.54 corresponds to PBA-PA₁-SC₂H₄C₆H₅ (theoretical mass = 2507.55) and the peak at 2609.59 corresponds to PBA-PA₂-SC₂H₄C₆H₅ (theoretical mass = 2609.60). Based on the peak intensities, PBA-PA_m-SC₂H₄C₆H₅ ($m = 1$ and 2) was generated (22%), and a large amount of PBA-PA_m-I ($m = 0$ and 1) remained unreacted (73%) (theoretical mass = 2523.45 and 2497.41). The peak at 2565.65 belongs to unidentified side products (totally 5%). The peaks at 2537.62, 2541.63 and 2595.62 belong to PBA-ene, PBA-OH and PBA-Lac, respectively, which were observed in the original PBA-I (Fig. S4a) and are excluded from the calculations.

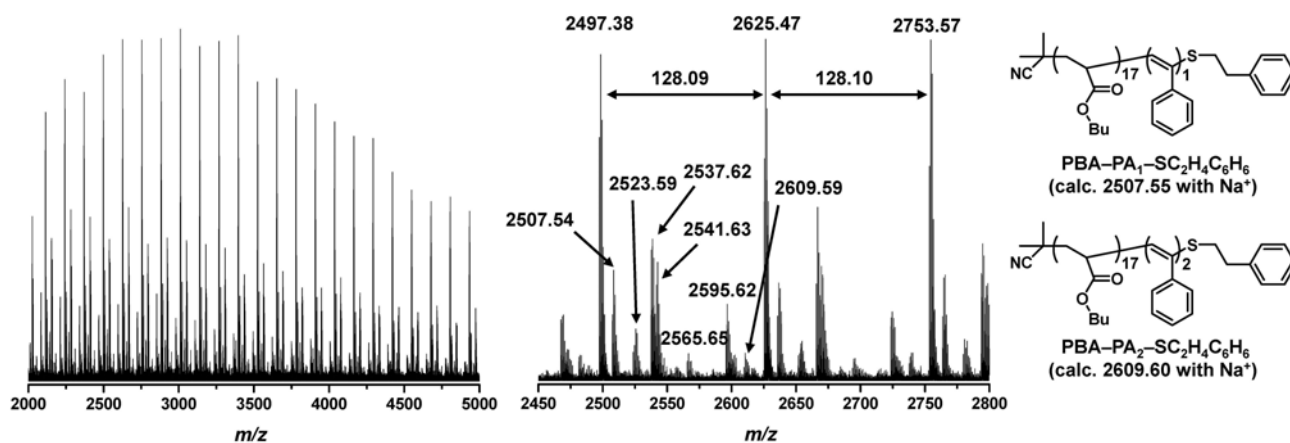


Fig. S17. MALDI-TOF-MS spectrum after the cross-coupling reaction of PBA-PA_m-I with 2-phenylethanethiol.

Fig. S18 shows the MALDI-TOF-MS spectrum for the cross-coupling of PBA-PA_m-I (with $m = 0$ (5%), $m = 1$ (86%), and $m = 2$ (9%) (Table 1, entry 2)) with 3,6-dioxa-1,8-octanedithiol. The peaks which correspond to PBA-PA₁-S(C₂H₄O)₂C₂H₄SH (theoretical mass = 2551.55) and PBA-PA₂-S(C₂H₄O)₂C₂H₄SH (theoretical mass = 2525.51) were not observed in the spectrum. The peaks at 2523.67 and 2497.44 correspond to the unreacted PBA-PA_m-I ($m = 0$ and 1) (86%) (theoretical mass = 2523.45 and 2497.41). The peaks at 2565.72 and 2600.70 belong to unidentified side products (14%). The peaks at 2537.68, 2541.68 and 2595.62 belong to PBA-ene, PBA-OH and PBA-Lac, respectively, which were observed in the original PBA-I (Fig. S4a) and are excluded from the calculations.

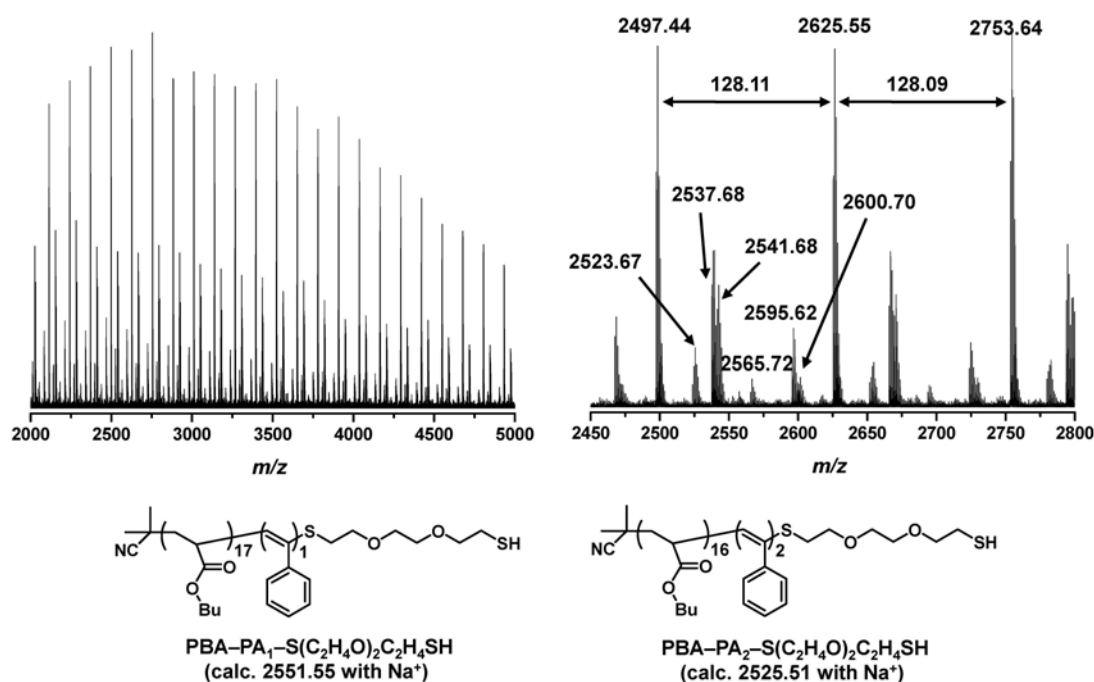


Fig. S18. MALDI-TOF-MS spectrum after the cross-coupling reaction of PBA-PA_m-I with 3,6-dioxa-1,8-octanedithiol.

15. ^1H NMR Analysis of PBA- PA_m -S-PEG.

Fig. S19 shows the ^1H NMR spectrum of the purified PBA- PA_m -S-PEG (Table 2, entry 3). The average number of the BA monomer units (the n value in Fig. S19) was approximately 30, as discussed above (Fig. S1). The average number of the PEG segments was determined to be approximately 0.6 from the peak areas of OCH_2 protons (a) of the BA monomer units (3.9–4.2 ppm) and OCH_3 protons (b) of the PEG segments (3.35–3.40 ppm).

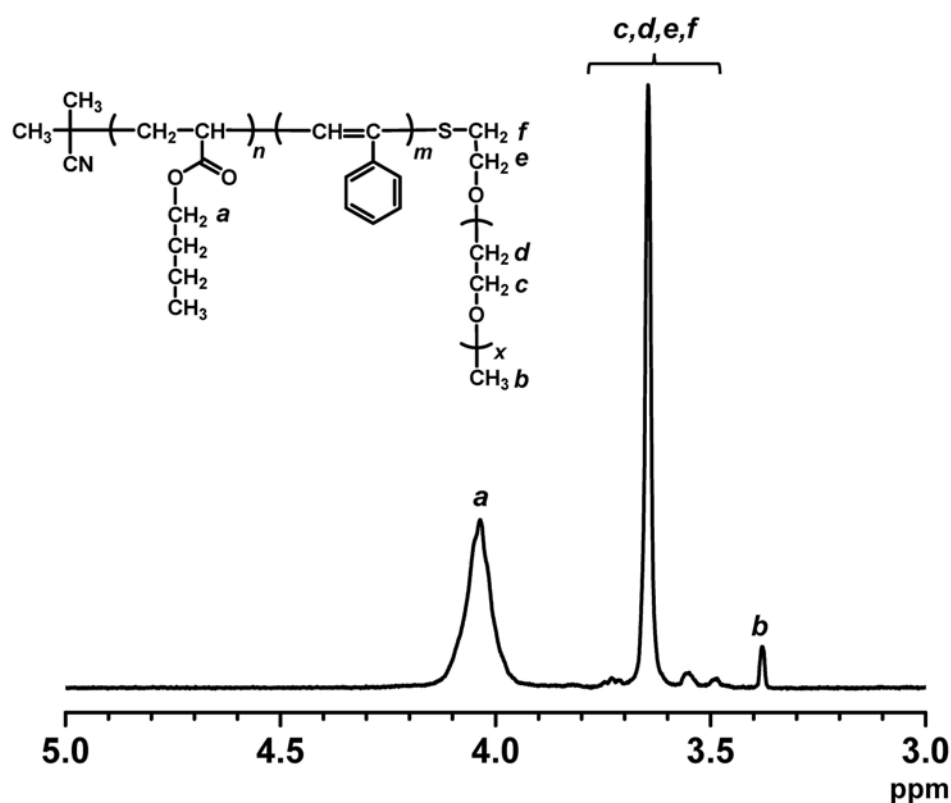


Fig. S19. ^1H NMR spectrum (CDCl_3) of PBA- PA_m -S-PEG (Table 2, entry 3).

16. CNT Dispersion Size Analysis.

The sizes of the dispersed CNT (43 μm with no polymer, 38 μm with PBA-I, and 6.4 μm with PBA-PA_m-I) mentioned in the manuscript refer to D_{50} (the diameter of the particle at the 50th percentile of the cumulative size distribution) given in Table S1.

Table S1. Mixtures of multi-walled CNT (110-170 nm diameter, 5-9 μm length) (1 mg), polymer (0 or 200 mg) in toluene (8 mL).^a

Entry	Polymer	CNT/Polymer (mg)	D_{10} (μm) ^a	D_{50} (μm) ^a	D_{90} (μm) ^a
1	None	1/0	9.5	43	280
2	PBA-I	1/200	8.8	38	190
3	PBA-PA-I	1/200	2.2	6.4	25

^a The D_{10} , D_{50} and D_{90} values refer to the diameters of the particle at the 10th, 50th and 90th percentile of the cumulative size distribution, respectively.

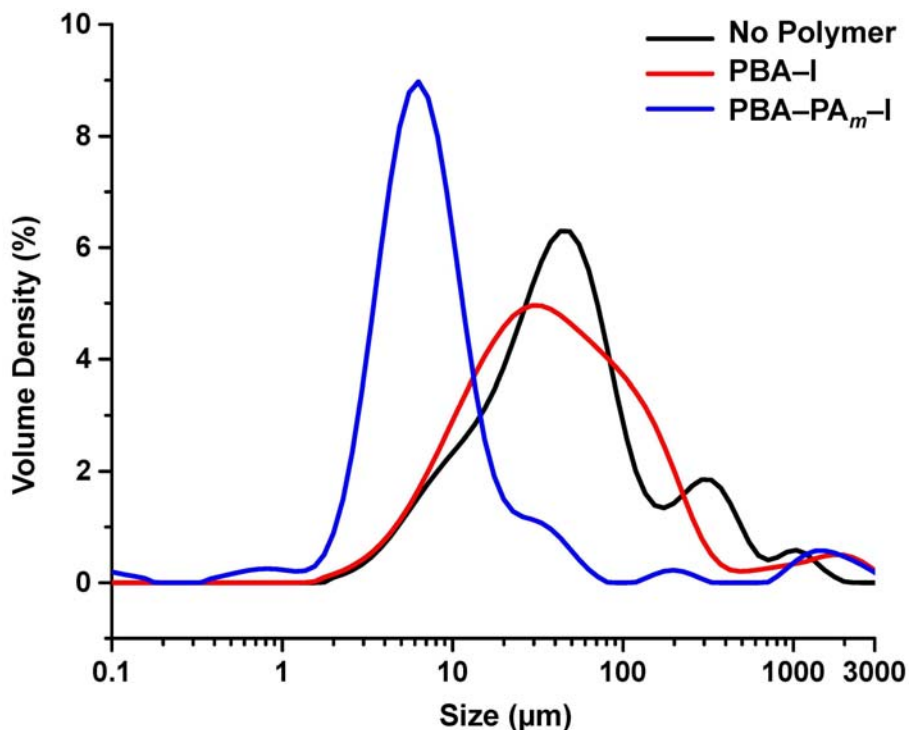


Fig. S20. Particle sizes distribution in Table S1.

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