Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Characterization of *N*-phenyl maleimide-terminated poly(ethylene glycol)s and their application to a tetra-arm poly(ethylene glycol) gels

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Spectral data

^{1}H NMR spectra

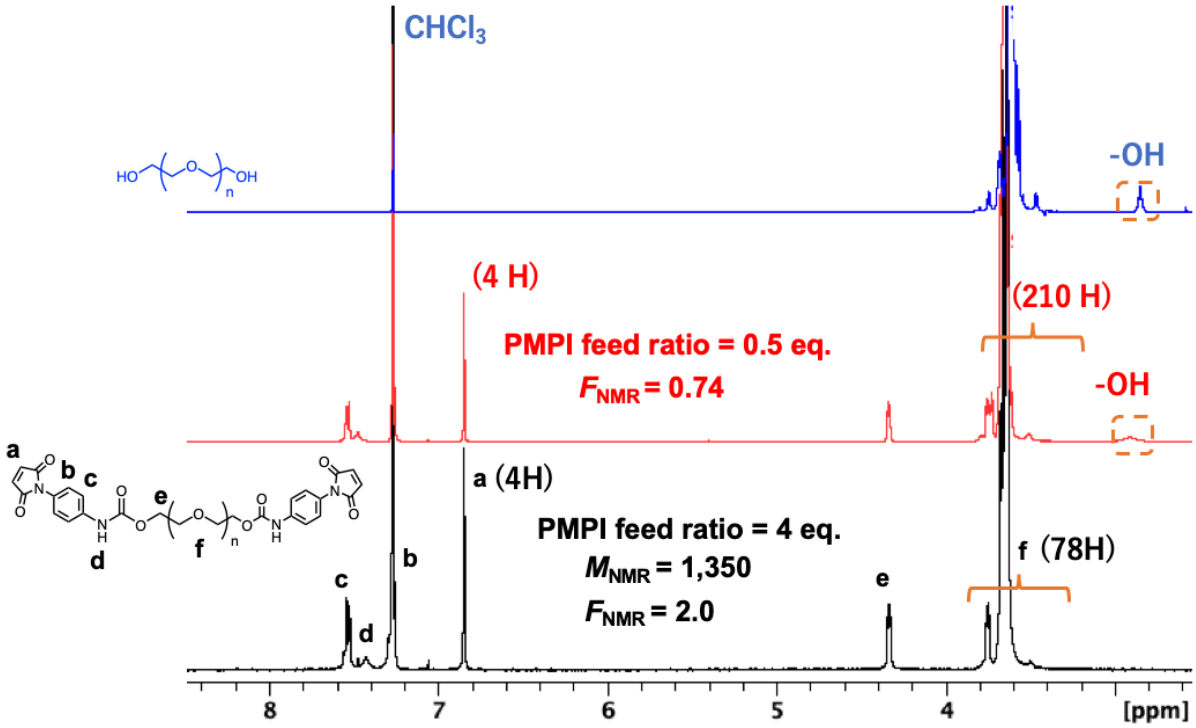

Figure S1. ^{1}H NMR spectra of the products in Runs 1 (red) and 2 (black) in Table 1, and their precursor PEG ($M_{n\ SEC}$ 920) (blue) (500 MHz, 25 °C, $CDCl_3$).

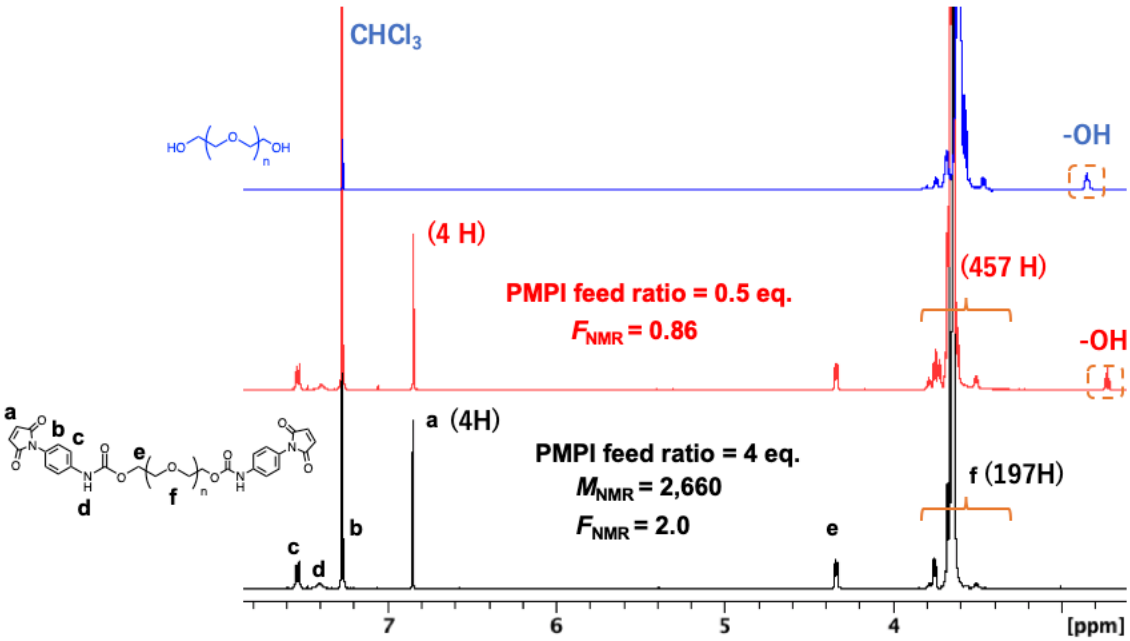

Figure S2. ^{1}H NMR spectra of the products in Runs 3 (red) and 4 (black) in Table 1, and their precursor PEG ($M_{n\ SEC}$ 1,900) (blue) (500 MHz, 25 °C, $CDCl_3$).

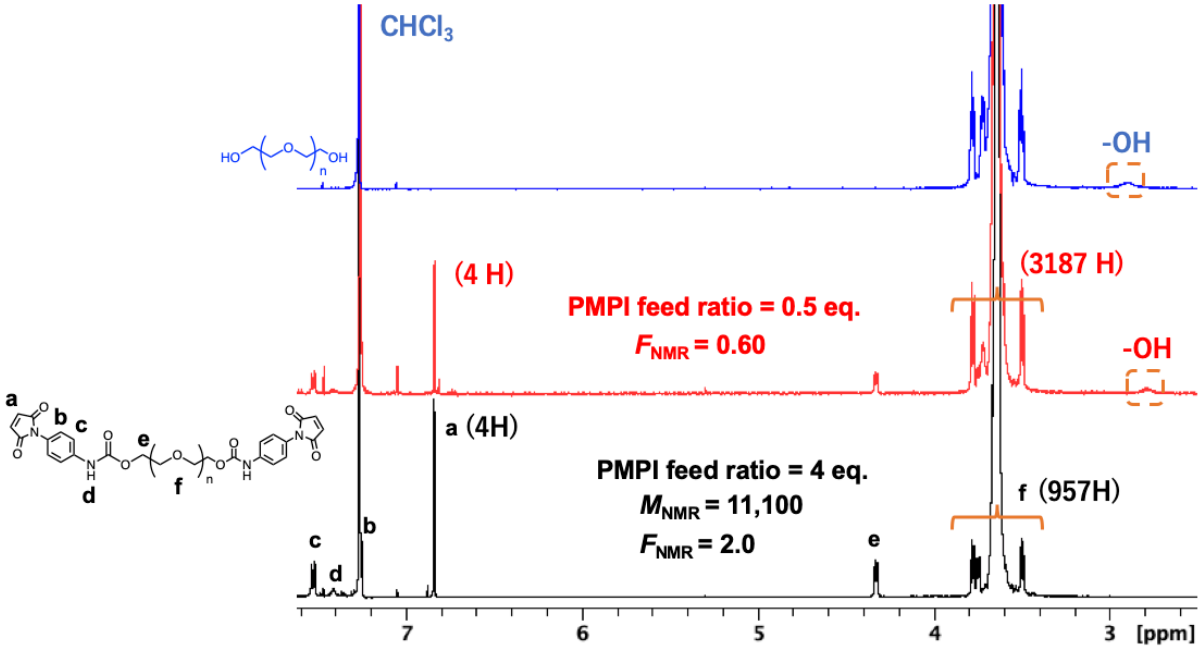

Figure S3. ^{1}H NMR spectra of the products in Runs 5 (red) and 6 (black) in Table 1, and their precursor PEG10k ($M_{n\ SEC}$ 7,900) (blue) (500 MHz, 25 °C, $CDCl_3$).

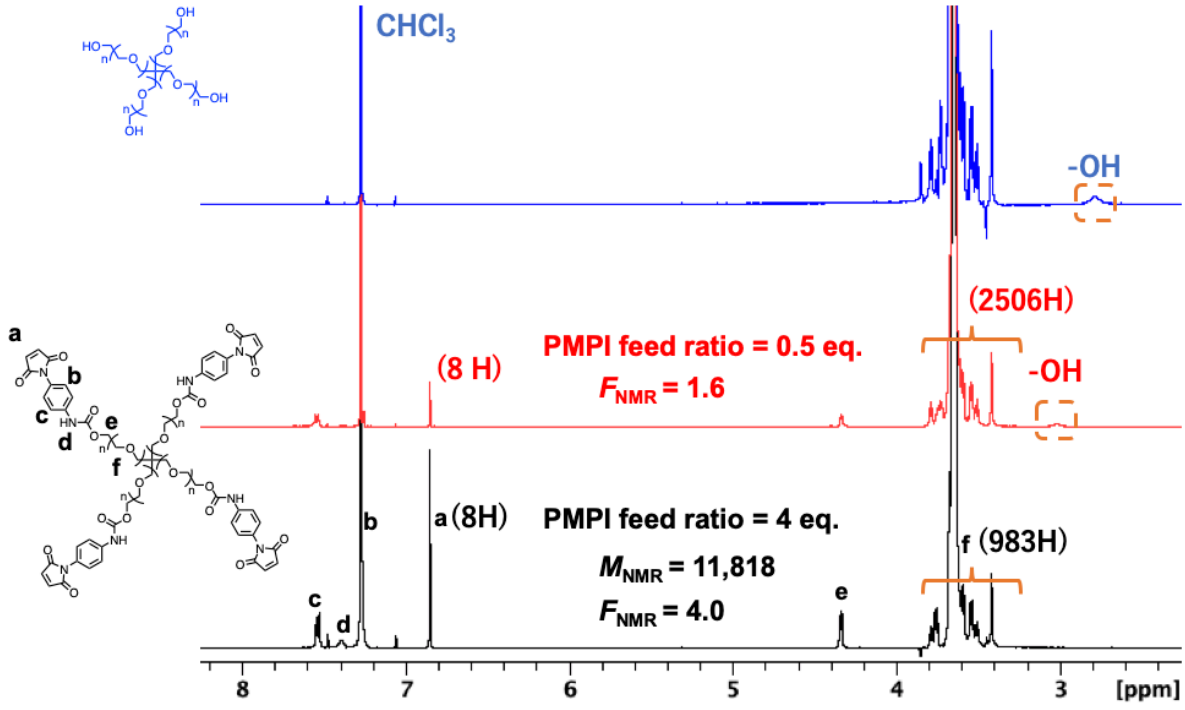

Figure S4. ^{1}H NMR spectra of the products in Runs 7 (red) and 8 (black) in Table 1, and their precursor TetraPEG ($M_{n\ SEC}$ 7,300) (blue) (500 MHz, 25 °C, $CDCl_3$).

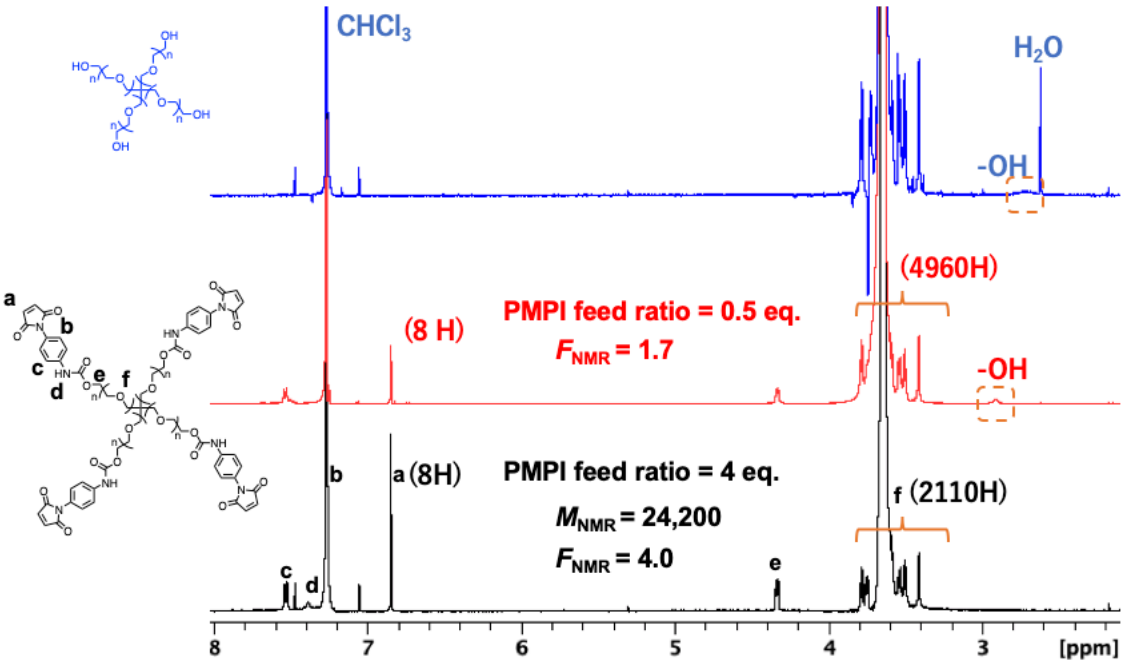

Figure S5. ^{1}H NMR spectra of the products in Runs 9 (red) and 10 (black) in Table 1, and their precursor TetraPEG20k ($M_{n\ SEC}$ 11,000) (blue) (500 MHz, 25 °C, $CDCl_3$).

^{13}C NMR spectra

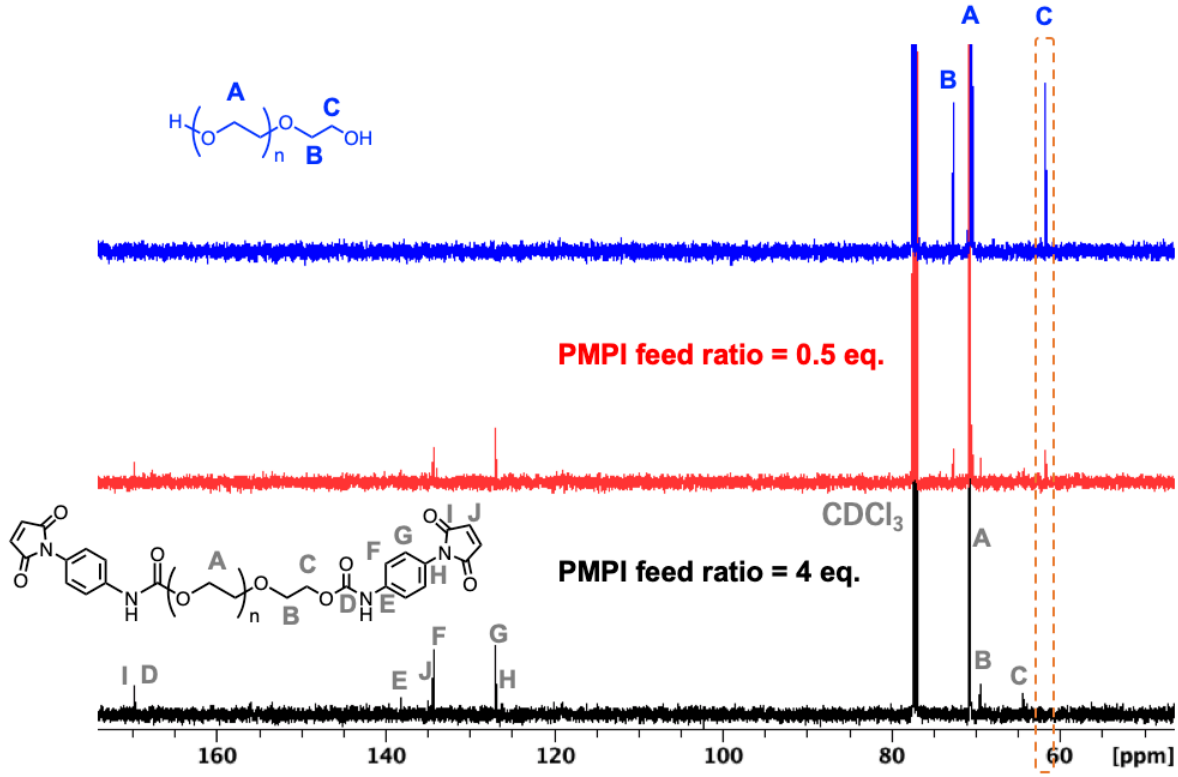

Figure S6. ^{13}C NMR spectra of the products in Runs 3 (red) and 4 (black) in Table 1, and their precursor PEG ($M_{n\ SEC}$ 1,900) (blue) (120 MHz, 25 °C, $CDCl_3$).

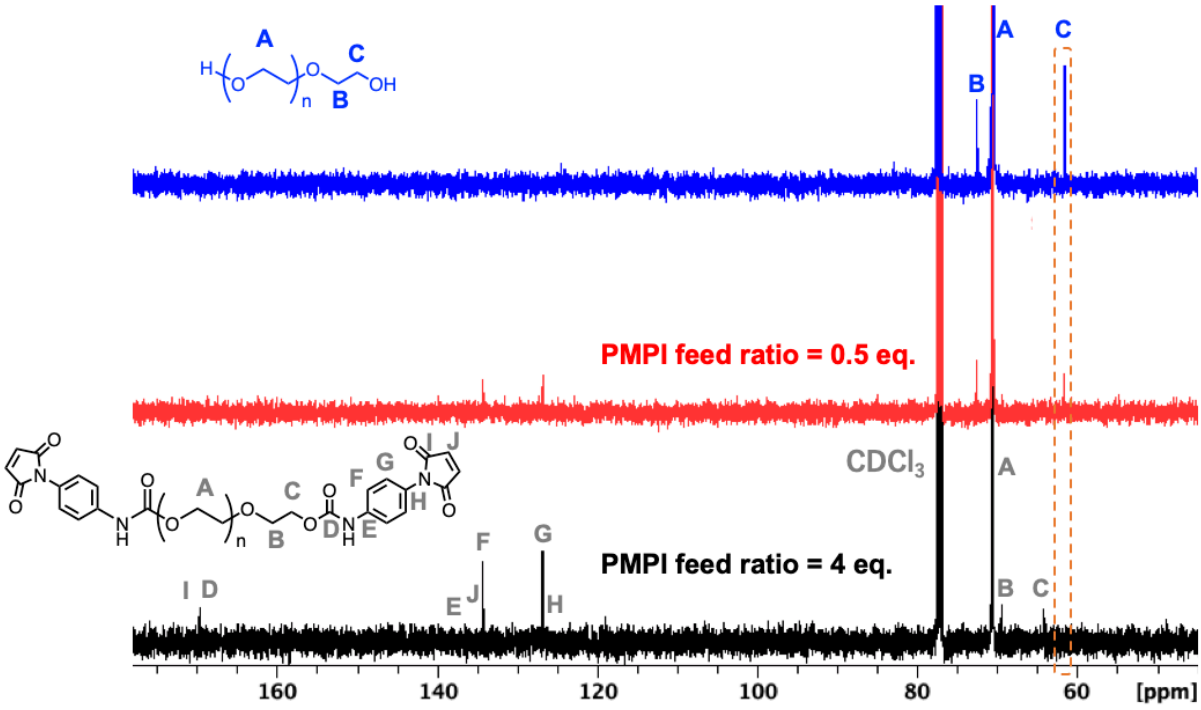

Figure S7. ^{13}CNMR spectra of the products in Runs 5 (red) and 6 (black) in Table 1, and their precursor PEG10k ($M_{n\,SEC}$ 7,900) (blue) (120 MHz, 25 °C, $CDCl_3$).

SEC curves

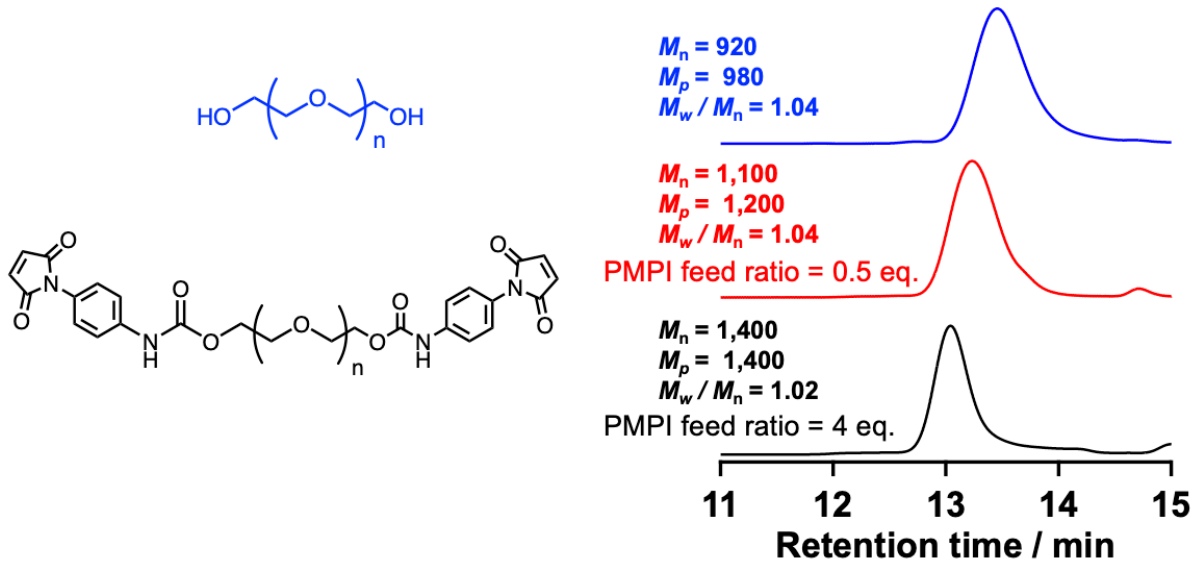

Figure S8. SEC charts of the products in Runs 1 (red) and 2 (black), and their precursor PEG1k (blue) (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by RI).

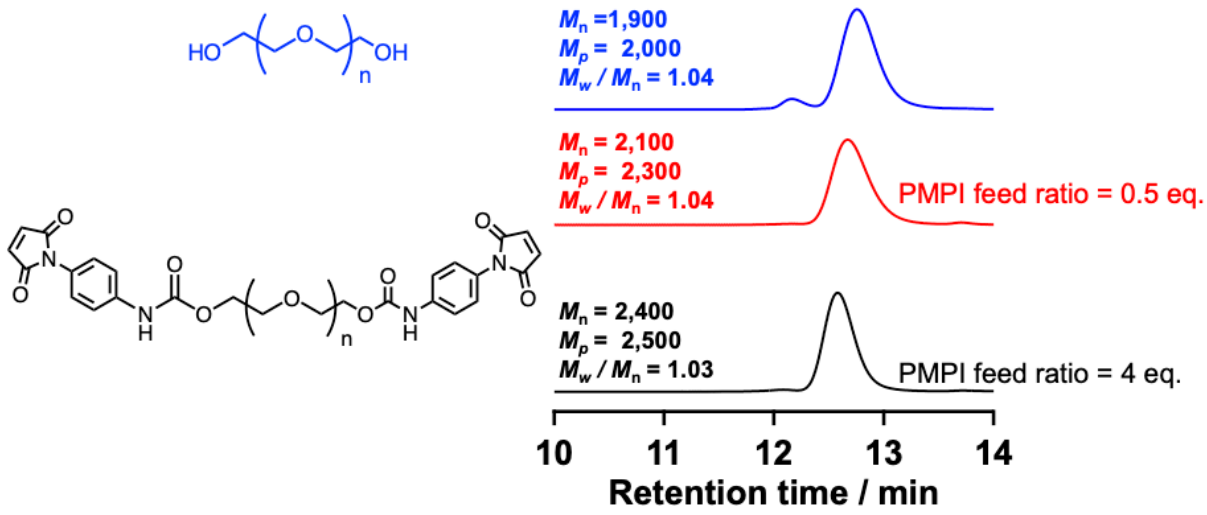

Figure S9. SEC charts of the products in Runs 3 (red) and 4 (black), and their precursor PEG2k (blue) (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by RI).

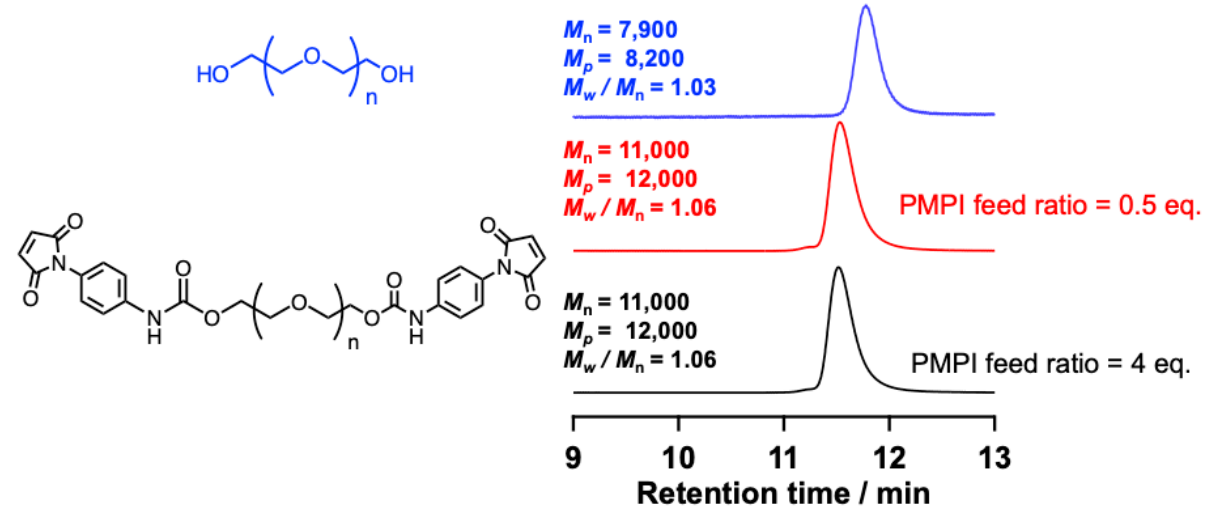

Figure S10. SEC charts of spectra of the products in Runs 5 (red) and 6 (black), and their precursor PEG10k (blue) (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by RI).

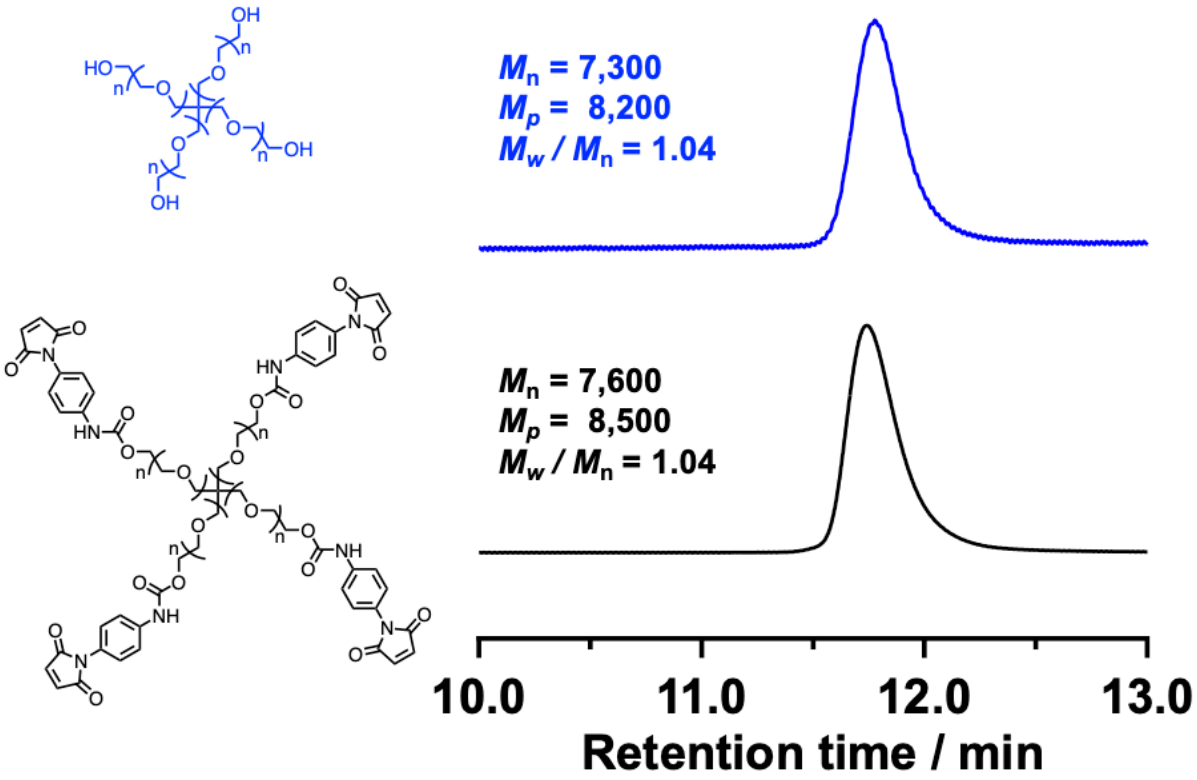

Figure S11. SEC charts of spectra of the product in Run 8 (black), and its precursor TetraPEG10k (blue) (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by RI).

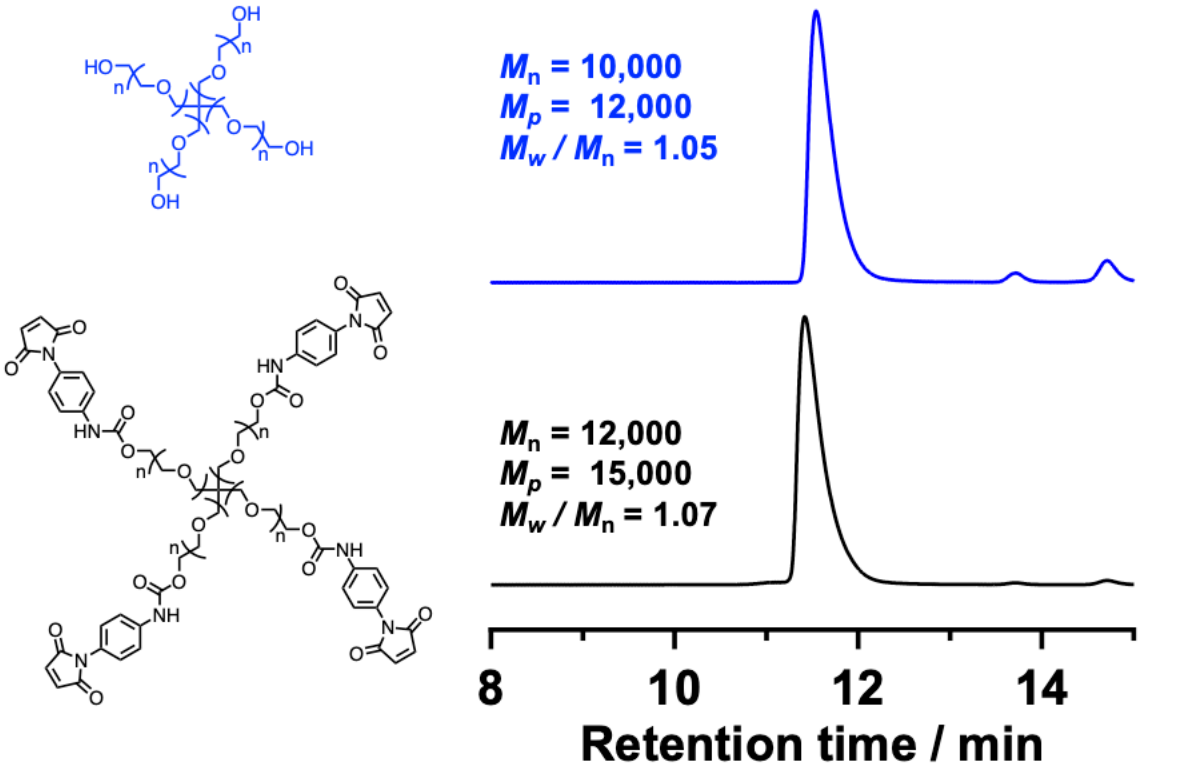

Figure S12. SEC charts of **Run10** (black), and their precursor TetraPEG20k (blue) (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by RI).

MALDI-TOF MS profiles

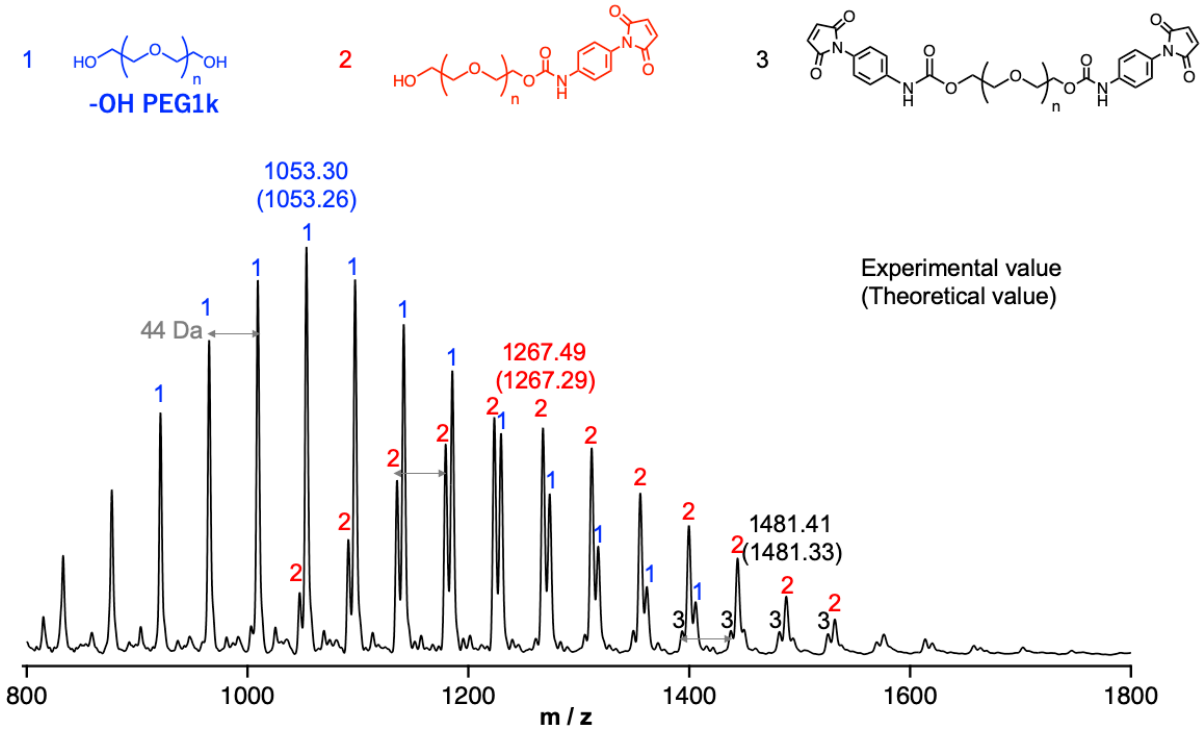

Figure S13. MALDI-TOF MS profile of the products in Run 1 in Table 1 (Matrix; DHBA).

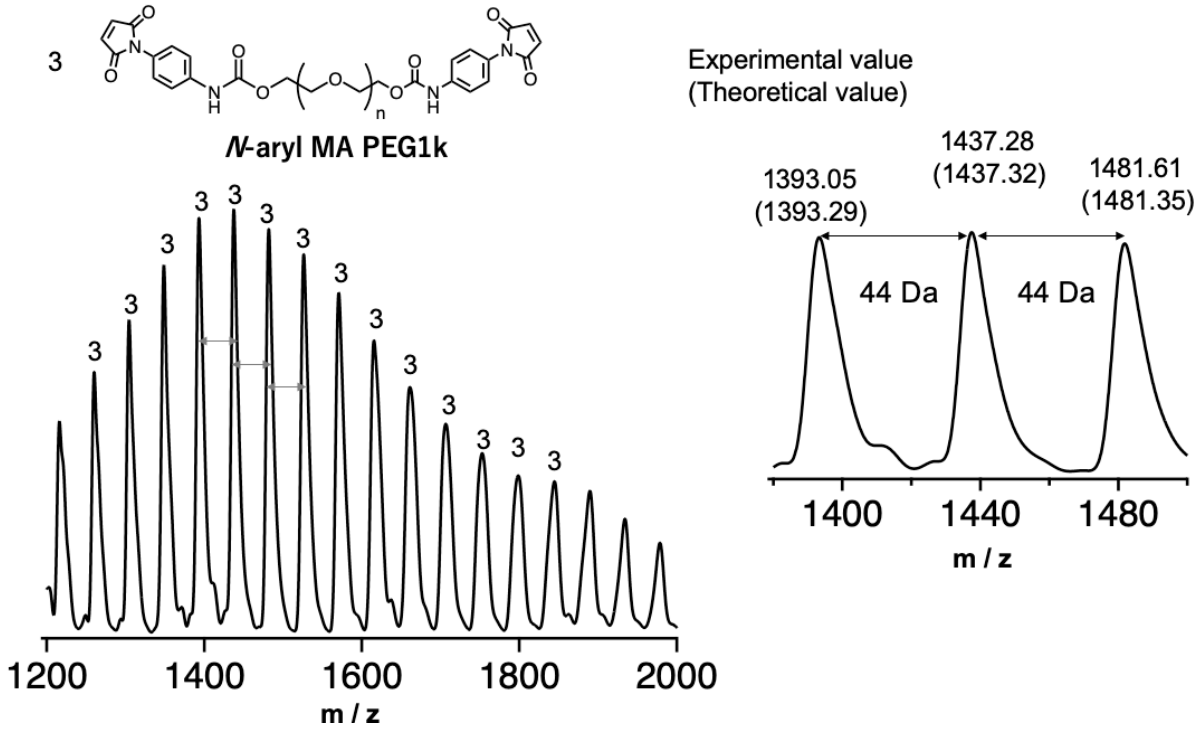

Figure S14. MALDI-TOF MS profile of the product in Run 2 in Table 1 (Matrix; Dith).

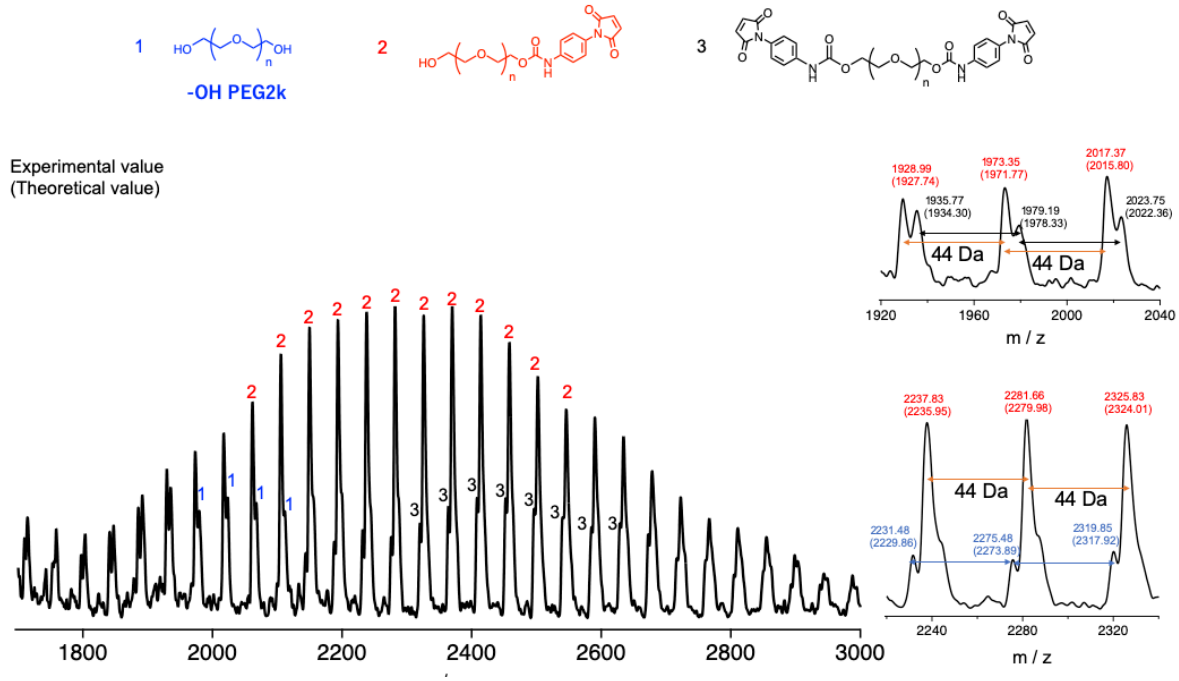

Figure S15. MALDI-TOF MS profile of the products in Run 3 in Table 1 (Matrix; Dith).

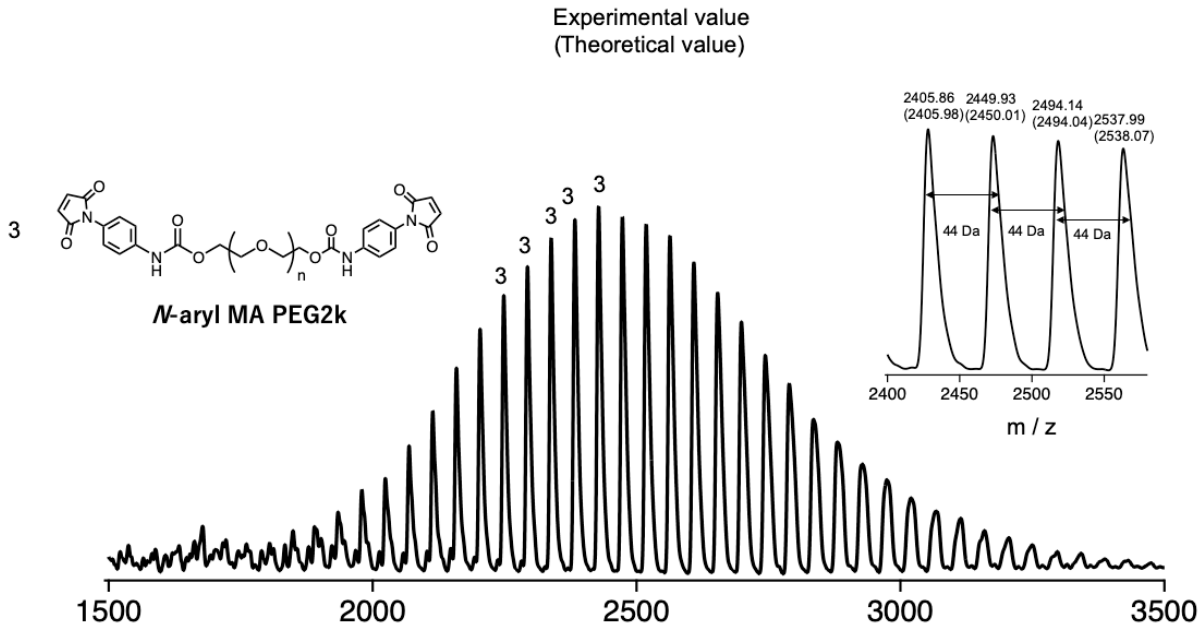

Figure S16. MALDI-TOF MS profile of the products in Run 4 in Table 1 (Matrix; Dith).

HPLC measurements

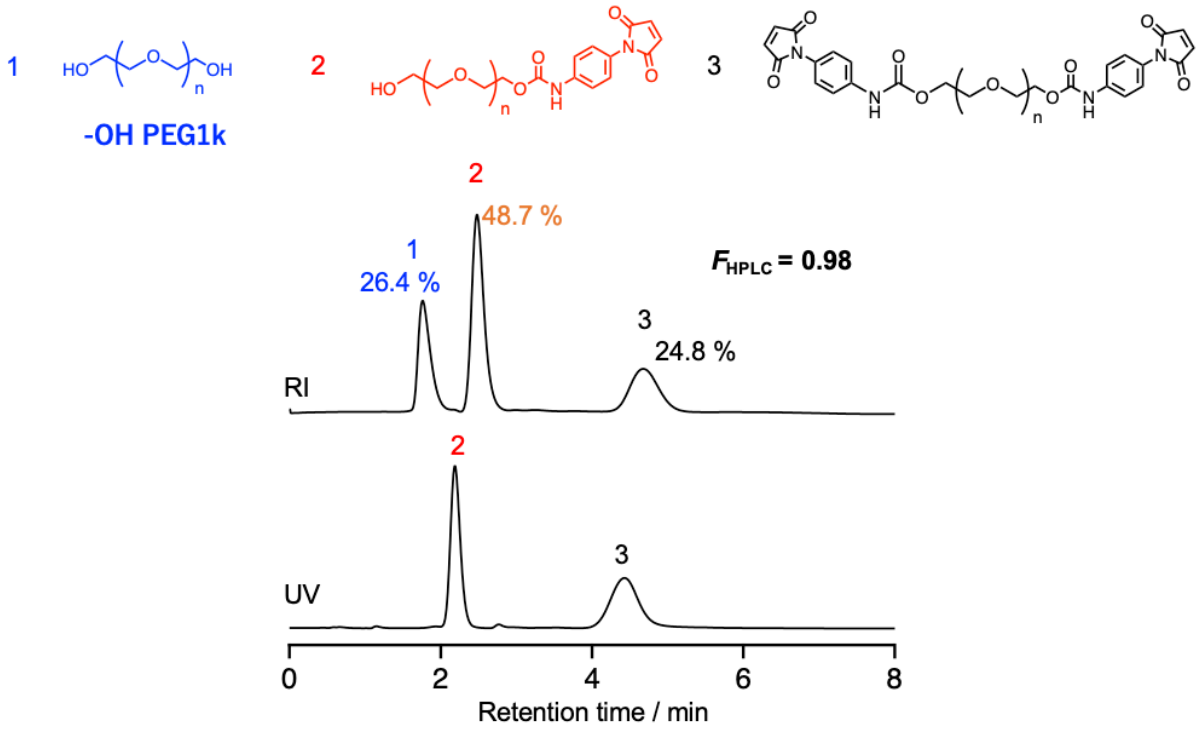

Figure S17. HPLC charts of the products in Run 1 in Table 1 (eluent, CH_3CN / water = 45 / 55; flow rate, 1.0 mL/min, detected by UV and RI).

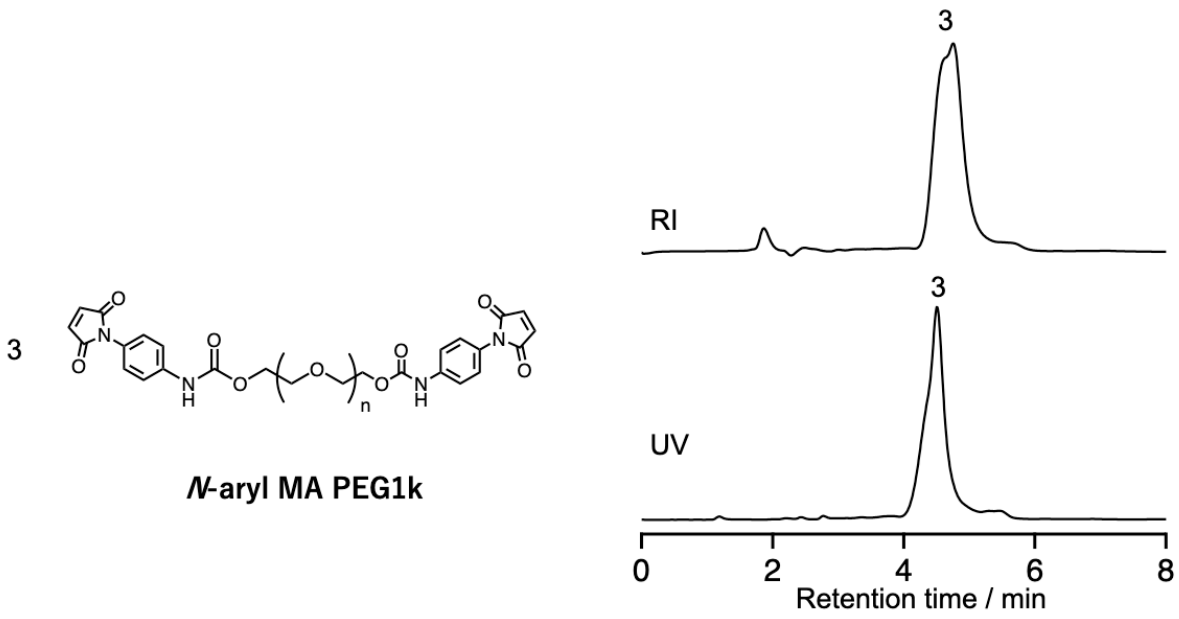

Figure S18. HPLC charts of the product in Run 2 in Table 1 (eluent, CH_3CN / water = 45 / 55 flow rate, 1.0 mL/min, detected by UV and RI).

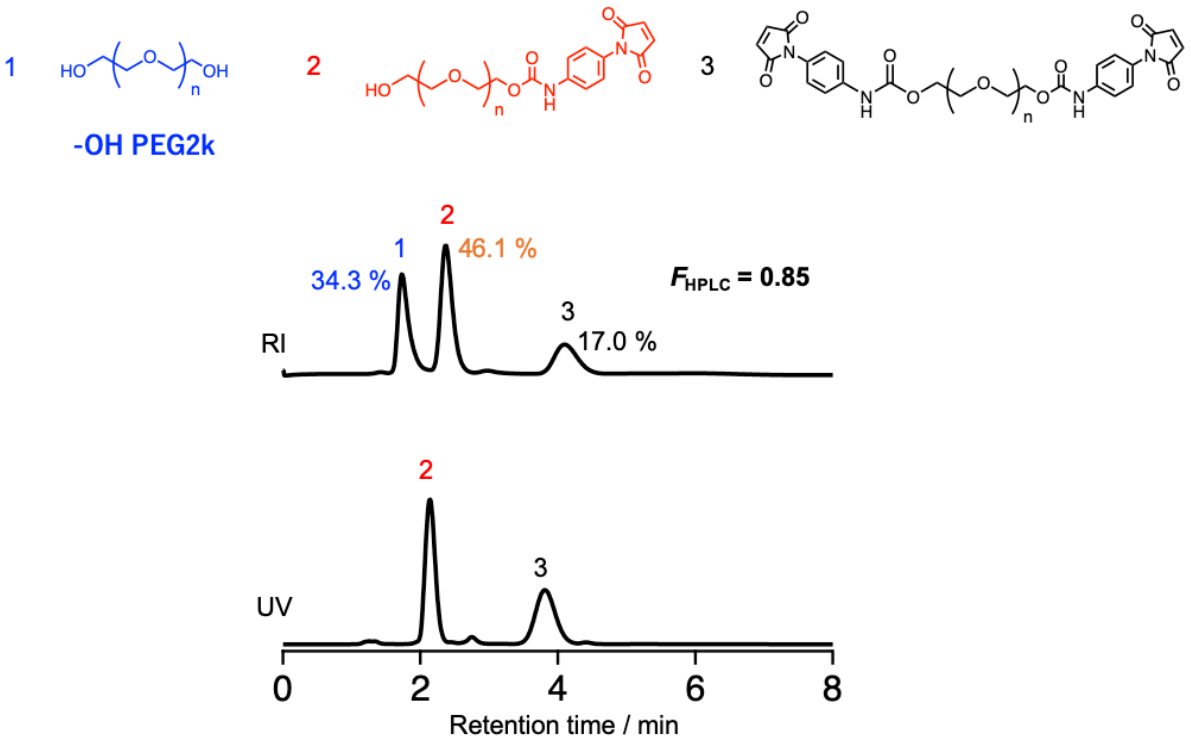

Figure S19. HPLC charts of the products in Run 3 in Table 1 (eluent, CH_3CN / water = 45 / 55; flow rate, 1.0 mL/min, detected by UV and RI).

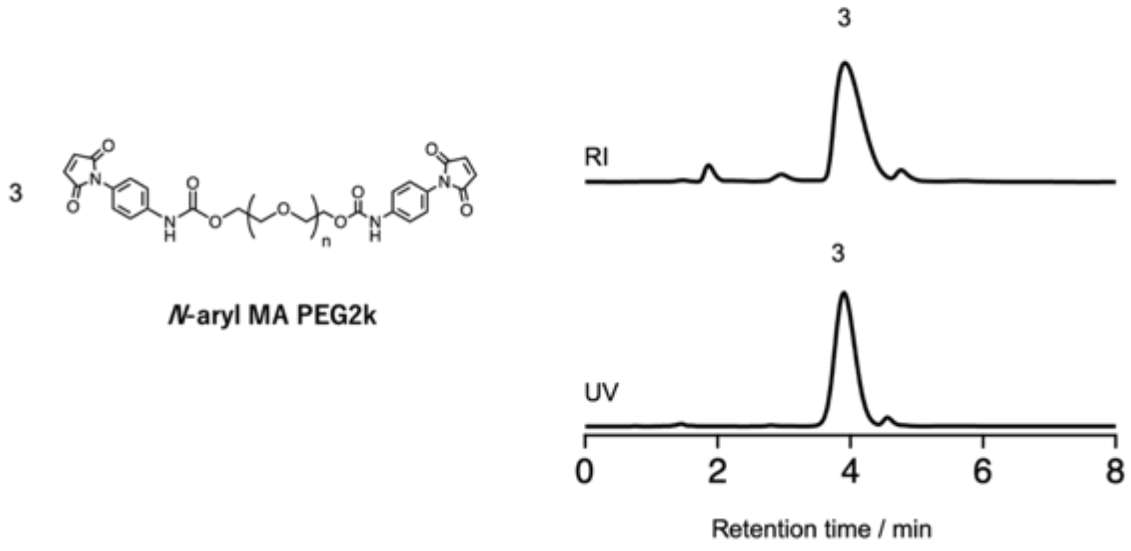

Figure S20. HPLC charts of the product in Run 4 in Table 1 (eluent, CH_3CN / water = 45 / 55; flow rate, 1.0 mL/min, detected by UV and RI).

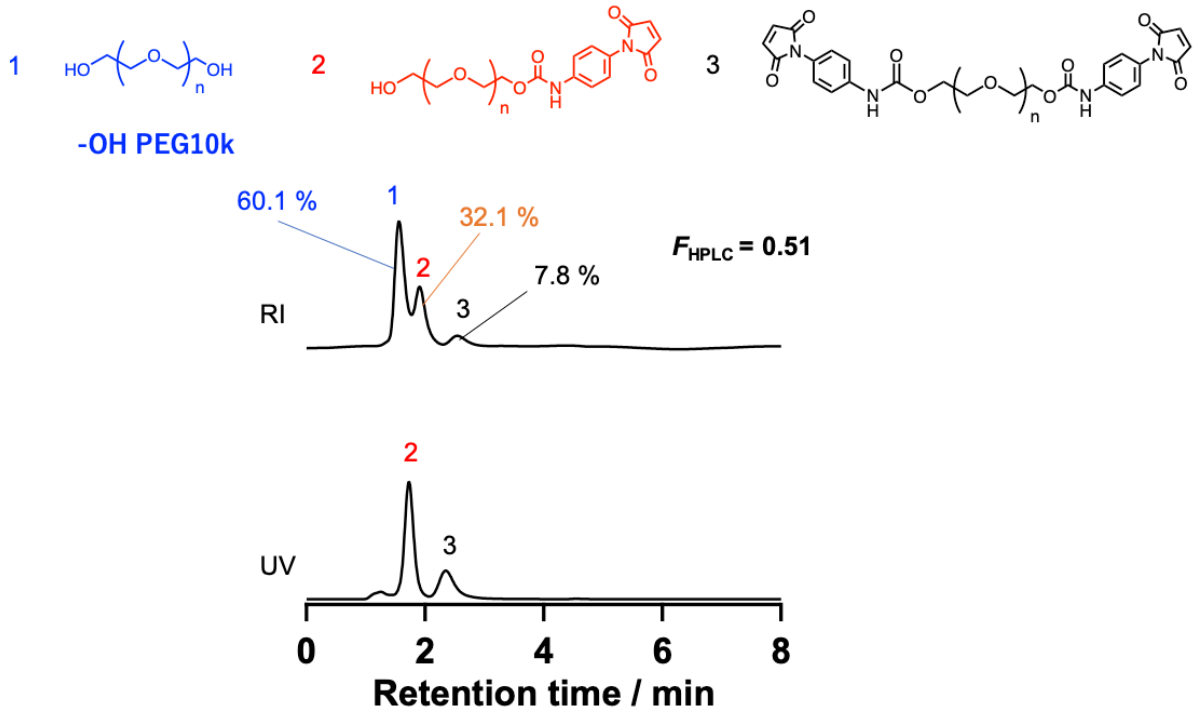

Figure S21. HPLC charts of the products in Run 5 in Table 1 (eluent, CH_3CN / water = 45 / 55; flow rate, 1.0 mL/min, detected by UV and RI).

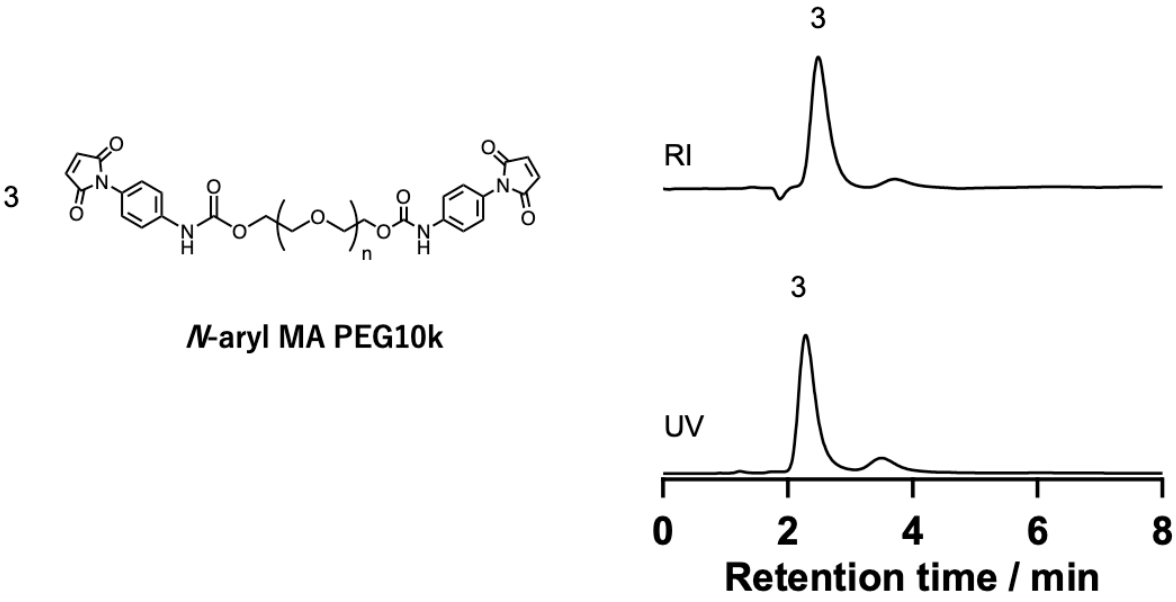

Figure S22. HPLC charts of the products in Run 6 in Table 1 (eluent, CH_3CN / water = 45 / 55; flow rate, 1.0 mL/min, detected by UV and RI).

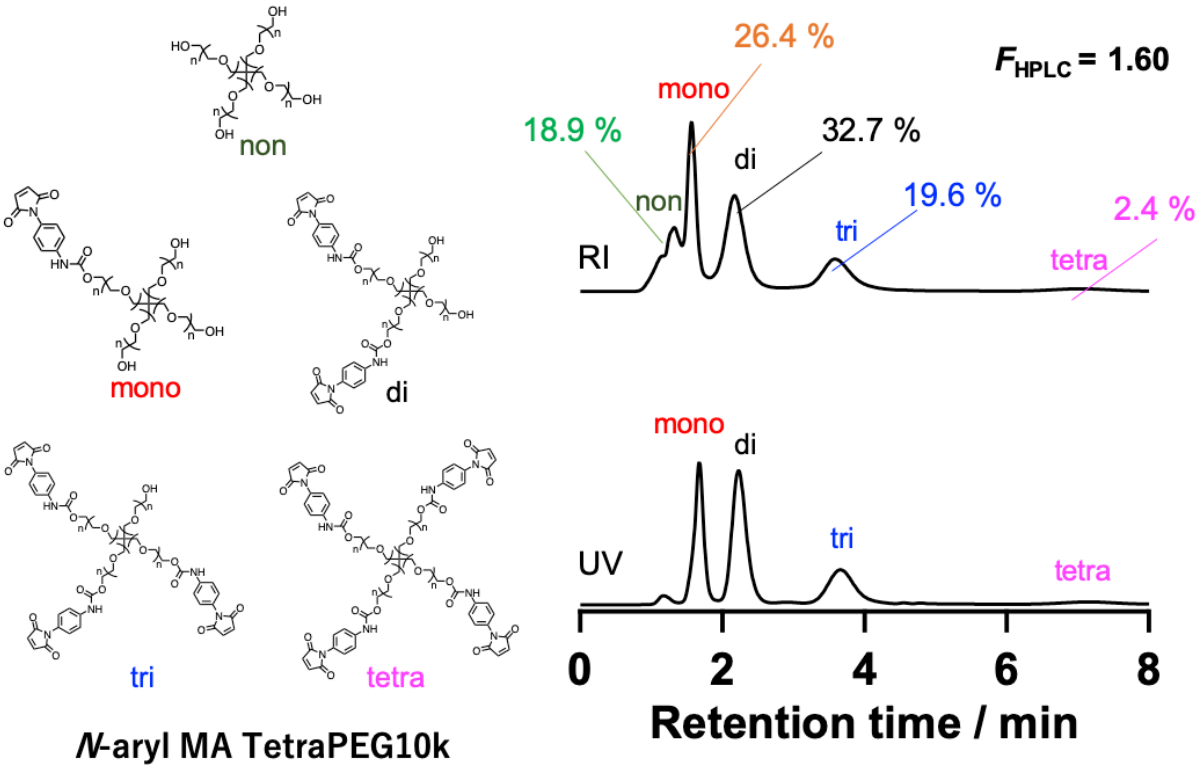

Figure S23. HPLC charts of the products in Run 7 in Table 1 (eluent, CH_3CN / water = 45 / 55; flow rate, 1.0 mL/min, detected by UV and RI).

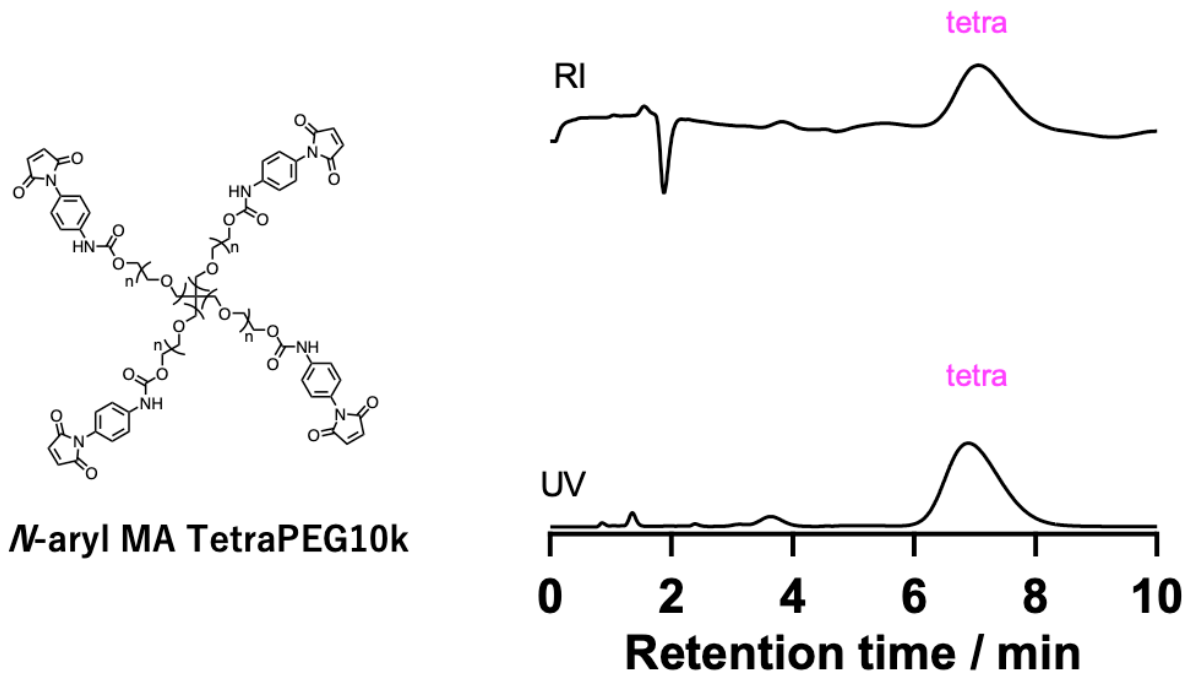

Figure S24. HPLC charts of the product in Run 8 in Table 1 (eluent, CH_3CN / water = 45 / 55; flow rate, 1.0 mL/min, detected by UV and RI).

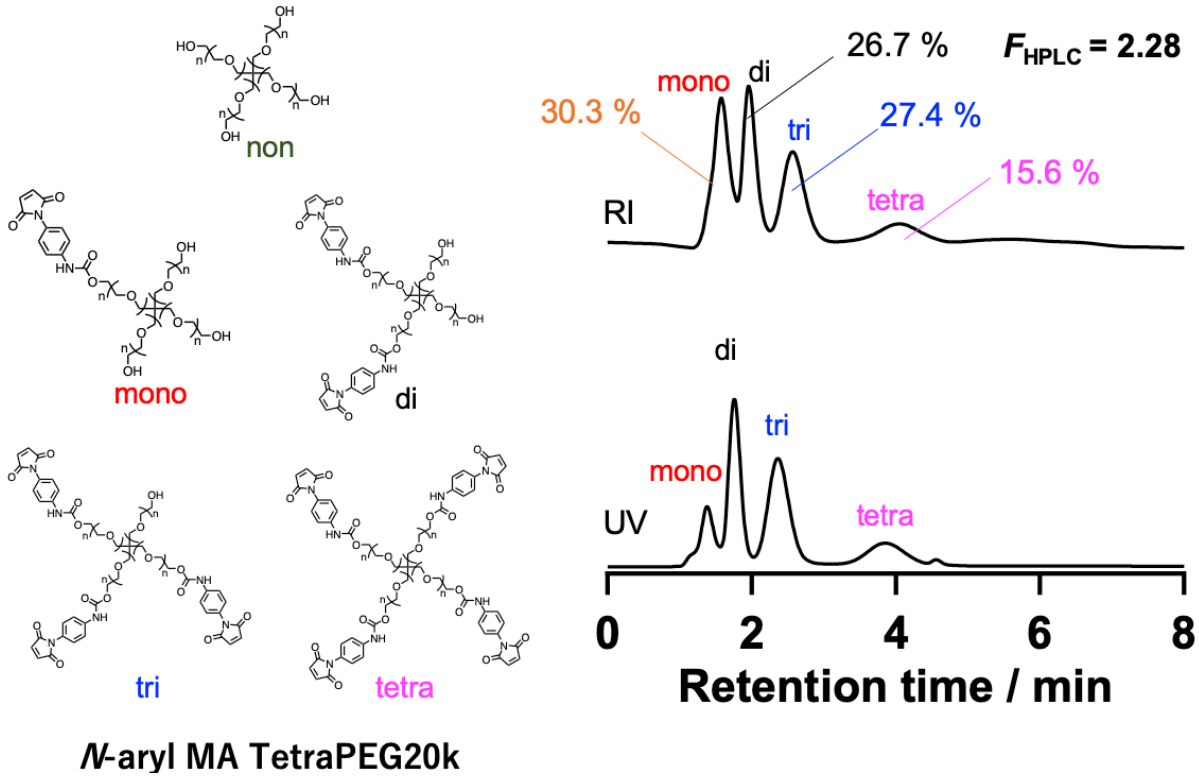

Figure S25. HPLC charts of the products in Run 9 in Table 1 (eluent, CH_3CN / water = 45 / 55; flow rate, 1.0 mL/min, detected by UV and RI).

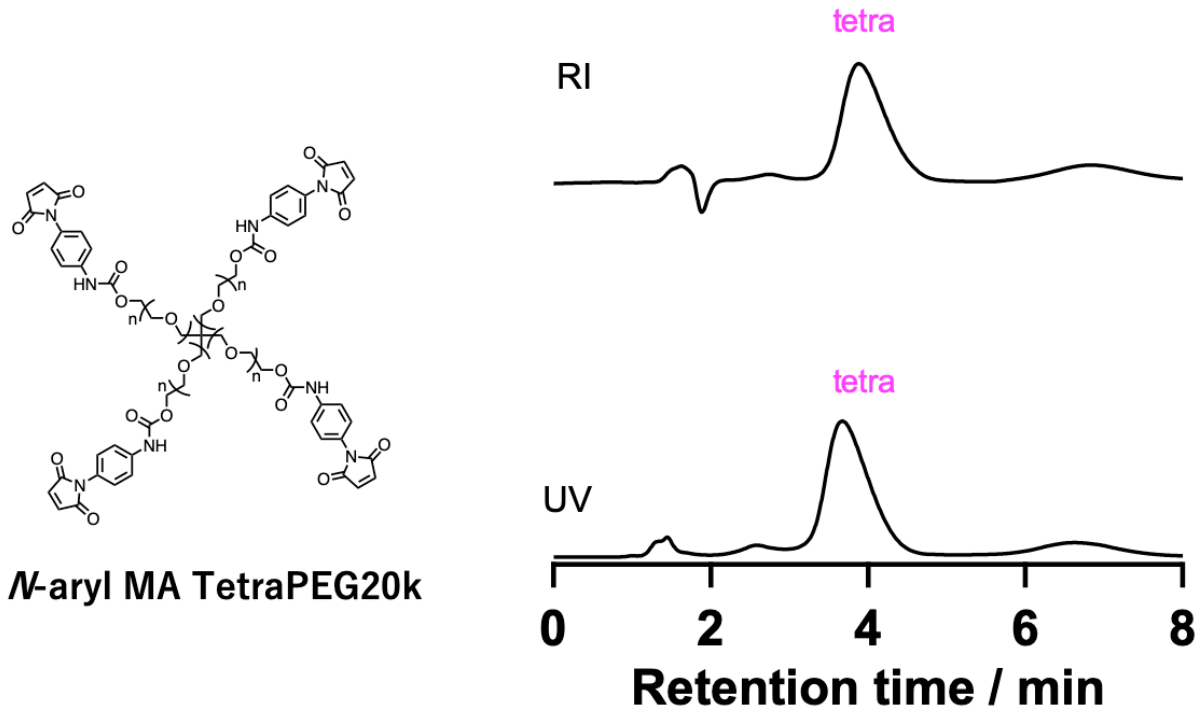

Figure S26. HPLC charts of the product in Run 10 in Table 1 (eluent, CH_3CN / water = 45 / 55; flow rate, 1.0 mL/min, detected by UV and RI).

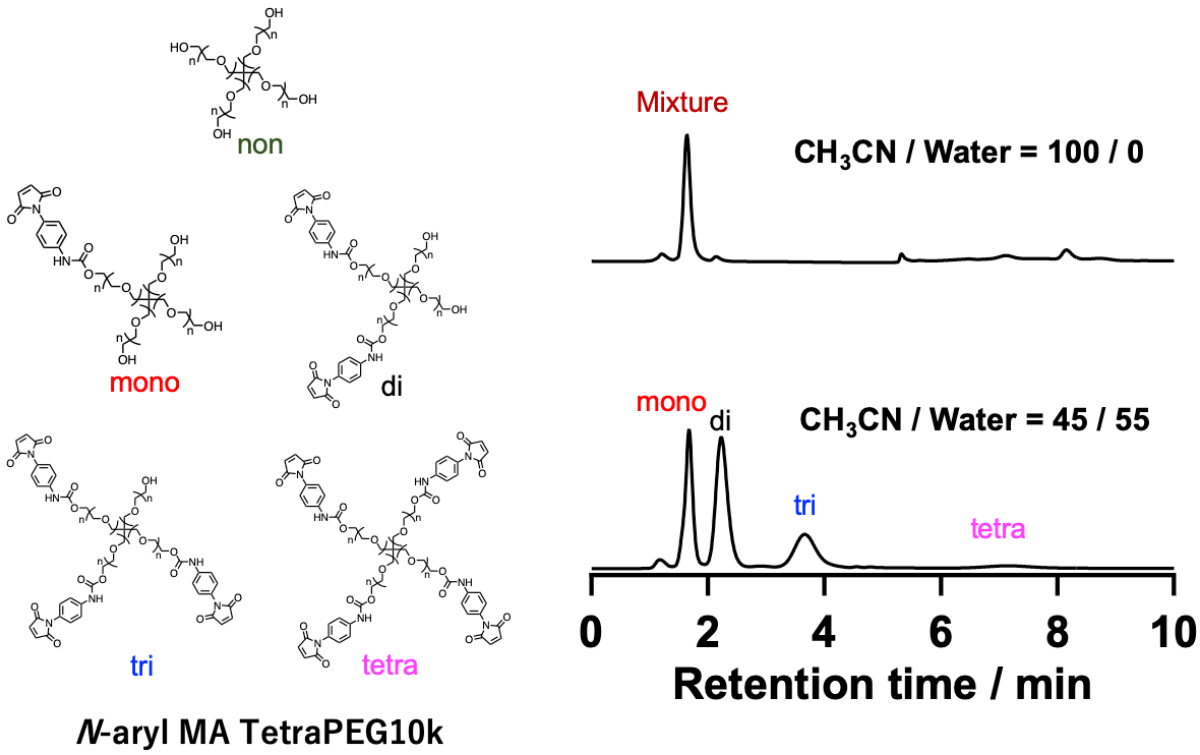

Figure S27. Effect of solvent composition in the dissolved sample. HPLC profiles of modified PEG prepared by CH_3CN or CH_3CN / water = 45 / 55 (HPLC eluent, CH_3CN / water = 45 / 55 vol%; flow rate, 1.0 mL/min on C18 column at 30 ºC detected by UV).

Reaction tracking

PMPI (120 mg, 560 µmol, 4.0 equivalents toward -OH groups) and TetraPEG (700 g, 35 µmol, M_n = ca. 20 000) were added to a round-bottomed flask. DCM (28 mL) and 2 drops of DBTDL were added under inert atmosphere.

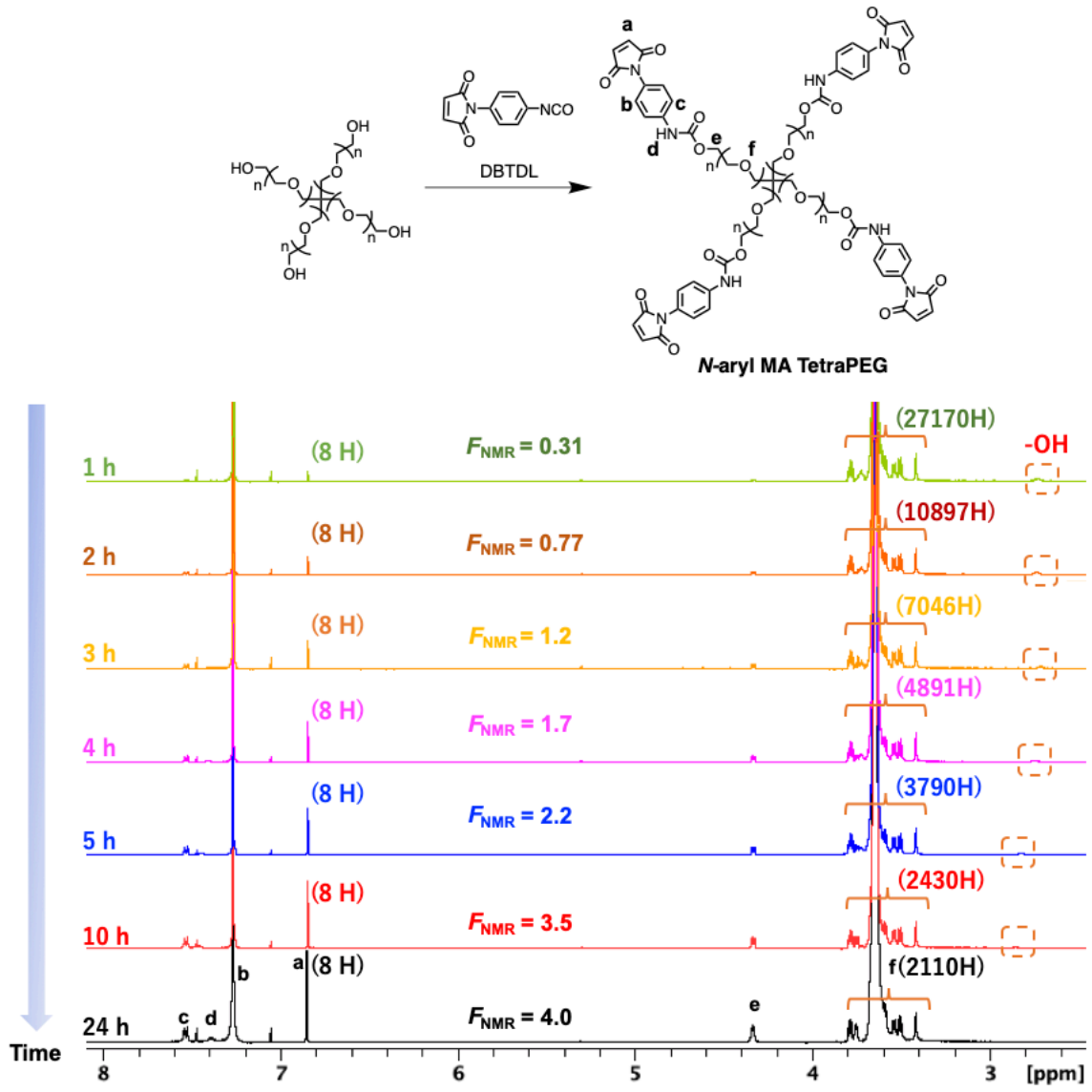

Figure S28. Changes in ^{1}H NMR spectra of the products in Run 10 in Table 1 (500 MHz, 25 °C, $CDCl_3$).

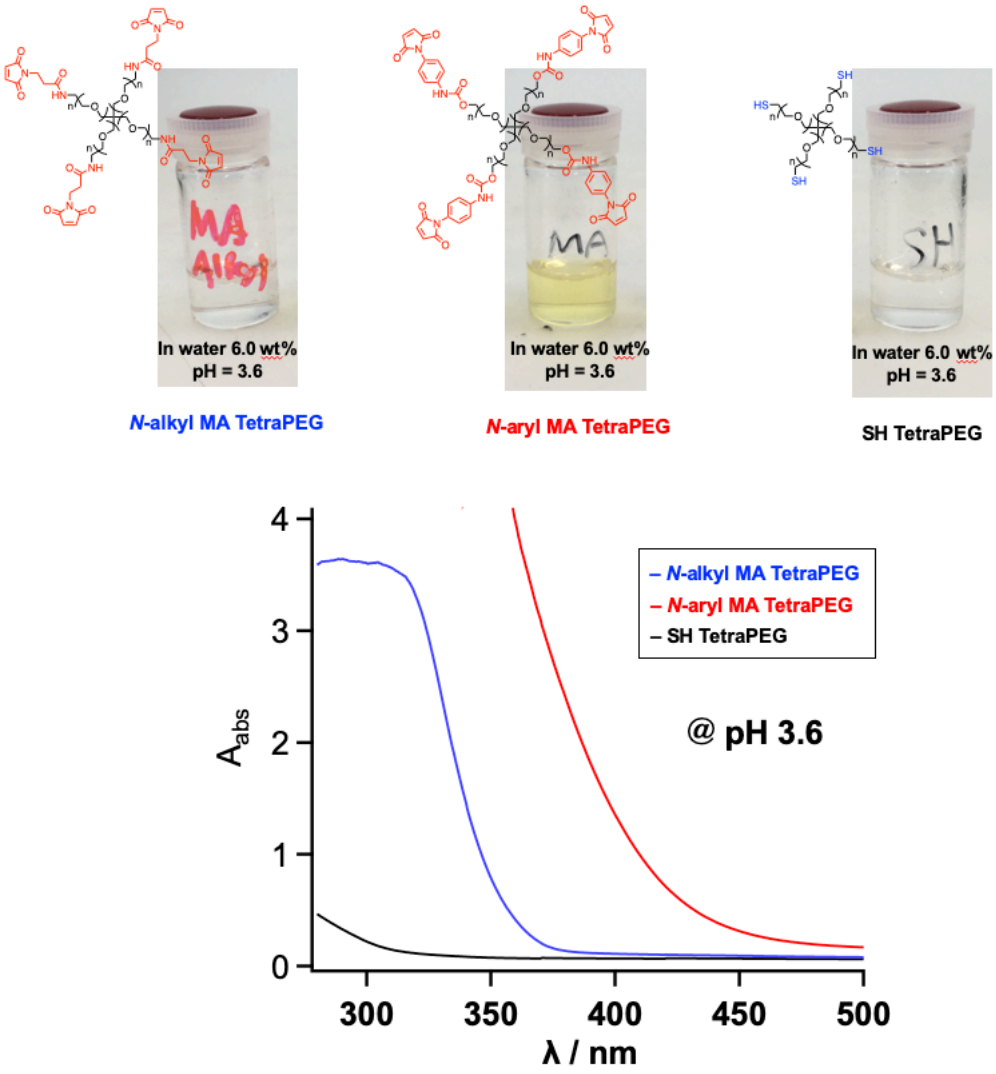

Figure S29. UV-vis spectra of various functional TetraPEGs at 6wt% before gelation experiment (in pH 3.6 buffer).

Table S1. pH dependence of gelation time*.

pH	*N*-aryl MA	*N*-alkyl MA
3.0	1000 sec	5000 sec
3.6	200 sec	1100 sec

*Gelation time was estimated by viscoelastic properties.