

Supporting Information

A Facile Metal-free “Grafting-from” Route from Acrylamide-based Substrate Toward Complex Macromolecular Combs

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Experimental Section

Chemicals

All chemicals were purchased from Sigma-Aldrich. Acrylamide (Am, 99%) was recrystallized three times from methanol. *N,N*-dimethylacrylamide (DMAm, 99%) and methyl iodide (CH₃I) was dried over CaH₂ and distilled before use. Ethylene oxide (EO, 99.5%), (±)-propylene oxide (PO, 99%), 1,2-butylene oxide (BO, 99%) and *tert*-butyl glycidyl ether (tBGE, 99%) were dried successively by CaH₂ and *n*-BuLi prior to graft polymerizations. Methyl methacrylate (MMA, 99%) and 2-(dimethylamino)ethyl methacrylate (DMAEMA, 98%) were purified by stirring successively with CaH₂ and trioctylaluminum followed by distillation. *N-tert*-butyl-*N*-(2-methyl-1-phenylpropyl)-*O*-(1-phenylethyl) hydroxylamine (NMPI), *tert*-butyl 1-phenyl-2- methylpropyl nitroxide (NMPNO), phosphazene base (*t*-BuP₄,

1M solution in *n*-hexane) and acetic acid (AcOH) were used as received. For anionic graft polymerization, tetrahydrofuran (THF) was dried successively by Na and *n*-BuLi.

Instrumentation

Size exclusion chromatography (SEC) with simultaneous UV and RI detection was conducted in *N,N*-dimethylformamide (DMF, with 0.1 wt % LiBr) at 70 °C using two identical PLgel columns (5 μm, MIXED-C) at a flow rate of 1.5 mL/min. Calibration was done with polystyrene standards. Nuclear magnetic resonance (NMR) measurements were carried out at room temperature using a Bruker AVANCEDIII 400 spectrometer operating at 400 MHz; CDCl₃ (Aldrich) was used as solvent. The integrals of the characteristic peaks, together with the theoretical molecular weight ($M_{n,theo}$) of the backbone, were used to calculate number-average molecular weight of the graft copolymers ($M_{n,NMR}$). Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC1/TC100 system in an inert nitrogen atmosphere. The samples were heated from room temperature to 150 °C, cooled to -150 °C and finally heated again to 150 °C at a heating/cooling rate of 10 °C/ min. The second heating curve was used to determine the glass transition temperature (T_g), melting temperature (T_m), and degree of crystallinity (X_{PEO}) when the polymer had poly(ethylene oxide) (PEO) segments. T_g was determined as the temperature corresponding to the middle (half-height) of the glass transition. T_m was determined from the endothermic maximum of the melting peak. X_{PEO} was calculated as the ratio

of measured melting enthalpy per gram of PEO to the heat fusion of 100% crystalline PEO (200 J/g).¹ Weight fraction of PEO (W_{PEO}) was calculated according to $M_{n,\text{NMR}}$.

Polymer Synthesis

Poly(N,N-dimethylacrylamide-co-acrylamide), CoAm. Typical procedure for CoAm193K: 25.0 mL of DMAm (24.1 g, 243 mmol), 0.374 g of Am (5.26 mmol), 41.5 mg of NMPI (0.127 mmol) and 1.4 mg of NMPNO (0.0064 mmol) were mixed and subject to 3 freeze-pump-thaw cycles; then the mixture was heated at 110 °C for 3 days. After quenching with rapid cooling, the product was dissolved in Milli-Q water and dialyzed in cellulose membrane (molecular weight cutoff: 1.0 kg/mol) against Milli-Q water for 3 days. After freeze-drying, 22.5 g product was obtained. Yield: 92%; $M_{n,\text{theo}} = 193$ kg/mol; $M_{n,\text{SEC}} = 260$ kg/mol, PDI (polydispersity index) = 1.26; ¹H NMR (400 MHz, CDCl₃): δ /ppm = 3.2-2.7 (–CON(CH₃)₂), 2.7-2.2 (–CH₂CHCO–), 1.9-1.0 (–CH₂CHCO–).

Poly(N,N-dimethylacrylamide-co-acrylamide)-g-poly(ethylene oxide), CoAm-EO. Typical procedure for CoAm193K-EO-1: 1.0 g CoAm193K (0.22 mmol –CONH₂) was dissolved in *ca.* 20 mL dry THF and filtered (through 1 μ m glass fiber filter) into the reaction flask. THF was removed slowly by cryo-evaporation followed by condensation of dry THF into the reactor to dissolve the polymer and cryo-evaporation of the THF again. After repeating this step twice, CoAm193K was dried thoroughly on vacuum line overnight with constant pumping. The next day, another 40 mL of dry THF was condensed into the reactor. After complete dissolution of CoAm193K, 0.22 mL *t*-BuP₄ solution (0.22mmol) was added dropwise with an

argon flow. The solution was stirred for 30 min and temperature was brought down to $-30\text{ }^{\circ}\text{C}$, after which 2.5 mL purified EO (2.2 g, 50 mmol) was condensed slowly into the reactor. Then the reactor was sealed by a stopcock and temperature was slowly elevated to $45\text{ }^{\circ}\text{C}$. After heating and stirring for 48 h, the viscosity of the solution apparently increased. 10 mL of the solution was taken out with an argon flow and injected quickly to a mixture of 5 mL THF and a few drops of AcOH. The sample solution was concentrated by evaporation of THF and the product was isolated by precipitation in *n*-hexane followed by drying in vacuum. $M_{n,\text{theo}} = 617\text{ kg/mol}$; $M_{n,\text{SEC}} = 638\text{ kg/mol}$, PDI = 1.17; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta/\text{ppm} = 3.8\text{-}3.4$ ($-\text{CH}_2\text{CH}_2\text{O}-$), 3.2-2.7 ($-\text{CON}(\text{CH}_3)_2$), 2.7-1.0 ($-\text{CH}_2\text{CHCO}-$).

To the rest of the polymerization solution, 2.0 mL purified MMA (18.7 mmol) was added with an argon flow, attempting to make diblock side chains. However, the solution gelled right away upon addition of MMA. The same occurred when DMAEMA was added to the solution of “living” CoAm193K-EO-2.

CoAm400K-EO-OH, *CoAm400K-EO-CH₃* and *CoAm400K-EO-DG*. CoAm400K-EO was prepared in the same manner as CoAM193K-EOs. 1.5 g CoAm400K (0.33 mmol $-\text{CONH}_2$), 70 mL THF, 0.38 mL *t*-BuP₄ solution (0.38 mmol, 1.15 equiv. of $-\text{CONH}_2$), and 4.5 mL EO (4.0 g, 90 mmol) were used. After polymerization at $45\text{ }^{\circ}\text{C}$ for 48 h, 10 mL of the solution was taken out and quenched with AcOH. The sample was precipitated in *n*-hexane, dried in vacuum, and termed as CoAm400K-EO-OH. $M_{n,\text{theo}} = 1456\text{ kg/mol}$; $M_{n,\text{SEC}} = 1152\text{ kg/mol}$, PDI = 1.28; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta/\text{ppm} = 3.8\text{-}3.4$ ($-\text{CH}_2\text{CH}_2\text{O}-$), 3.2-2.7 ($-\text{CON}(\text{CH}_3)_2$), 2.7-1.0 ($-\text{CH}_2\text{CHCO}-$).

To the rest of the “living” CoAm400K-EO solution, 0.1 mL CH₃I (1.6 mmol, *ca.* 5 equiv. of alkoxide) was added for quenching. The yellowish color of the solution faded right away. The solution was stirred at room temperature overnight to ensure complete methylation of the ends of PEO side chains. Then, 20 mL of the solution was taken out. The solvent was evaporated. The product was dissolved in Milli-Q water, dialyzed in cellulose membrane (molecular weight cutoff: 1.0 kg/mol) against Milli-Q water for 3 days, freeze-dried and termed as CoAm400K-EO-CH₃. $M_{n,theo} = 1457$ kg/mol; $M_{n,SEC} = 1157$ kg/mol, PDI = 1.28; ¹H NMR (400 MHz, CDCl₃): $\delta/ppm = 3.8-3.4$ (–CH₂CH₂O–), 3.36 (–OCH₃), 3.2-2.7 (–CON(CH₃)₂), 2.7-1.0 (–CH₂CHCO–).

The solvent and excess of CH₃I in the solution of CoAm400K-EO-CH₃ remaining in the reaction flask were removed by cryo-evaporation. New THF (dried) was condensed to repeat this step twice so as to ensure complete removal of CH₃I. Finally the remaining solid was dissolved in 50 mL of THF, and 0.2 mL *t*-BuP₄ solution (0.2 mmol) was added to activate (deprotonate) the secondary amide moieties. 1 h later, temperature was decreased to 10 °C (lower temperature was not achievable due to the crystallization of PEO side chains), and 5.0 mL EO (4.4 g, 100 mmol) was condensed into the reaction flask. Afterwards, temperature was slowly increased to 45 °C and the polymerization was allowed to proceed at this temperature for 48 h. After quenching with 0.2 mL AcOH, solvent was evaporated, and the solid product was dissolved in Milli-Q water, dialyzed in cellulose membrane (molecular weight cutoff: 1.0 kg/mol) against Milli-Q water for 3 days, freeze-dried and termed as CoAm400K-EO-DG.

Due to the existence of large quantity of linear (low-molecular-weight) byproduct, the crude product was fractionated using chloroform as solvent and cyclohexane as precipitant. Finally the fractionated product was precipitated in *n*-hexane and dried in vacuum. $M_{n,theo} = 3211$ kg/mol (assuming 100% incorporation of EO monomer in the graft copolymer), $M_{n,SEC} = 1712$ kg/mol, PDI = 1.18; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta/\text{ppm} = 3.8\text{-}3.4$ ($-\text{CH}_2\text{CH}_2\text{O}-$), 3.36 ($-\text{OCH}_3$), 3.2-2.7 ($-\text{CON}(\text{CH}_3)_2$), 2.7-1.0 ($-\text{CH}_2\text{CHCO}-$).

Poly(N,N-dimethylacrylamide-co-acrylamide)-g-poly(propylene oxide) and Poly(N,N-dimethylacrylamide-co-acrylamide)-g-[poly(propylene oxide)-b-poly(ethylene oxide)].

Graft polymerization of PO from CoAm400K was conducted in the same manner as EO, using 1.5 g CoAm400K (0.33 mmol $-\text{CONH}_2$), 50 mL THF, 0.38 mL *t*-BuP₄ solution (0.38 mmol, 1.15 equiv. of $-\text{CONH}_2$), and 4.5 mL PO (3.7 g, 64 mmol). After polymerization at 45 °C for 72 h, 10 mL sample solution was taken out of the reactor and quenched with AcOH. Solvent was evaporated and the sample (CoAm400K-PO-OH) was dried in vacuum. $M_{n,theo} = 1327$ kg/mol (assuming 100% incorporation of PO monomer in the graft copolymer), $M_{n,SEC} = 878$ kg/mol, PDI = 1.26; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta/\text{ppm} = 3.65\text{-}3.45$ ($-\text{CH}_2\text{CH}(\text{CH}_3)\text{O}-$), 3.44-3.27 ($-\text{CH}_2\text{CH}(\text{CH}_3)\text{O}-$), 3.21-2.81 ($-\text{CON}(\text{CH}_3)_2$), 2.66-1.17 ($-\text{CH}_2\text{CHCO}-$), 1.17-1.00 ($-\text{CH}_2\text{CH}(\text{CH}_3)\text{O}-$).

The rest of the solution with “living” poly(propylene oxide) (PPO) side chains was cooled to 0 °C, followed by condensation of 5.0 mL of purified EO (4.4 g, 90 mmol) into the reactor. Temperature was increased slowly to 45 °C again. After 48 h, the

solution became very viscous. 0.2 mL CH₃I (3.2 mmol) was added to quench the reaction (and methylate the ends of the PPO-*b*-PEO side chains). Solvent was evaporated and the crude product was purified by fractionation using chloroform as solvent and *n*-hexane as precipitant. The fractionated product, CoAm400K-(PO-*b*-EO), was dried in vacuum at 35 °C for 3 days. $M_{n,theo} = 2569$ kg/mol (assuming 100% incorporation of PO and EO monomers in the graft copolymer), $M_{n,SEC} = 1472$ kg/mol, PDI = 1.25; ¹H NMR (400 MHz, CDCl₃): $\delta/ppm = 3.77-3.59$ (–CH₂CH₂O–), 3.59-3.45 (–CH₂CH(CH₃)O–), 3.44-3.27 (–CH₂CH(CH₃)O–), 3.21-2.81 (–CON(CH₃)₂), 2.66-1.17 (–CH₂CHCO–), 1.17-1.00 (–CH₂CH(CH₃)O–).

Poly(N,N-dimethylacrylamide-co-acrylamide)-g-poly(1,2-butylene oxide-co-ethylene oxide). 1.5 g CoAm400K (0.33 mmol –CONH₂), 50 mL THF, 0.38 mL *t*-BuP₄ solution (0.38 mmol, 1.15 equiv. of –CONH₂), and 3.6 mL BO (3.0 g, 41 mmol) were used and the reaction was conducted in the same manner as CoAm400K-EO and CoAm400K-PO. After stirring at 45 °C for 72 h, 10 mL sample solution was taken out of the reactor, quenched with AcOH and analyzed by SEC. No increase of the molecular weight was shown, indicating that the graft polymerization did not occur. Then, 5.0 mL (4.4 g, 100 mmol) of purified EO was condensed into the rest of the reaction solution at 0 °C. Temperature was increased slowly to 45 °C again. After 48 h, the solution became apparently viscous. 0.2 mL CH₃I (3.2 mmol) was added to methylate the ends of the side chains. Solvent was evaporated and the crude product was purified by fractionation using chloroform/*n*-hexane. The fractionated product,

CoAm400K-(BO-*co*-EO), was dried in vacuum at 35 °C for 3 days. $M_{n,theo} = 2373$ kg/mol (assuming 100% incorporation of BO and EO monomers in the graft copolymer), $M_{n,SEC} = 1556$ kg/mol, PDI = 1.26; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta/\text{ppm} = 3.9\text{-}3.2$ (polyether main chain protons), 3.21-2.75 ($-\text{CON}(\text{CH}_3)_2$), 1.66-1.39 ($-\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{O}-$), 0.97-0.81 ($-\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{O}-$).

Poly(N,N-dimethylacrylamide-co-acrylamide)-g-poly(tert-butyl glycidyl ether-co-ethylene oxide). The same procedure was followed alike CoAm400K-(BO-*co*-EO). 1.59 g CoAm400K (0.35 mmol $-\text{CONH}_2$), 50 mL THF, 0.40 mL *t*-BuP₄ solution (0.40 mmol, 1.15 equiv. of $-\text{CONH}_2$), and 5.2 mL tBGE (4.8 g, 37 mmol) were used in the first place. No grafting occurred after heating at 45 °C for 72 h, as indicated by SEC (molecular weight was not increased). Then, 3.0 mL (2.6 g, 60 mmol) of purified EO was condensed into the solution, which was then heated at 45 °C for another 48 h, followed by addition of 0.2 mL CH_3I . The crude product was purified by fractionation using chloroform/*n*-hexane. The fractionated product, CoAm400K-(tBGE-*co*-EO), was dried in vacuum at 35 °C for 3 days. $M_{n,theo} = 2252$ kg/mol (assuming 100% incorporation of tBGE and EO monomers in the graft copolymer), $M_{n,SEC} = 1138$ kg/mol, PDI = 1.31; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta/\text{ppm} = 3.86\text{-}3.46$ (polyether main chain protons), 3.44-3.31 ($-\text{CH}_2\text{OC}(\text{CH}_3)_3-$), 3.24-2.28 ($-\text{CON}(\text{CH}_3)_2$), 1.91-1.21 ($-\text{CH}_2\text{CHCO}-$), 1.20-1.02 ($-\text{CH}_2\text{OC}(\text{CH}_3)_3-$).

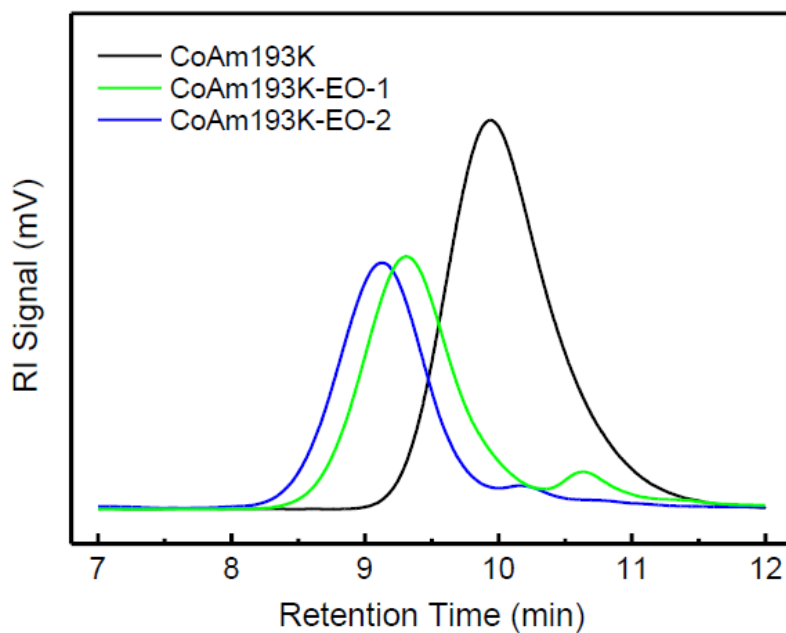


Figure S1 SEC traces of CoAm193K and products from graft polymerizations of EO with feed ratio (EO:CoAm193K, w/w) being 2.2:1 (CoAm193K-EO-1) and 3:1 (CoAm193K-EO-2); concentration (of injected polymer solution) = 3 mg/mL

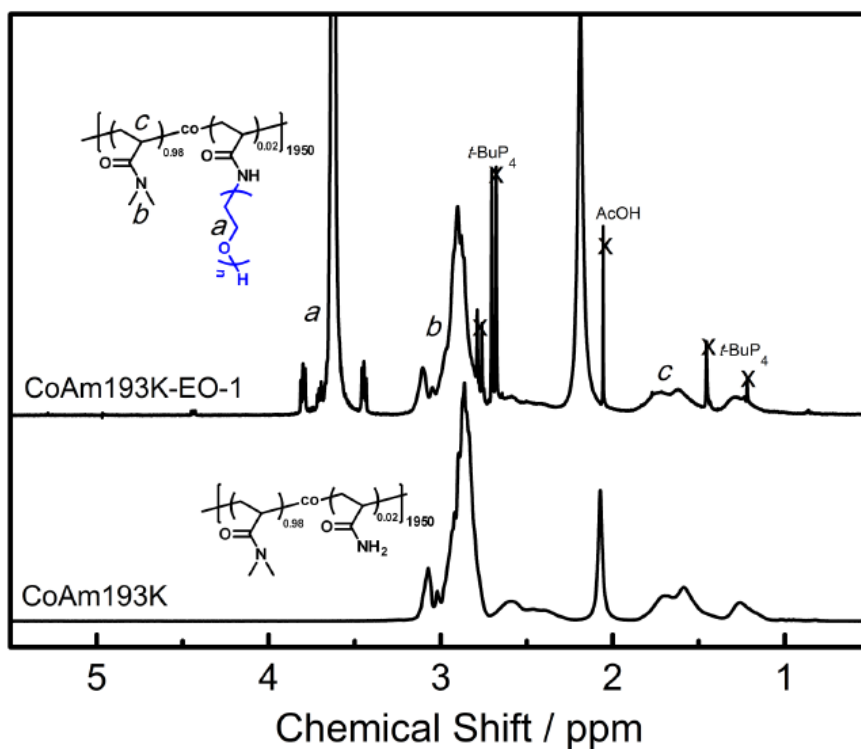


Figure S2 ¹H NMR spectra of CoAm193K and CoAm193K-EO-1

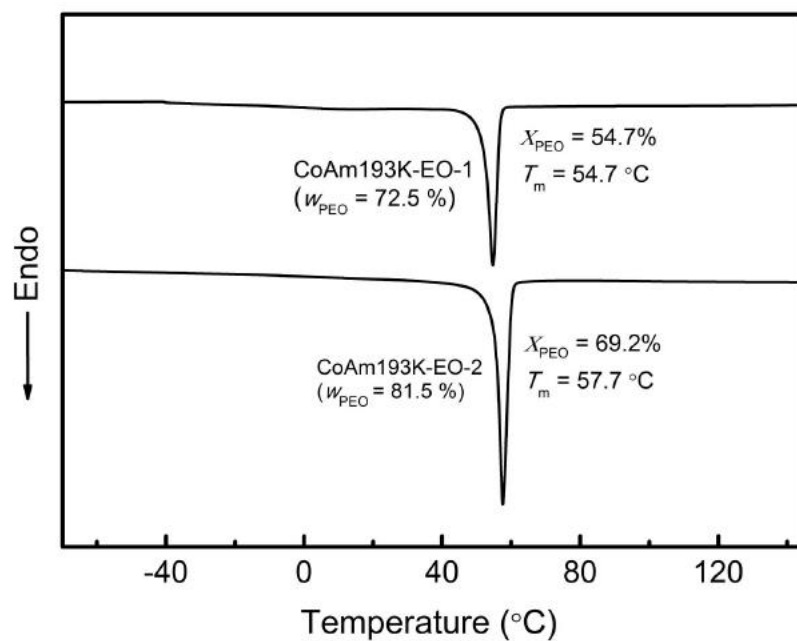
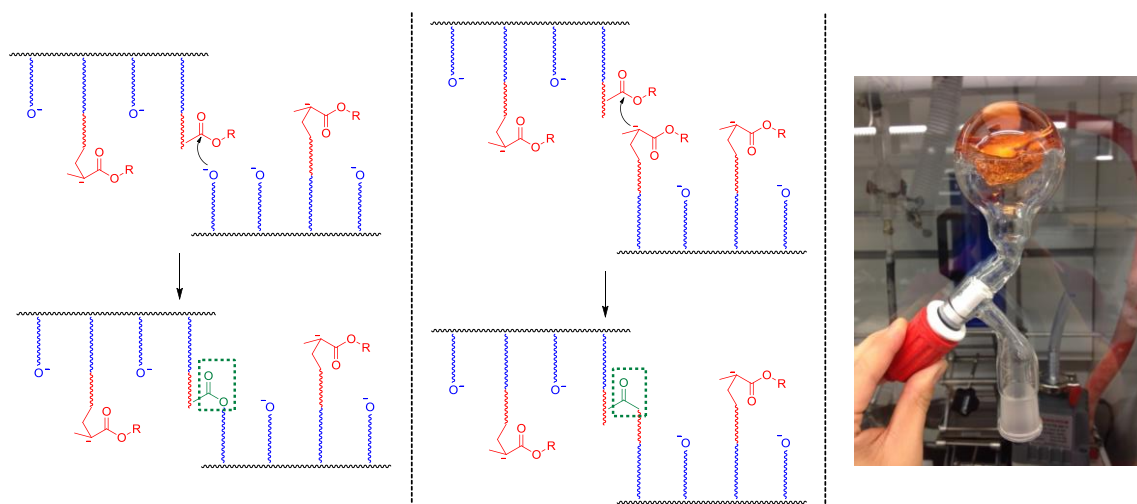


Figure S3 DSC traces (second heating curves) of CoAm193K-EOs



Scheme S1 Proposed gelation mechanism upon addition of methacrylate to "living" PEO side chains: formation of intermacromolecular ester (left) and ketone (middle) groups, and photograph of a gelled reaction mixture (right)

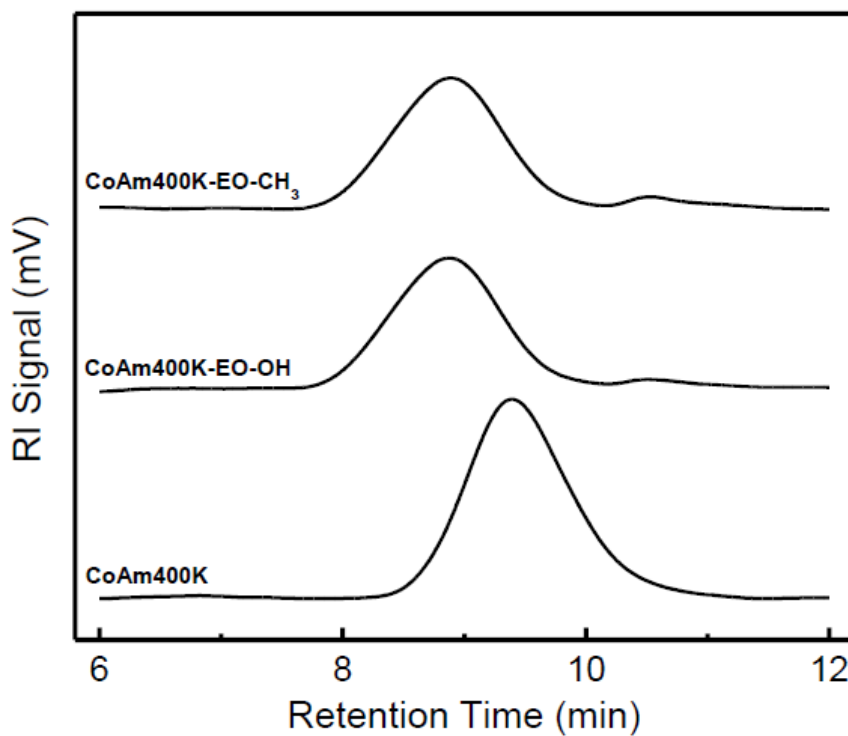


Figure S4 SEC traces of CoAm400K and the products from anionic graft polymerization of EO followed by different quenching methods

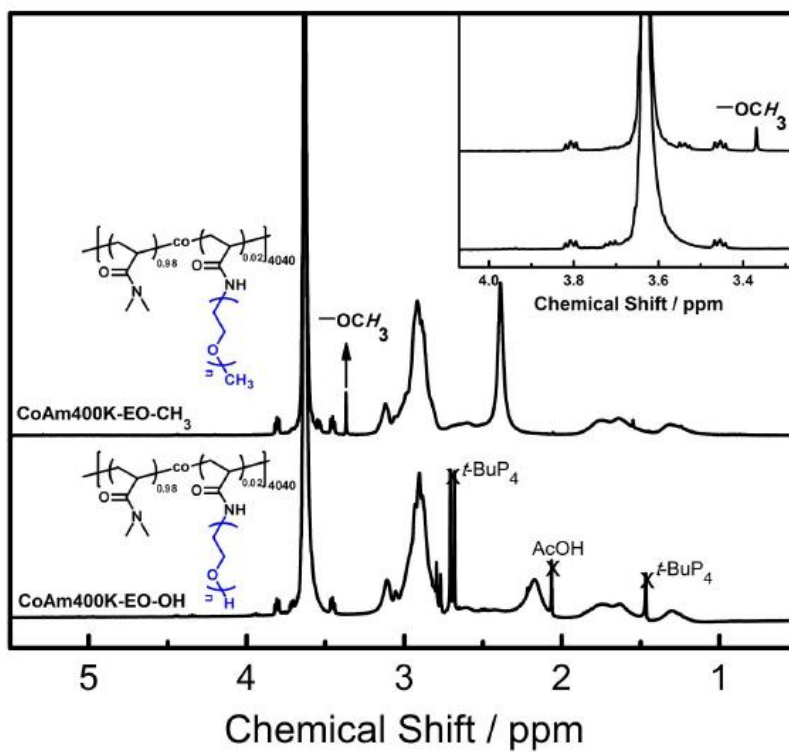


Figure S5 ¹H NMR spectra of CoAm400K-EO-OH and CoAm400K-EO-CH₃; insert: enlarged area of ether protons

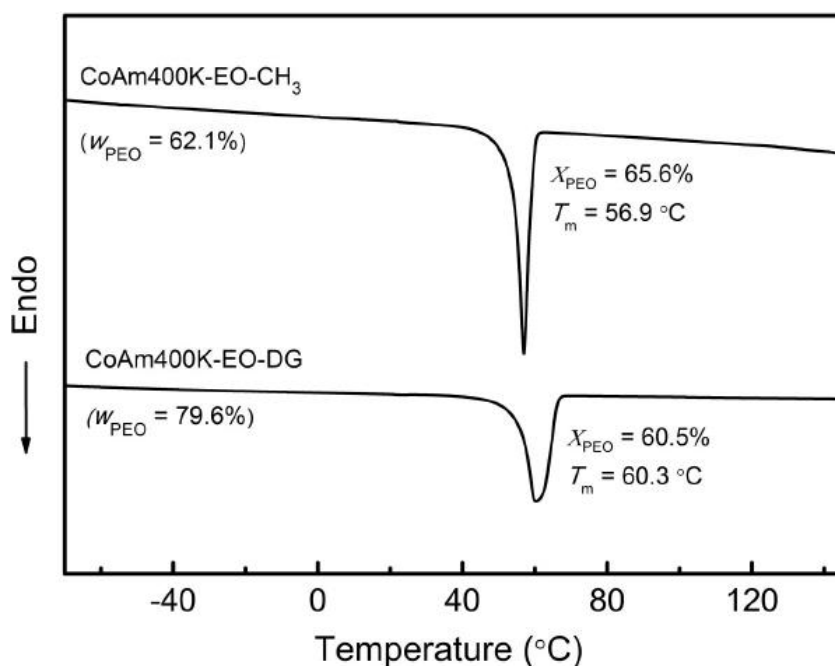


Figure S6 DSC traces (second heating curves) of single (CoAm400K-EO-CH₃) and double-graft (CoAm400K-EO-DG) macromolecular combs based on CoAm400K

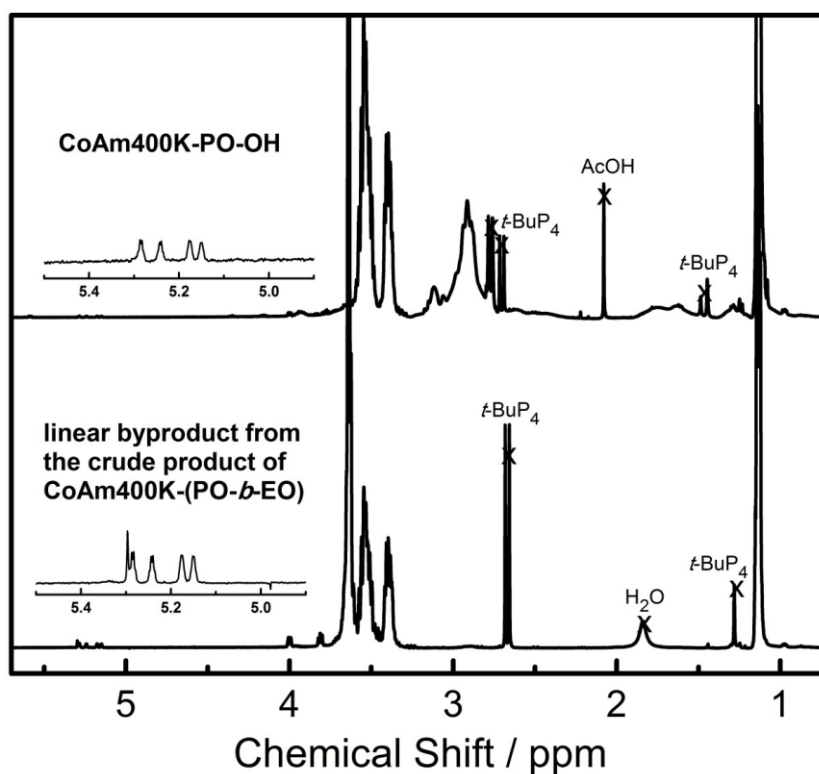


Figure S7 ¹H NMR spectra of CoAm400K-PO-OH (upper spectrum) and linear byproduct fractionated from crude CoAm400K-(PO-*b*-EO) (lower spectrum): the existence of C=C proton (5.12-5.31 ppm) demonstrates the occurrence of chain transfer to PO monomers during the graft polymerization

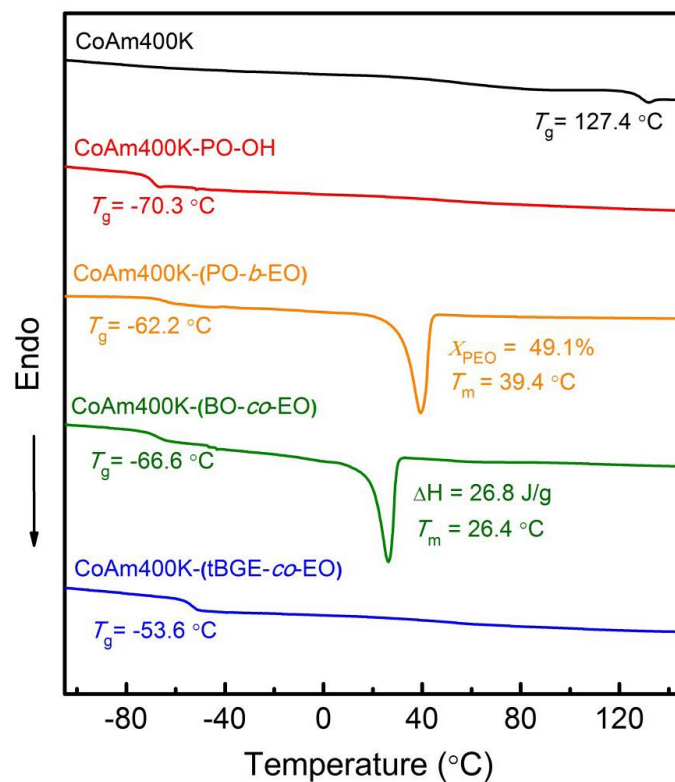


Figure S8 DSC traces (second heating curves) of the complex macromolecular combs (fractionated) based on CoAm400K

References

1. G. Floudas, R. Ulrich and U. Wiesner, *J. Chem. Phys.*, 1999, **110**, 652.