Supporting Information

One-Pot Synthesis of Brush-Like Polymers via Integrated Ring-Opening Metathesis Polymerization and Polymerization of Amino Acid *N*-Carboxyanhydrides

Hua Lu,[†] *Jing Wang,*[‡] *Yao Lin,*[‡]* *Jianjun Cheng*[†]*

[†]Department of Materials Science and Engineering, University of Illinois at Urbana–Champaign, Urbana, IL, 61801

[‡] Polymer Program, Institute of Materials Science and Department of Chemistry, University of Connecticut, Storrs, CT 062691

General:

Materials. All chemicals were purchased from Sigma-Aldrich (St. Louis, Mo) unless otherwise specified. Anhydrous dimethylformamide (DMF) was dried by a column packed with 5Å molecular sieves. Dichloromethane (DCM) and tetrahydrofuran (THF) were dried by an alumina column and stored in a glove box. Anhydrous $CDCl_3$ was prepared by treating commercial $CDCl_3$ (Sigma, St. Louis, Mo) with $CaSO_4$ overnight, followed by distillation under nitrogen. The purified $CDCl_3$ was stored in the presence of 4Å MS. Deuterated trifluoroacetic acid (CF_3CO_2D, TFA-*d*) was purchased from Alfa-Aesar (Ward Hill, MA). H-Glu(OBn)-OH and H-Lys(Z)-OH were purchased from Chem-Impex International (Des Plaines, IL) and used as received. C1,[1] C2,[1] NCAs, M1, M2 and M4[2] were prepared by following previously reported procedures.

Instrumentation. NMR spectra were recorded on a Varian UI400 MHz, a UI500NB MHz or a VXR-500 MHz spectrometer. Tandem gel permeation chromatography (GPC) experiments

were performed on a system equipped with an isocratic pump (Model 1100, Agilent Technology, Santa Clara, CA), a DAWN HELEOS 18-angle laser light scattering detector (also known as multi-angle laser light scattering (MALLS) detector, Wyatt Technology, Santa Barbara, CA) and an Optilab rEX refractive index detector (Wyatt Technology, Santa Barbara, CA). The detection wavelength of HELEOS was set at 658 nm. Separations were performed using serially connected size exclusion columns (100Å, 500Å, 10^3Å and 10^4Å Phenogel columns, 5 μm, 300 × 7.8 mm, Phenomenex, Torrance, CA) at 60°C using DMF containing 0.1 M LiBr as the mobile phase. The *d*n/*d*c values were found to be 0.095-0.110 for the brush polymers depending on the molecular weight. The MALLS detector is calibrated using pure toluene with no need for external polymer standards and can be used for the determination of the absolute molecular weights of both linear polymer and branched polymers. The molecular weights of all polymers were determined based on the *d*n/*d*c value of each sample calculated offline by using the internal calibration system processed by the ASTRA V software version 5.1.7.3 provided by Wyatt Technology.[3] All polymer samples were prepared at 10 mg/mL using DMF containing 0.1M LiBr. Twenty microliters of such solution (0.2 mg sample) was injected into GPC for each analysis. Low resolution electrospray ionization Mass spectrometry (ESI-MS) was performed on a Waters Quattro II Mass Spectrometer. Laser Desorption/Ionization-Time of Flight mass spectrometry (MALDI-TOF MS) spectra were collected on an Applied Biosystems Voyager-DE™ STR system. Infrared spectra were recorded on a Perkin Elmer 100 serial FTIR spectrophotometer calibrated with polystyrene film. TEM experiments were performed on a Philips EM300 Electron Microscope at an accelerating voltage of 80 kV. Circular dichroism measurements were carried out on a JASCO J-700 CD Spectrometer. The path length of the quartz cell was 0.1 cm, and the concentration of polymer was 2 mg/mL in trifluoroethanol (TFE).

General Procedure of ROMP Polymerization and Copolymerization. In a glove box, M2 (22 mg, 0.08 mmol) and M4 (51 mg, 0.2 mmol) were mixed in anhydrous THF (0.9 mL). Ruthenium catalyst C1 (3.5 mg, 0.004 mmol) in DCM (0.1 mL) was added to the monomer

mixture. The reaction mixture was stirred at room temperature for 30 min. After the polymerization was complete (monitored by TLC), the reaction was quenched by pouring the reaction mixture into ethyl vinyl ether (2 mL) to terminate the ROMP. The precipitated solid was collected by centrifugation, washed with diethyl ether (3 × 2 mL) and dried under vacuum (82-90% isolated yield). The MW of the resulting polymer was determined by GPC (M_n = 1.62 × 10^4 g/mol, dn/dc = 0.134, M_w/M_n = 1.04). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.38-7.22, 5.59, 4.61, 3.50, 3.21, 2.90, 1.86-1.62, 1.22-0.98.

General Procedure for Converting The *N*-TMS Amine Group of the ROMP Polymer to *N*-Boc ROMP Polymer To perform the GPC analysis of the homo-polymer P4 and P5, the *N*-TMS group of the polymer was converted to the *tert*-butoxycarbonyl (Boc) group, a more stable amine-protecting group. M2 (14 mg. 0.05 mmol) and C1 (0.44 mg. 0.5 μmol) were mixed in THF (0.5 mL) and stirred for 2 h. The ROMP was quenched by adding ethyl vinyl ether (0.1 mL) and MeOH (0.1 mL) to the polymerization solution. $(Boc)_2O$ (50 mg, 0.23 mmol) was then added to the solution. The mixture was stirred overnight at room temperature. Petroleum ether (5 mL) was added to the reaction mixture. The resulting precipitate was collected by centrifugation, washed by petroleum ether (2×5 mL) and dried under vacuum. The polymer was dissolved in $CDCl_3$ for ^{1}H NMR analysis. Based on the NMR analysis, nearly 100 % of the *N*-TMS group was replaced by Boc (Figure S3). Excellent signal/noise ratio was observed in GPC analysis. The M_n and MWD of the N-Boc protected ROMP polymer were 2.76 × 10^4 g/mol and 1.13, respectively (dn/dc = 0.136).

General procedure for the Preparation of Brush-Like Polymers. In a glove box, M2 (14.5 mg, 0.05 mmol) and M4 (75 mg, 0.3 mmol) were mixed in anhydrous THF (1 mL). Ruthenium catalyst C1 (4.4 mg, 0.005 mmol) in DCM (0.1 mL) was added to the monomer mixture. The reaction solution was stirred at room temperature for 1 h. After M2 and M4 were completely consumed (monitored by TLC), THF was removed under vacuum in a glove

box. Anhydrous DMF (1 mL) was then added to dissolve the resulting polymer (P4). A small portion of the solution was taken out for GPC analysis of the MW of P4 (M_n = 1.25 × 10^4 g/mol, dn/dc = 0.134, M_w/M_n = 1.02). Glu-NCA (395 mg, 1.5 mmol) in DMF (2 mL) was added to the remaining P4 solution. After the Glu-NCA was completely consumed (monitored by following the anhydride band of NCA at 1790 cm^{-1} using FTIR), the ruthenium catalyst was removed by pouring the reaction mixture into ethyl vinyl ether (5 mL). The resulting polymer (P4-*g*-Glu_{30}) was precipitated with diethyl ether (20 mL), collected by centrifugation, washed with diethyl ether (3 × 20 mL) and then dried under vacuum (68-75% isolated yield). The MW of the brush-like polymer P4-*g*-Glu_{30} was determined by GPC (M_n = 5.51× 10^4 g/mol, dn/dc = 0.110, M_w/M_n = 1.05). The dn/dc values of the brushed polymers (Table 2) were found to range from 0.095 to 0.11, depending on the polypeptide chain lengths. ^{1}H NMR ($CDCl_3$/TFA-*d* mixture (v/v: 85/15 to 50/50), 500 MHz): δ 8.24, 7.39-7.25, 5.59-5.40, 5.08, 4.61, 4.57, 3.50, 2.90, 2.44, 2.11, 1.92, 1.18.

General Procedure of the Kinetic Studies of NCA Polymerizations Mediated by M2 and *N*-TMS ROMP

The solution for the kinetic study of M2-initiated Glu-NCA polymerization at a M/I (NCA/M2) ratio of 100:1 was prepared by dissolving Glu-NCA (156 mg, 0.6 mmol) in dry DMF (3.0 mL) followed by the addition of M2 (0.1 M in DMF, 60 μL) to the Glu-NCA solution. The kinetic study of NCA polymerization was performed by monitoring the intensity of the NCA infrared anhydride band at 1790 cm^{-1} at various time intervals by injecting an aliquot of polymerization solution into a Wilmad 0.1 mm KBr cell. The polymerization rate constant was obtained by plotting the log of the NCA concentration versus time and fitting the data using the standard rate expressions (Figure S6). A standard working curve was prepared by using Glu-NCA at selected concentrations.

The solution for the kinetic study of ROMP polymer-initiated Glu-NCA polymerization at a M/I (NCA/M2) ratio of 100:1 was prepared as follows: M4 (25 mg, 0.1 mmol) and M2 (7.8 mg,

0.03 mmol) were dissolved in anhydrous THF (0.6 mL) in a glove box, to which Grubbs catalyst (C1) in THF (0.01 M, 0.1 mL) was added in one portion. The mixture was stirred at room temperature for 2 h followed by the evaporation of the solvent under high vacuum. DMF (300 μL) was then added to dissolve the polymer to prepare a stock solution with an *N*-TMS concentration of 0.1 M. The ROMP stock solution (0.1 M in DMF, 60 μL) was added in one portion into a vigorously stirred DMF solution of Glu-NCA (156 mg, 0.6 mmol, 3 mL). The experiments to determine the polymerization kinetics were performed in a similar manner to those mentioned above (Figure S6).

Objective: To study whether M2 can initiate controlled polymerization of Glu-NCA and Lys-NCA

Table S1. M2 Initiated NCA Polymerization in DMF at Room Temperature

entry	M (M/I)	M_n (expected) (x 10^3 g/mol)	M_n (obtained) (x 10^3 g/mol)	M_w/M_n
1	Glu-NCA (50)	10.9	12.3	1.15
2	Glu-NCA (100)	21.9	23.8	1.17
3	Glu-NCA (200)	43.8	43.3	1.15
4	Lys-NCA (50)	13.1	13.3	1.09
5	Lys-NCA (100)	26.2	22.7	1.04
6	Lys-NCA (200)	52.4	41.2	1.05

M2 initiated controlled polymerization of γ-benzyl-L-glutamate NCA (Glu-NCA) and ε-Cbz-L-lysine NCA (Lys-NCA). The resulting M2-poly(γ-benzyl-L-glutamate) (M2-PBLG) and M2- poly(ε-Cbz-L-lysine) (M2-PZLL) have the expected MWs and narrow MWDs.

Objective: To confirm that the TMS groups on the monomer M2 can be well preserved during ROMP of M2 or a mixture of M2 and M4 in the presence of a Grubbs catalyst.

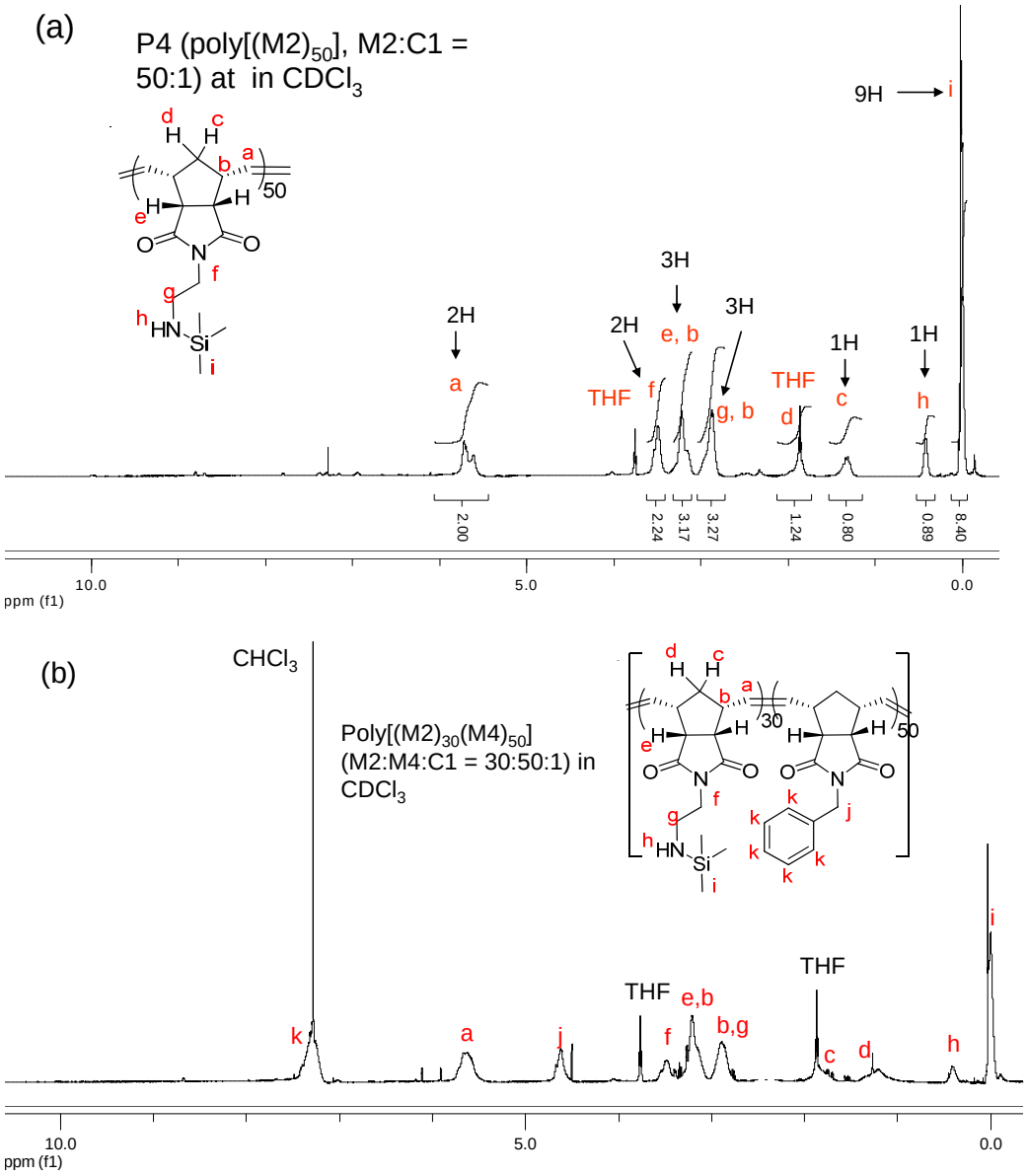


Figure S1. (a) P4 (Poly[(M2)$_{50}$], prepared at an M2/C1 ratio of 50:1, was analyzed by ^{1}H NMR (in $CDCl_3$) before being quenched by ethyl vinyl ether to confirm that the *N*-TMS group of M2 stayed intact during the ROMP to form P4. (b) Analysis of poly(M2/M4) at a C1/M2/M4 ratio of 1:30:50. The *N*-TMS group also stayed intact during the formation of poly(M2/M4) random copolymer. The NMR spectra were collected on UI500NB NMR spectrometer.

Objective: To show that the pendant TMS groups on the random copolymers P9 ([$(M2)_{18}(M4)_{50}$], Table 2) can be completely removed by quenching the ROMP solution with ethyl vinyl ether.

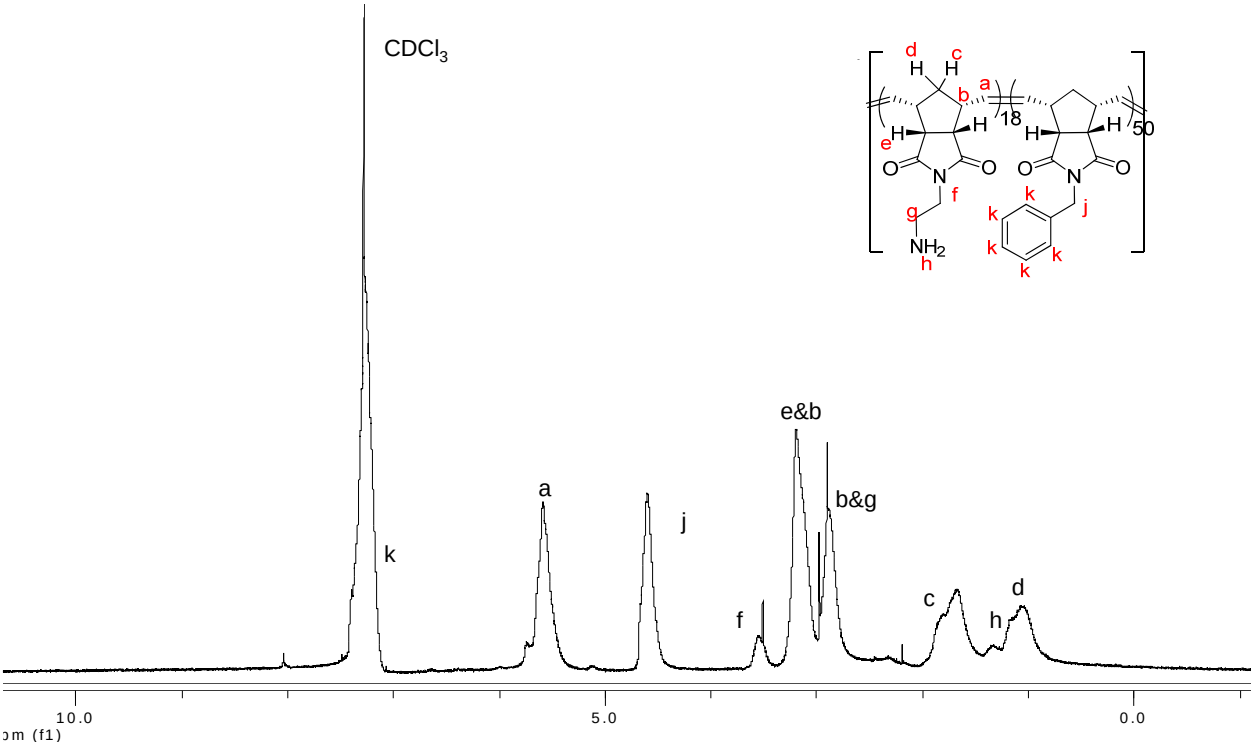


Figure S2. The ^{1}H NMR ($CDCl_3$) spectrum of the random copolymer P9 after it was quenched with ethyl vinyl ether.

Objective: To show that the pendant TMS groups on P5 ([$(M2)_{100}$]) can be quantitatively converted to the Boc group so that the resulting polymer can be analyzed by GPC

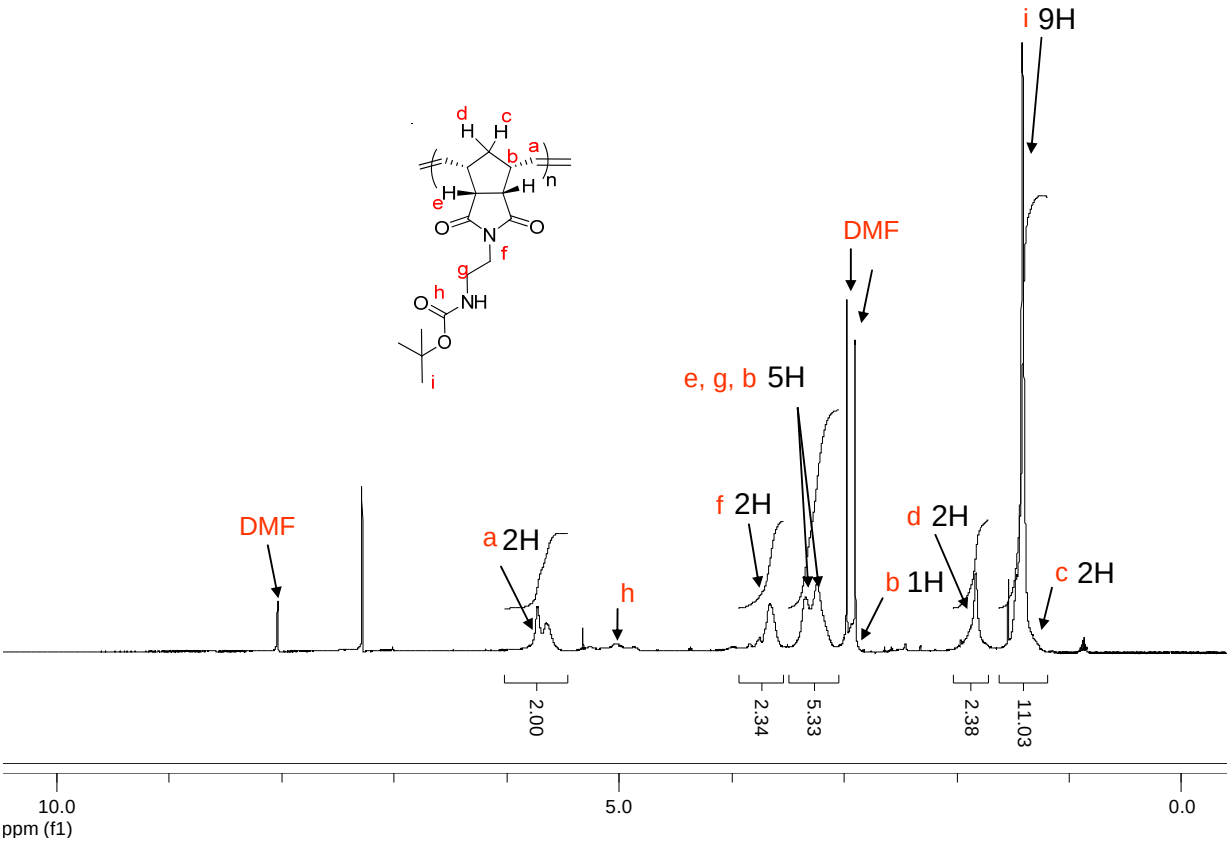


Figure S3. The ^{1}H NMR spectrum of P5 after its -NH-TMS group was converted to -NH-Boc (in $CDCl_3$).

Based on the integration of the Boc and other protons, it is apparent that the conversion from -NH-TMS to -NH-Boc is quantitative. This experiment also demonstrates that the -NH-TMS was indeed completely preserved on M2 during ROMP, as show in Figure S1a.

Objective: To show the NMR spectrum of the brush polymer P7-*g*-Glu_{30}

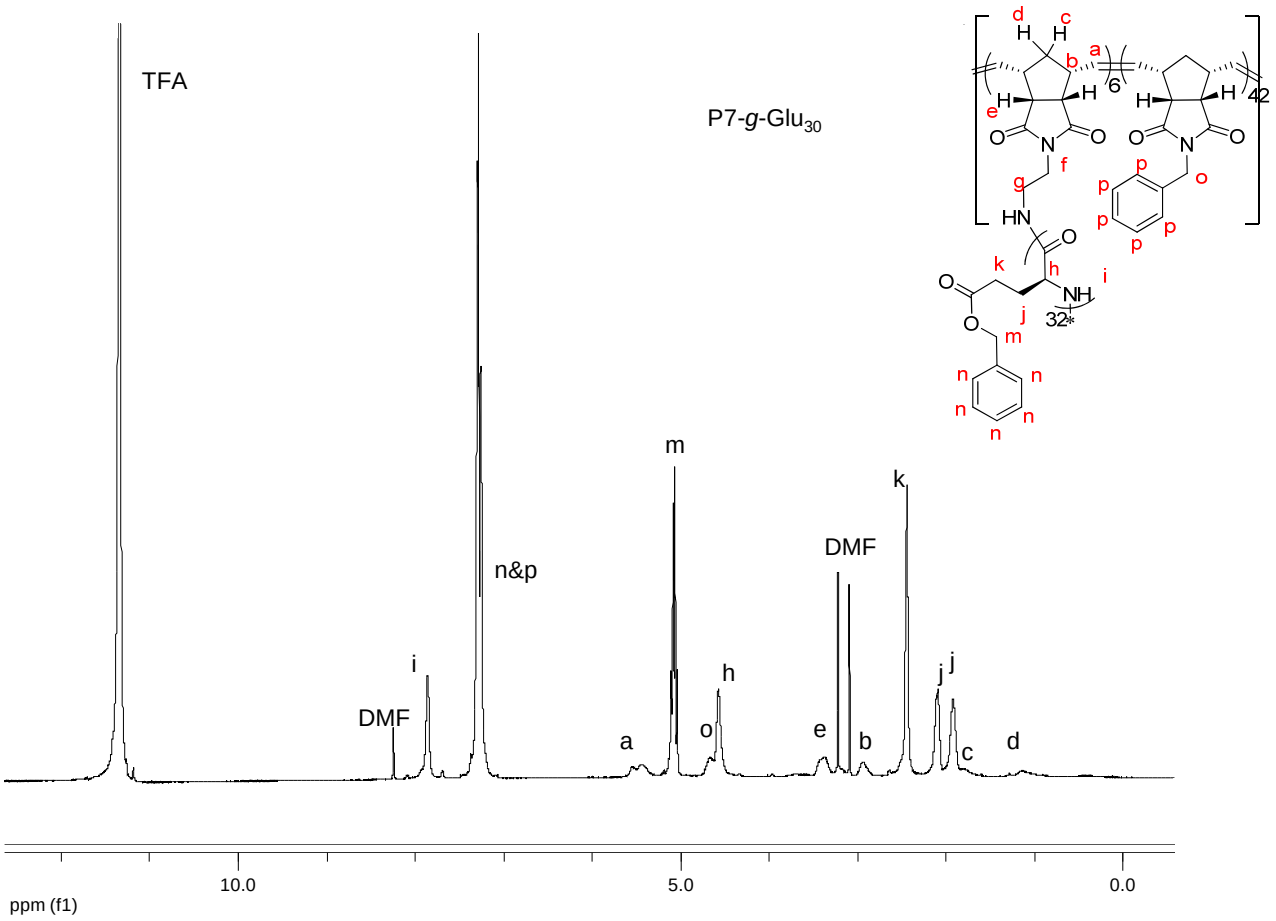


Figure S4. The ^{1}H NMR spectrum of the brush-like polymer P7-*g*-Glu_{30}. TFA-*d* was used as the NMR solvent. The NMR spectrum was collected on a UI500NB NMR spectrometer.

Objective: To study whether the poly(norbornene)-*g*-PBLG, instead of low-MW PBLG homopolymer, was predominately generated during $(M2)_{11}(M4)_2$-*g*-$(Glu)_{30}$ (an *N*-TMS containing poly(norbornene))-mediated Glu-NCA polymerization.

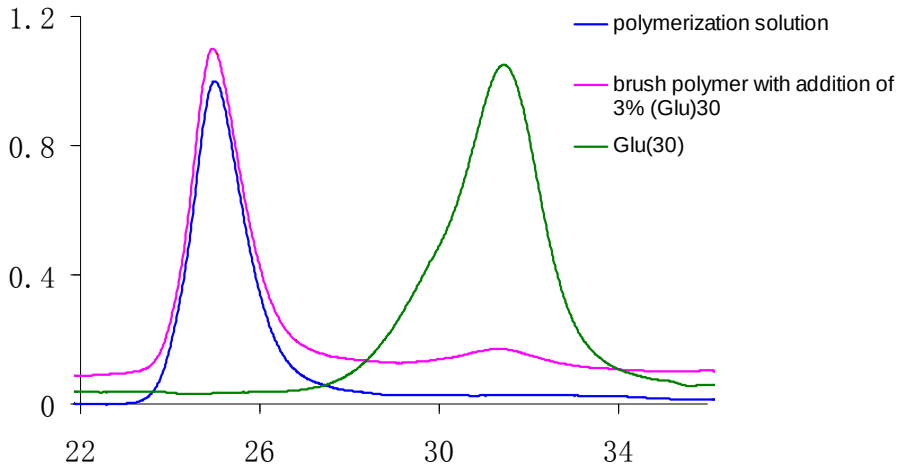


Figure S5 Overlay of the GPC curves (reflective index signal) of the polymerization solution for the synthesis of $(M2)_{11}(M4)_2$-*g*-$(Glu)_{30}$ (blue) (direct injection into GPC without purification), PBLG ($(Glu)_{30}$) prepared at a Glu-NCA/M2 ratio of 30:1 (green), and the $(M2)_{11}(M4)_2$-*g*-$(Glu)_{30}$ with the addition of 3 wt% of $(Glu)_{30}$ (magenta).

Experimental: In a glove box, M4 (25 mg, 0.1 mmol) and M2 (11 mg, 0.04 mmol) were dissolved in dry THF (0.6 mL). Grubbs catalyst C1 in THF (0.01 M, 0.2 mL) was added to the M2/M4 solution in one portion. The mixture was stirred at room temperature for 1 h, followed by evaporation of the solvent under vacuum for 2 h. The resulting ROMP polymer was dissolved in DMF (1.5 mL), and the solution was divided into three portions (0.5 mL for each portion). Glu-NCA (102 mg, 0.4 mmol) was added to one portion (0.5 mL of the ROMP polymer solution), and the solution was stirred overnight. After the Glu-NCA was completely consumed (monitored by following the anhydride band of NCA at 1790 cm^{-1} by FR-IT), the ruthenium catalyst was removed by adding ethyl vinyl ether (0.1 mL) to the reaction mixture. A small portion of the solution (0.1 mL) was taken out, diluted to 0.5 mL by DMF, and used for

GPC analysis directly (**Sample 1**). The rest of the polymer solution was precipitated with diethyl ether (10 mL), collected by centrifuge and dried under vacuum. The purified brush polymer $(M2)_{11}(M4)_2$-*g*-$(Glu)_{30}$ (67 mg) was obtained (**Sample 2**). The DMF-ether supernatant was transferred from the centrifuge tube to a separate, pre-weighed 20 mL vial; the solvent mixture was removed under vacuum to give sample 3 (2.0 mg). **Sample 3** was dissolved in DMF (0.1 mL) to make a solution at 20 mg/mL and injected into GPC for MW analysis.

$(Glu)_{30}$ (Sample 4) was prepared by mixing a DMF solution of Glu-NCA (78 mg, 0.3 mmol, 0.5 mL) and a DMF solution of M2 (0.1 M, 0.1 mL). The polymerization was complete in 3 h. The $(Glu)_{30}$ was precipitated, washed with ether (2 × 10 mL) and dried under vacuum to give 40 mg of **Sample 4**. Stock solutions of **Sample 2** (10 mg/mL) and **Sample 4** (10 mg/mL) were prepared separately using DMF containing 0.1M LiBr. **Sample 2** (100 μL) and **Sample 4** (3 μL) were then mixed and injected into GPC.

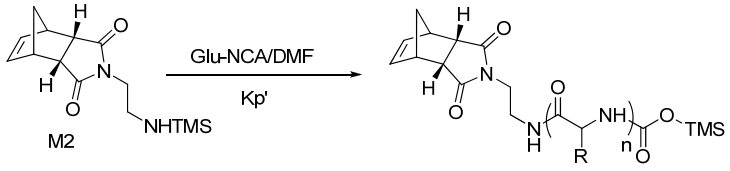
Interpretation of the GPC data: The blue curve shows the GPC results (RI signal) of the bulk polymerization solution (**Sample 1**) without any precipitation or separation. Both LS and RI detectors showed very smooth baseline along the low MW region (30-40 min), indicating that the small amount of **Sample 3** collected from the ether solution has a very low MW. To confirm this, we analyzed **Sample 3** with GPC. As expected, very weak RI signals and nearly no LS signals were obtained when **Sample 3** was injected into GPC; the LS and RI data were insufficient to give reliable measurement of the MW of **Sample 3**. To further confirm that formation of PBLG was negligible during $(M2)_{11}(M4)_2$-mediated Glu-NCA polymerization, we prepared $(Glu)_{30}$ (**Sample 4**) through M2-mediated Glu-NCA polymerization at a Glu-NCA/M2 ratio of 30:1. **Sample 4** was analyzed by GPC (green, Figure S5, M_n = 6.5 × 10^3 g/mol, MWD = 1.20). We mixed **Sample 4** (3 wt%) with **Sample 2** and then analyzed the mixture by GPC (Megenta, Figure S5). The GPC analysis clearly showed that the 3% of **Sample 4** in **Sample 2** is detectable. Thus, the side reaction for generating homo PBLG in $(M2)_{11}(M4)_2$ mediated Glu-NCA polymerization is negligible.

Objective:

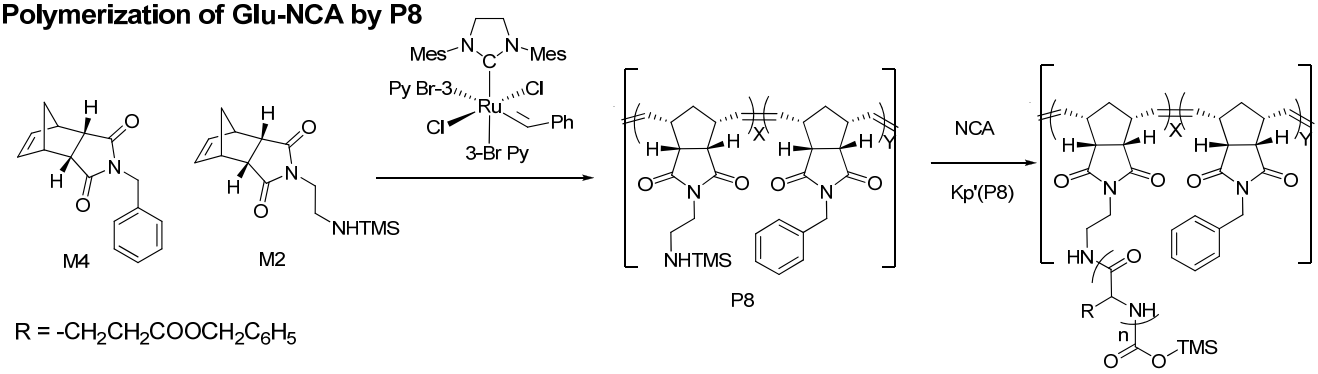
(1) To estimate roughly how many of the pendant –NH-TMS on a ROMP random polymer (e.g., P8 selected in this study) can function as the initiator for ROP of NCA by comparing the polymerization rate constant of P8-initiated NCA polymerization with that of M2-initiated polymerization (Figure S6a and Figure S6b) using kinetic analysis.

(2) To study whether the pendant –NH-TMS of P8 can initiate a controlled, living polymerization by analyzing the M_n's versus Glu-NCA conversions by terminating the ROP of Glu-NCA at selected monomer conversions (Figure S6c).

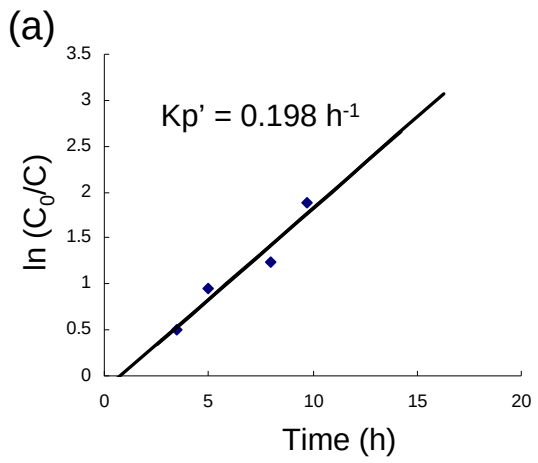
Polymerization of Glu-NCA by M2

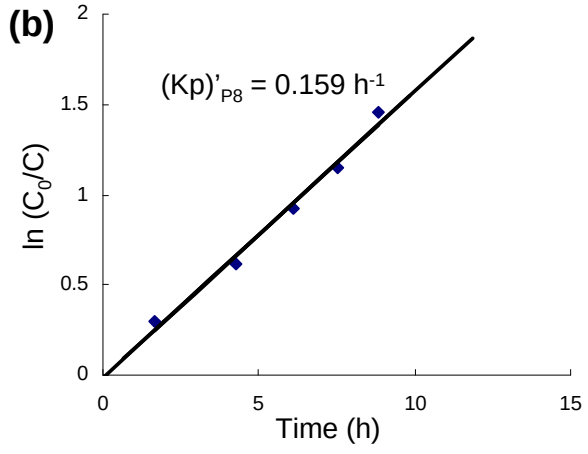


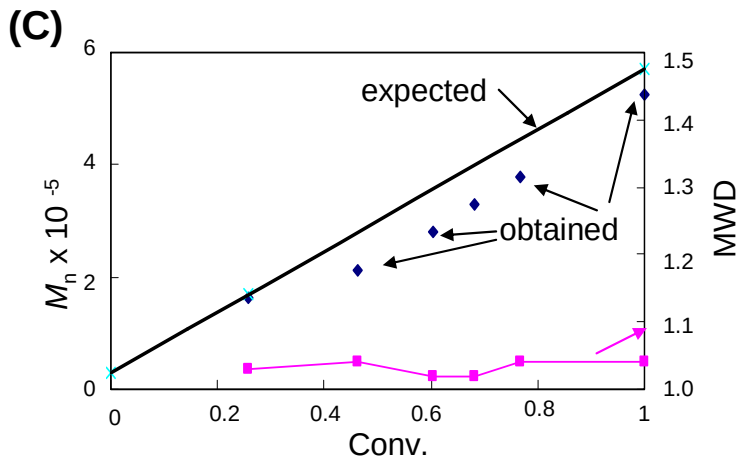
Polymerization of Glu-NCA by P8



R = -$CH_2CH_2COOCH_2C_6H_5$







conversion (%)	M_n (x 10^5 g/mol) (cal.)	M_n (x 10^5 g/mol) (obt.)	M_w/M_n
25.7	1.68	1.62	1.03
46.2	2.79	2.12	1.04
60.3	3.55	2.80	1.02
68.2	3.98	3.30	1.02
76.6	4.43	3.78	1.04
100.0	5.70	5.25	1.04

Figure S6. The kinetic study of M2-initiated Glu-NCA polymerization at a Glu-NCA/M2 ratio of 100:1. The initial Glu-NCA concentration was 52 mg/mL. The polymerization rate constant was obtained by plotting the log of the NCA concentration versus time and fitting the data using a standard rate expression: $-d[\text{Glu-NCA}]/dt = K_p[\text{NHTMS}][\text{Glu-NCA}] = K_p'[\text{Glu-NCA}]$. K_p' ($K_p[\text{NHTMS}]$), the slope of the plot shown above in Figure S6a, was found to be 0.198 h^{-1}. (b) The kinetic study of P8-initiated Glu-NCA polymerization at a Glu-NCA/M2 ratio of 100:1. The initial Glu-NCA concentration was 52 mg/mL. The polymerization rate constant was obtained by plotting the log of the NCA concentration versus time and fitting the data using a standard rate expression: $-d[\text{Glu-NCA}]/dt = (K_p)_{P8}[\text{NHTMS}]_{P8}[\text{Glu-NCA}] = (K_p)'_{P8}[\text{Glu-NCA}]$. $(K_p)'_{P8}$ ($(K_p)_{P8}[\text{NHTMS}]_{P8}$), the slope of the plot shown in Figure S6b, was found to be 0.159 h^{-1}. (c) The plot of M_n of P8-*g*-Glu_{100} versus the conversion of Glu-NCA for P8-initiated Glu-NCA polymerization terminated at selected monomer conversions.

Interpretation of data

The rate constants of the Glu-NCA polymerization initiated by M2 and P8 with identical concentrations of *N*-TMS were obtained from the kinetic studies shown in Figure S6a and Figure S6b, respectively. Both polymerizations proved to be first order with respect to the NCA concentration. The kinetic equations for M2 (1) and P8-initiated polymerizations (2) are expressed as

$$-d[\text{Glu-NCA}]/dt = K_p[\text{NHTMS}][\text{Glu-NCA}] = K_p'[\text{Glu-NCA}] \quad (1)$$

$$-d[\text{Glu-NCA}]/dt = (K_p)_{P8}[\text{NHTMS}_{P8}][\text{Glu-NCA}] = (K_p)'_{P8}[\text{Glu-NCA}] \quad (2)$$

Kp', which is K_p[NHTMS], is equal to 0.198 h^{-1}. $(K_p)'_{P8}$, which is $(K_p)_{P8}[NHTMS_{P8}]$, is equal to 0.159 h^{-1}. As we have shown previously in Figure S1 and Figure S3, the *N*-TMS groups are quantitatively preserved during the ROMP process. Thus, the initial [NHTMS] ($[NHTMS]_0$) should be identical to initial $[NHTMS_{P8}]$ (($[NHTMS_{P8}]_0$). The P8-initiated Glu-NCA polymerization proceeds at a rate (0.159 h^{-1}) roughly 80% relative to the rate of M2-initiated Glu-NCA polymerization. There are four possibilities:

(1) If K_p is substantially smaller than $(K_p)_{P8}$, which means that the actual [NHTMS] should be substantially larger than the actual $[NHTMS_{P8}]$, only a small portion of the -NH-TMS of P8 participated in initiating Glu-NCA polymerization. However, it is unlikely that K_p is substantially smaller than $(K_p)_{P8}$. The probability is therefore very low that only a small portion of the –NH-TMS group of P8 acts as an initiator of the Glu-NCA polymerization to form very long PBLG arms in the resulting P8-*g*-PBLG..

(2) If K_p is identical to $(K_p)_{P8}$, which is likely to happen, the actual amount of -NH-TMS of P8 ($[NHTMS_{P8}]$) participating in the initiation of Glu-NCA polymerization should be 80% compared to that of M2 ([NHTMS]). Because of the linear correlation between MW and conversion, the MW of the PBLG arm in P8-*g*-PBLG should be roughly 25% larger than the expected MW.

(3) If K_p is slightly larger than $(K_p)_{P8}$, which is highly likely to occur because of the increased steric bulkiness around the –NH-TMS in P8, the actual amount of -NH-TMS of P8 ($[NHTMS_{P8}]$) participating in the initiation of Glu-NCA polymerization should be very close to that of M2 ([NHTMS]). Because of the linear correlation between MW and conversion, the MW of the PBLG arm in P8-*g*-PBLG should therefore be very close

to the expected MW.

(4) K_p is substantially larger than $(K_p)_{P8}$, which means that the actual [NHTMS] should be substantially smaller than the actual [$NHTMS_{P8}$]. This is very unlikely to happen.

It is reasonable to conclude that K_p is nearly identical to or slightly larger than $(K_p)_{P8}$ and that the actual amount of -NH-TMS of P8 ([$NHTMS_{P8}$]) that participated in the initiation of Glu-NCA polymerization should be close or slightly smaller than that of M2 ([NHTMS]).

The linear correlation of the M_n values of the P8-*g*-PBLG ($M_w/M_n < 1.1$) with the conversion of NCA monomer suggests that P8-mediated NCA polymerizations proceeded in a highly controlled manner.

Objective: To analyze whether the PBLG arm in the brush-like polymers still adopt a helical conformation.

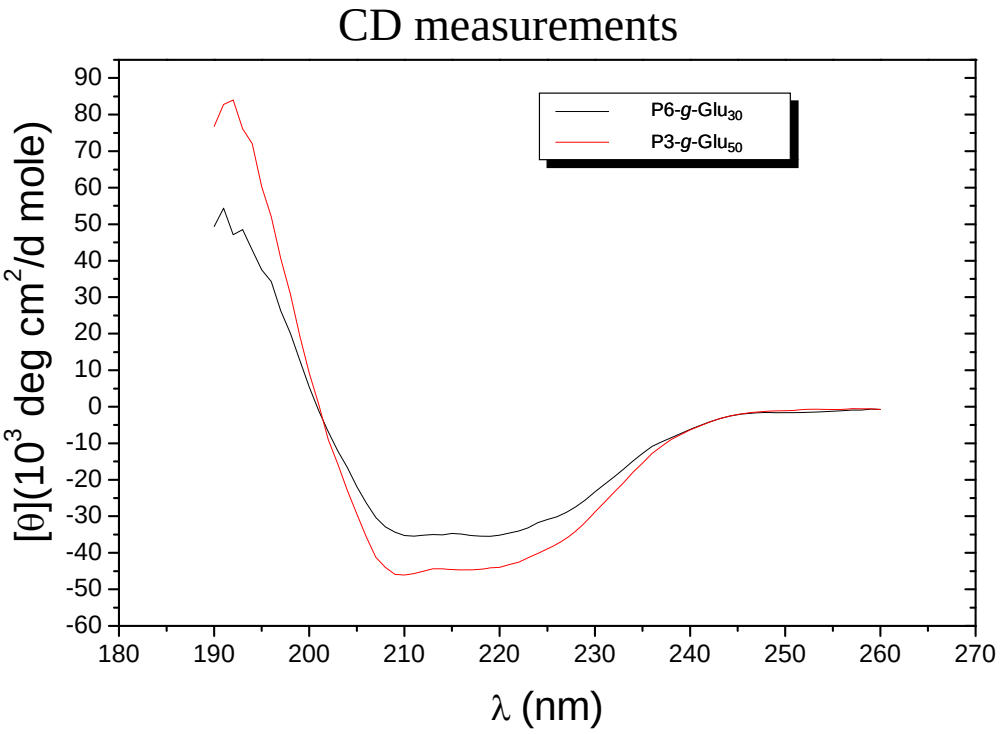


Figure S7. CD analysis of PBLG grafted to ROMP polymers (P6-*g*-Glu_{30} and P3-*g*-Glu_{50}) in TFE (2.0 mg/mL for P6-*g*-$Glu_{30;}$ 1.8 mg/mL for P3-*g*-Glu_{50}).

The two negative bands at 208 and 222 nm and the positive band at 192 nm of the CD spectra of P6-*g*-Glu_{30} and P3-*g*-Glu_{50} suggest that the PBLG still adopts a helical conformation when grafted to poly(norbornene) .

Objective: To evaluate whether PBLG in the brush-like polymers still adopts a helical conformation by analyzing the ^{1}H NMR spectra of the P6-*g*-Glu$_{30}$ in a helicogenic solvent (e.g., DMF) that favors the formation of the α-helical conformation of PBLG and in a non-helicogenic solvent (e.g., TFA) that disrupts the helical conformation of PBLG.

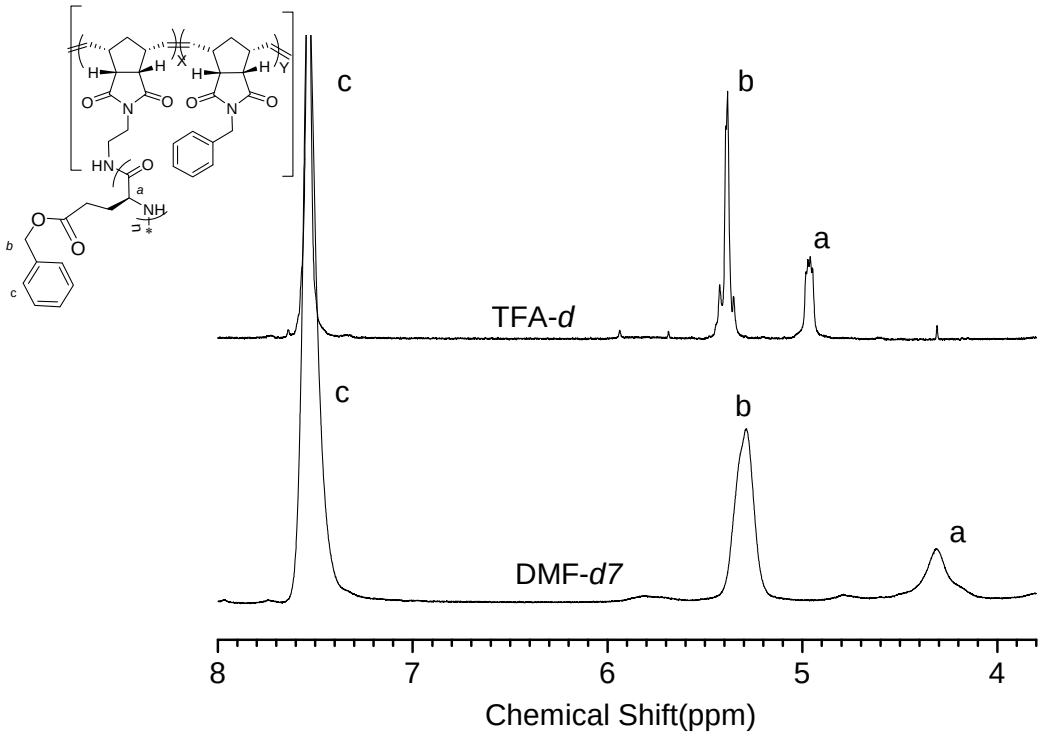


Figure S8. ^{1}H NMR spectrum of the brush polymer P6-*g*-Glu$_{30}$ (10 mg/mL) in DMF-*d*7 and TFA-*d*.

It is known that PBLG adopts a helical conformation in DMF and a random coil conformation in TFA. The change of the chemical shift of the protons in P6-*g*-Glu$_{30}$ and the line broadening (in DMF) suggest a random coil conformation in TFA and the helical conformation in DMF. This study further demonstrated that PBLG should adopt an α-helical conformation in a helicogenic solvent and confirmed the α-helical conformation of P6-*g*-Glu$_{30}$ by the CD analysis.

Objective: To preliminarily study whether brush-like polymers can form nanometer-sized aggregates with the addition of non-solvent to solution containing poly(norbornene)-*g*-PBLG

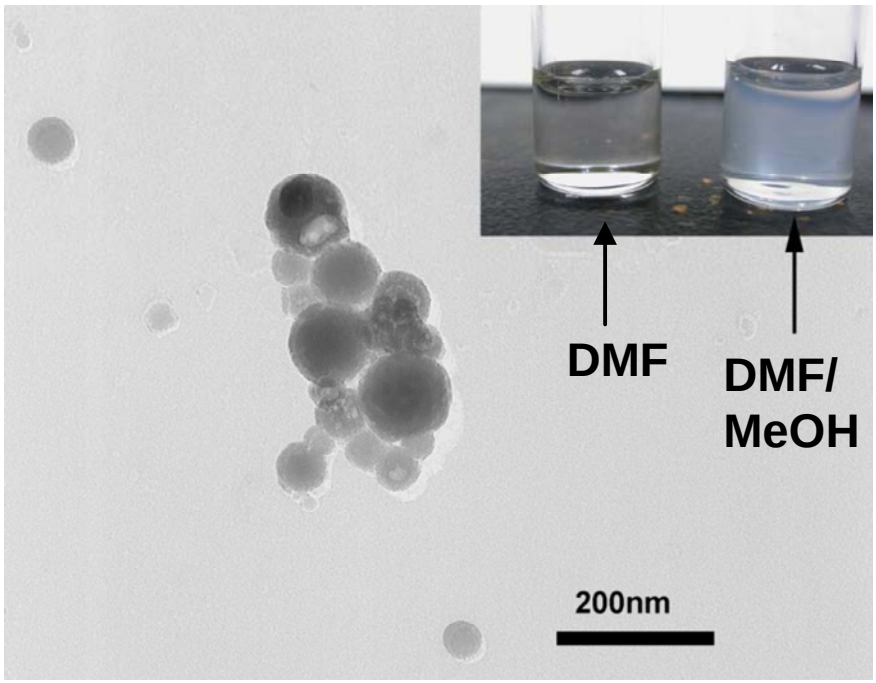


Figure S9. TEM analysis of P7-*g*-Glu_{30} in MeOH/DMF. Inset: (Left) a solution of P7-*g*-Glu_{30} in DMF; (Right) a solution of P7-*g*-Glu_{30} micelles in a mixture of MeOH/DMF.

Experimental

P7-*g*-Glu_{30} (0.45 mg) was dissolved in DMF (0.5 mL) followed by dropwise addition of methanol (0.25 mL) under sonication. Strong Tyndall light scattering was observed when a laser beam was passed through the dispersion, indicating formation of assemblies or aggregates. This sample was then analyzed by TEM. The solution was first cast onto a carbon-coated copper grid and allowed to air dry at room temperature. The samples were then stained with RuO_4 vapor at room temperature for 30 min before the TEM analysis. (Figure S9)

This preliminary study demonstrated the formation of nanometer-sized aggregates when MeOH was added to a DMF solution of P7-*g*-Glu_{30}. The formation of nano-aggregates was

likely through a self-assembly process. It is beyond the scope of this study to completely understand the structure of these nano-aggregates and to control the self-assembly of poly(norbornene)-*g*-PBLG bush-like polymers. Studies on the self-assembly of poly(norbornene)-*g*-PBLG are underway, and the results will be reported in due course.

(1) Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2002**, *41*, 4035-4037.
(2) Lu, H.; Cheng, J. J. *J. Am. Chem. Soc.* **2008**, *130*, 12562-12563.
(3) (a) Schappacher, M.; Deffieux, A. *Macromolecules* **2000**, *33*, 7371-7377; (b) Parent, J. S.; Sengupta, S. S.; Kaufman, M.; Chaudhary, B. I. *Polymer* **2008**, *49*, 3884-3891.