

Supporting Information

Experimental Formulation of Photonic Crystal Properties for Hierarchically Self-Assembled POSS-Bottlebrush Block Copolymers

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S1. Experimental Section

S1.1. Materials

Aminopropyl-heptasobutyl POSS ($\text{NH}_2\text{C}_3\text{H}_6\text{POSS}$) was purchased from Hybrid Plastics. All other materials were purchased from available suppliers (Sigma-Aldrich, TCI, Fisher Scientific, etc.) and used without further purification unless otherwise noted. Tetrahydrofuran (THF) was distilled over sodium naphthalenide and degassed at 10^{-6} Torr. Hexane was distilled over 1,1-diphenylhexyllithium and degassed at 10^{-6} Torr. Lithium chloride (LiCl) was dried with stirring at $150\text{ }^\circ\text{C}$ for 24 h at 10^{-6} Torr. A 1.4 M *sec*-butyllithium (*s*-BuLi) solution in cyclohexane was degassed, appropriately diluted in hexane, divided into clean glass ampules equipped with break-seals at 10^{-6} Torr, and stored at $-30\text{ }^\circ\text{C}$. 1,1-Diphenylethylene (DPE) and benzyl methacrylate (BzMA) were distilled over calcium hydride (CaH_2) at reduced pressure and then redistilled over CaH_2 at 10^{-6} Torr. DPE, LiCl, and BzMA were appropriately diluted in THF, divided into clean glass ampules equipped with break-seals at 10^{-6} Torr, and stored at $-30\text{ }^\circ\text{C}$. A Grubbs third generation catalyst, $\text{Ph}-\text{CH}=\text{Ru}(\text{Cl})_2(\text{H}_2\text{IMes})(\text{pyridine})_2$ (**G3**), was prepared according to a previously reported procedure.^{S1}

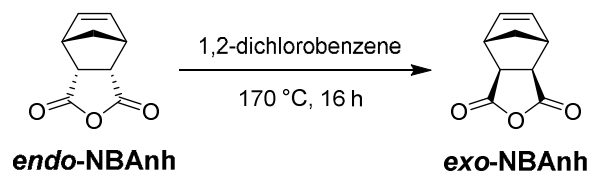
S1.1.2. Instruments and Analyses.

Proton and carbon-13 nuclear magnetic resonance (^1H and ^{13}C NMR) spectra were recorded using a JNM-ECX 400 NMR spectrometer (JEOL) in chloroform-*d* (CDCl_3 , 99.8% atom D, contains 0.03 vol% tetramethylsilane (TMS)) at $25\text{ }^\circ\text{C}$. Number-average molecular weight (M_n) and dispersity (D) values of the polymers were measured using a size exclusion chromatography-multiangle laser light scattering (SEC-MALLS) equipped with a 515 HPLC pump (Waters), a set of four Styragel columns connected in series (HR 0.5, HR 1, HR 3, and HR 4 with pore sizes of

50, 100, 500, and 1000 Å, respectively, Waters), a miniDAWN TREOS light scattering detector (Wyatt Technology) and an Optilab T-rEX refractive index detector (Wyatt Technology). The SEC-MALLS was operated in THF/triethylamine (98/2 v/v) with an elution rate of 1.0 mL/min at 40 °C. Thermogravimetric analysis (TGA) measurement was performed on a TGA Q50 (TA Instruments) at a heating rate of 10 °C/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC) measurement was performed on a DSC Q20 (TA Instruments) at heating and cooling rates of 2 °C/min under a nitrogen atmosphere. Wide-angle X-ray scattering (WAXS) profiles were recorded using a Rigaku D/max-2500 diffractometer with Cu-K α radiation ($\lambda = 1.54$ Å) at 40 kV and 100 mA. Scanning electron microscopy (SEM) images were obtained on a Hitachi S-4700 (Hitachi High-Technologies Corporation) at an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) images were obtained on a Tecnai G2 S-Twin (FEI) at an accelerating voltage of 300 kV. Reflectance spectra were recorded using a LAMBDA 750 UV/Vis/NIR spectrophotometer equipped with an integrating sphere (Perkin Elmer). Processing of numerical data was performed on an OriginPro 2017 (OriginLab).

S1.3. Synthesis Procedures for *exo*-Norbornene Derivatives and Monomers

S1.3.1. *cis*-5-Norbornene-*exo*-2,3-dicarboxylic anhydride (*exo*-NBAnh)

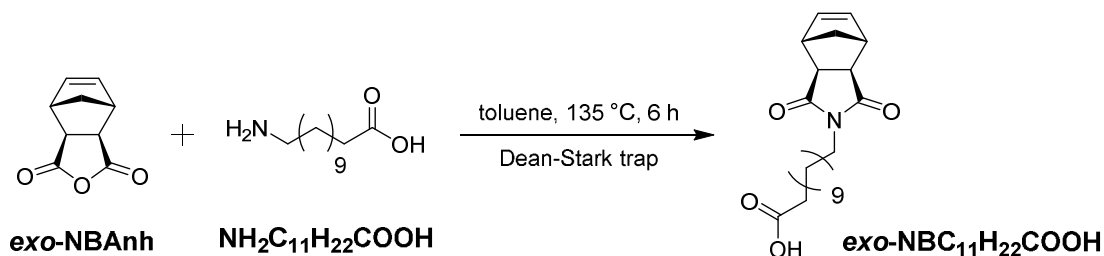


The presented synthetic procedure is similar to a previously reported method.^{S2} A two-neck 500 mL flask equipped with a Dimroth condenser was charged with nitrogen for 30 min. To the flask were added *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride (*endo*-NBAnh, 100 g, 609

mmol) and 1,2-chlorobenzene (100 mL). The solution was stirred at 170 °C for 16 h. After cooling at room temperature, the crystal solids were isolated by filtration and repeatedly recrystallized from ethyl acetate four times to afford *exo*-NBAnh as a white crystal (25.8 g, 26%).

exo-NBAnh: ¹H NMR (CDCl₃ with 0.03% v/v TMS, 400 MHz): δ (ppm) 6.33 (s, 2H), 3.45 (s, 2H), 2.99 (s, 2H), 1.66 (d, 1H, *J* = 10.0 Hz), 1.44 (d, 1H, *J* = 10.0 Hz). ¹³C NMR (CDCl₃ with 0.03% v/v TMS, 100 MHz): δ (ppm) 171.67, 138.01, 48.85, 46.93, 44.17.

S1.3.2. 12-(*cis*-5-Norbornene-*exo*-2,3-dicarboximido)dodecanoic acid (*exo*-NBC₁₁H₂₂COOH)

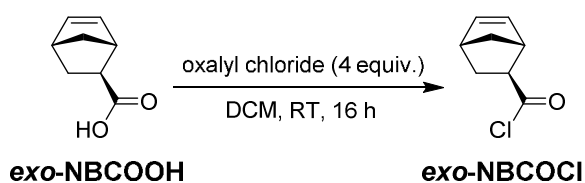


The presented synthetic procedure is modified from a previously reported method.^{S3} A two-neck 100 mL flask equipped with a Dean-Stark trap was charged with nitrogen for 30 min. To the flask were added toluene (25 mL), *exo*-NBAnh (7.22 g, 30.5 mmol) and 12-aminolauric acid (NH₂C₁₁H₂₂COOH, 5.00 g, 30.5 mmol). The reaction mixture was stirred at 135 °C for 16 h. After the reaction was complete, the mixture was cooled and concentrated at reduced pressure. The residual mixture was dissolved in dichloromethane (DCM, 25 mL) and then washed with 0.1 N aqueous solution of hydrochloric acid (HCl, 25 mL) and brine (25 mL). The organic layer was dried over Na₂SO₄, filtered, and concentrated at reduced pressure. The crude product was puri-

fied by silica gel column chromatography in hexane/ethyl acetate = (5/5 v/v) to yield *exo*-NBC₁₁H₂₂COOH as a white solid (7.90 g, 72%).

exo-NBC₁₁H₂₂COOH: ¹H NMR (CDCl₃ with 0.03% v/v TMS, 400 MHz): δ (ppm) 6.28 (s, 2H), 3.44 (t, 2H, *J* = 7.6 Hz), 3.27 (s, 2H), 2.66 (s, 2H), 2.34 (t, 2H, *J* = 7.4 Hz), 1.62 (quint, 2H, *J* = 7.4 Hz), 1.53 (m, 2H), 1.37–1.18 (m, 16H). ¹³C NMR (CDCl₃ with 0.03% v/v TMS, 100 MHz): δ (ppm) 179.66, 178.22, 137.89, 47.87, 45.23, 42.76, 38.83, 34.08, 29.44, 29.41, 29.37, 29.22, 29.13, 29.08, 27.79, 26.98, 24.73.

S1.3.3. *exo*-5-Norbornene-2-carbonyl chloride (*exo*-NBCOCl)

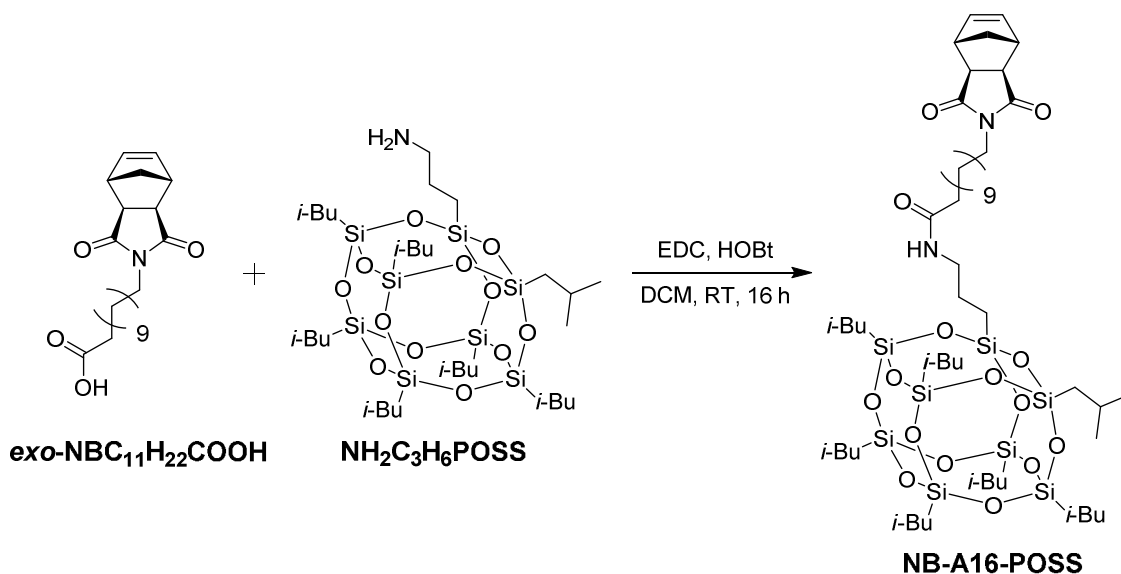


The presented synthetic procedure is similar to a previously reported method.^{S4} A one-neck 100 mL flask equipped with a pressure-equalizing 60 mL dropping funnel was charged with nitrogen for 30 min. To the flask was added oxalyl chloride (12.3 mL, 145 mmol), and to the dropping funnel were added 5-*exo*-norbornene-2-carboxylic acid (*exo*-NBCOOH, 5 g, 36.2 mmol) and DCM (40 mL). The flask was cooled in an ice bath with stirring for 10 min, and the solution of *exo*-NBCOOH in DCM was slowly added dropwise to the oxalyl chloride. The ice bath was removed from the flask, and the reaction mixture was stirred at room temperature for 16 h. After the removal of the DCM and oxalyl chloride by evaporation under reduced pressure, the residual mixture was distilled at 10⁻⁶ Torr to afford *exo*-NBCOCl as a colorless liquid. The isolated prod-

uct was appropriately diluted in THF, divided into clean glass ampoules equipped with break-seals at 10^{-6} Torr, and stored at -30 °C (4.24 g, 75%).

exo-NBCOCl: ^1H NMR (CDCl_3 with 0.03% v/v TMS, 400 MHz): δ (ppm) 6.20 (q, 1H, $J = 2.9$ Hz), 6.11 (q, 1H, $J = 3.1$ Hz), 3.27 (s, 1H), 2.97 (s, 1H), 2.72 (qd, 1H, $J = 4.5, 1.6$ Hz), 2.01 (dt, 1H, $J = 12.4, 4.0$ MHz), 1.54–1.39 (m, 3H). ^{13}C NMR (CDCl_3 with 0.03% v/v TMS, 100 MHz): δ (ppm) 176.76, 139.08, 134.95, 56.38, 46.98, 46.35, 41.93, 31.29.

S1.3.4. 3-(12-(*cis*-5-Norbornene-*exo*-2,3-dicarboximido)dodecanoylamino)propylheptaisobutyl POSS (NB-A16-POSS)

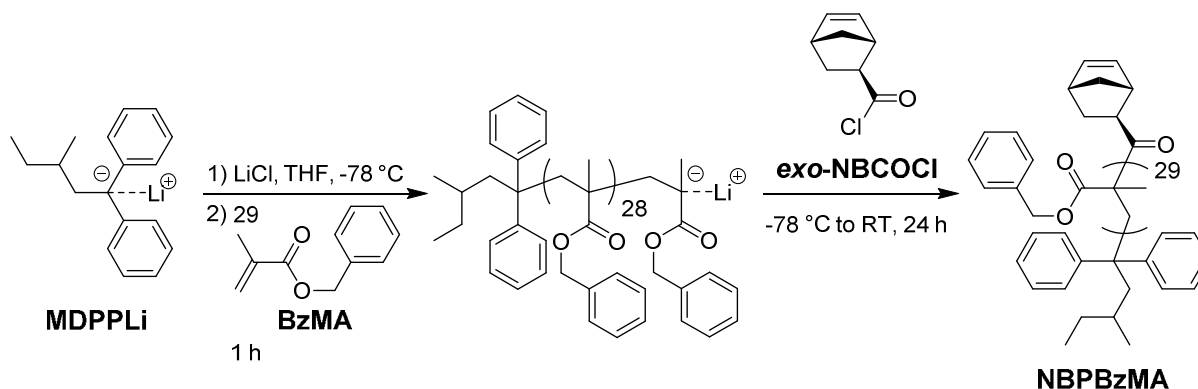


A two-neck 100 mL flask was charged with nitrogen for 30 min. To the flask were added DCM (60 mL), *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC, 1.64 g, 8.58 mmol), 1-hydroxybenzotriazole hydrate (HOBT, 1.16 g, 8.58 mmol), *exo*-NBC₁₁H₂₂COOH (2.07 g, 5.72 mmol) and NH₂C₃H₆POSS (5.00 g, 5.72 mmol). The reaction mixture was stirred at room temperature. After 16 h, the solution was cooled and concentrated at reduced pressure. The

crude product was purified by silica gel column chromatography in hexane/ethyl acetate (initially 8/2 v/v and subsequently 6/4 v/v). The recovered solid was precipitated in cool methanol, filtered, and dried under vacuum to afford **NB-A16-POSS** as a white powder (3.69 g, 53%).

NB-A16-POSS: ^1H NMR (CDCl_3 with 0.03% v/v TMS, 400 MHz): δ (ppm) 6.28 (s, 2H), 5.42 (s, 1H), 3.44 (t, 2H, $J = 7.6$ Hz), 3.26 (s, 2H), 3.29–3.17 (m, 4H), 2.66 (s, 2H), 2.13 (t, 2H, $J = 7.6$ Hz), 1.84 (m, 7H), 1.66–1.44 (m, 8H), 1.24 (m, 14H), 0.95 (d, 42H, $J = 6.4$ Hz), 0.59 (dd, 16H, $J = 6.8, 1.2$ Hz). ^{13}C NMR (CDCl_3 with 0.03% v/v TMS, 100 MHz): δ (ppm) 178.08, 172.95, 137.88, 47.86, 45.22, 42.76, 41.73, 38.79, 36.99, 29.65–29.25, 29.14, 27.80, 26.98, 25.89, 25.73, 23.91, 23.14, 22.55, 9.53. ^{29}Si NMR (CDCl_3 with 0.03% v/v TMS, 79.4 MHz): δ (ppm) –67.13, –67.28, –67.38.

S1.3.5. *exo*-5-Norbornene-2-carbonyl-end poly(benzyl methacrylate) (NBPBzMA)



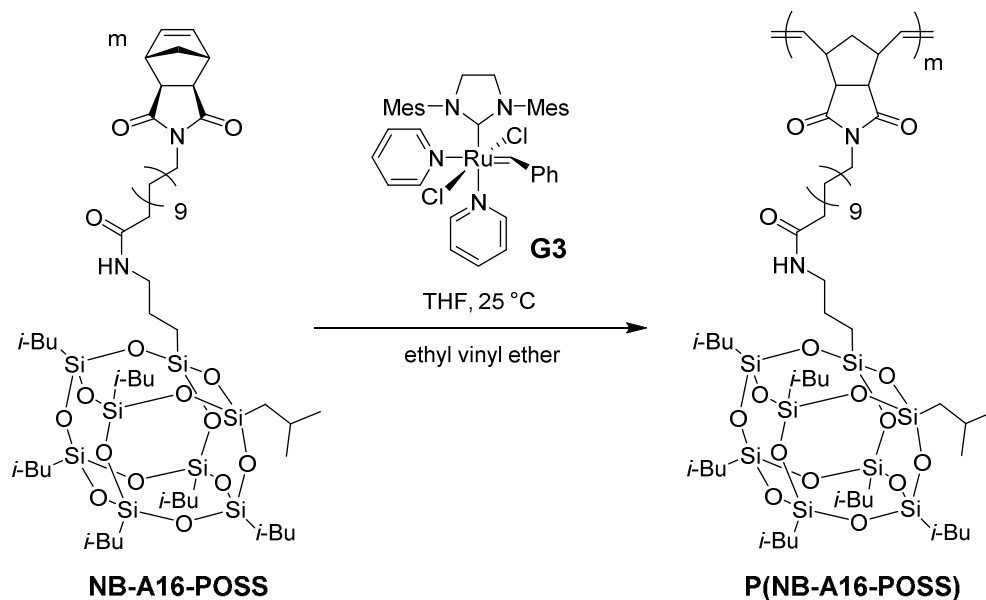
The anionic polymerization was carried out in a clean glass reactor equipped with break-seals that had been prewashed with a 1,1-diphenylhexyllithium solution in heptane at 10^{-6} Torr. A solution of *s*-BuLi (0.270 mmol) in heptane (5.6 mL) was transferred into the reaction flask and cooled to -78 °C. A solution of DPE (0.529 mmol) in THF (5.8 mL) was added to generate 3-methyl-1,1-diphenylpentyl lithium (MDPPLi) as a initiator. After 30 min, a LiCl (1.25 mmol)

solution in THF (5.6 mL) was added to the initiator solution. A solution of BzMA (7.03 mmol) in THF (10 mL) was then added to the initiator solution to allow the polymerization. After 1 h, a solution of *exo*-NBCOCl (0.856 mmol) in THF (6.0 mL) was added to the polymerization mixture for the ω -end-caption. The reaction mixture was allowed to stand for 24 h slowly elevating the temperature from $-78\text{ }^{\circ}\text{C}$ to room temperature. The resulting polymer was isolated by the precipitation in methanol, filtration, and drying under vacuum.

NBPBzMA: $M_n = 5.44\text{ kDa}$ ($M_{n,\text{theo}} = 4.95\text{ kDa}$ at $[\text{BzMA}]_0/[\textit{s}\text{-BuLi}]_0 = 26.0$). $D = 1.02$. ^1H NMR (CDCl_3 with 0.03% v/v TMS, 400 MHz): δ (ppm) 7.41–7.01 (br), 6.09–5.66 (br), 5.17–4.50 (br), 2.10–0.40 (br). ^{13}C NMR (CDCl_3 with 0.03% v/v TMS, 100 MHz): δ (ppm) 177.14, 135.24, 128.62, 66.86, 54.25, 44.87, 18.57.

S1.4. ROMP Procedures for Polymers

S1.4.1. Poly[3-(12-(*cis*-5-Norbornene-*exo*-2,3-dicarboximido)dodecanoylamino)propylheptaisobutyl POSS] (P(NB-A16-POSS))



All ROMP experiments were carried out in a glove box charged with nitrogen. The total volumes of THF for homopolymerization mixture were set according to $[M]_0 = 0.1$ or 0.4 M. **NB-A16-POSS** (M: 100 mg, 0.0821 mmol) was dissolved in THF in a 10 mL vial, and then the solution was stirred. A 0.01 M solution of **G3** (I) in THF (164, 82, 33, 16 or 8 μ L corresponding to $[M]_0/[I]_0 = 50, 100, 250, 500$ or $1,000$, respectively) was rapidly added via syringe to allow the polymerization. The volume of added **G3** was set according to $[M]_0/[I]_0$. After final conversion, the polymerization was quenched by adding 2 droplets of ethyl vinyl ether. The resulting polymer was isolated by precipitation in acetonitrile, filtration, and drying under vacuum.

P(NB-A16-POSS): ^1H NMR (CDCl_3 with 0.03% v/v TMS, 400 MHz): δ (ppm) 5.89–5.23 (br), 3.80–2.50 (br), 2.13 (t, $J = 7.4$ Hz), 1.84 (m), 1.68–1.44 (br), 1.25 (s), 0.95 (d, $J = 6.4$ Hz), 0.59 (d, $J = 6.8$ Hz). ^{13}C NMR (CDCl_3 with 0.03% v/v TMS, 100 MHz): δ (ppm) 178.32, 173.00, 131.96, 41.78, 38.73, 37.01, 29.86–29.14, 27.82, 27.08, 25.96, 25.75, 23.93, 23.15, 22.56, 9.56. ^{29}Si NMR (CDCl_3 with 0.03% v/v TMS, 79.4 MHz): δ (ppm) –67.14, –67.38.

S1.4.2. Poly[3-(12-(*cis*-5-Norbornene-*exo*-2,3-dicarboximido)dodecanoylamino)propylheptaisobutyl POSS]-*block*-poly(*exo*-5-norbornene-2-carboxylate-graft-benzyl methacrylate) (P(NB-A16-POSS)-*b*-P(NB-*g*-BzMA))

NB-A16-POSS (M_A) was dissolved in THF according to $[M_A]_0 = 0.4$ M in 10 mL vials. With vigorous stirring, an appropriate volume of 0.01 M **G3** (I) in THF according to $[M_A]_0/[I]_0$ was rapidly added via a syringe to the monomer solution to allow the homopolymerization. After the complete conversion of **NB-A16-POSS**, an appropriate volume of 0.1 M **NBPBzMA** in THF was subsequently added via a syringe according to the weight ratio of the two monomers ($M_A:M_B = 33:67, 50:50$ or $67:33$ wt:wt) in the homopolymerization mixture to allow block co-

polymerization. When precipitation occurred, a minimal volume of THF was added to the block copolymerization mixtures to redissolve the precipitates. After stirring for 24 h, the polymerization was quenched by adding 2 droplets of ethyl vinyl ether. The resulting polymer was isolated by precipitation in methanol, filtration, and drying under vacuum.

P(NB-A16-POSS)-*b*-P(NB-*g*-BzMA) (50-4): ^1H NMR (CDCl_3 with 0.03% v/v TMS, 400 MHz): δ (ppm) 7.37–7.00 (br), 5.87–5.36 (br), 3.78–2.50 (br), 2.13 (t, $J = 7.4$ Hz), 1.84 (m), 2.00–0.40 (br). ^{13}C NMR (CDCl_3 with 0.03% v/v TMS, 100 MHz): δ (ppm) 177.16, 173.06, 135.34, 131.89, 128.47, 66.87, 54.21 45.01, 41.80, 37.05, 29.61, 27.88, 27.07, 26.01, 25.80, 23.97, 23.17, 22.56, 18.52, 16.59, 9.57. ^{29}Si NMR (CDCl_3 with 0.03% v/v TMS, 79.4 MHz): δ (ppm) –67.14, –67.38.

S1.5. Preparation of 1D PC Films Based on P(NB-A16-POSS)-*b*-P(NB-*g*-BzMA)s.

Glass and silicon substrates ($1.25 \times 1.25 \text{ cm}^2$) were washed with deionized water, acetone and isopropyl alcohol in sequence and then dried. To a 20 mL vial with a glass or silicon substrate lying on the bottom, a **P(NB-A16-POSS)-*b*-P(NB-*g*-BzMA)** solution in THF (50 mg/3 mL) was added. The vial was left open at room temperature under the ambient pressure to evaporate the solvent. The dried film were taken out of the vial and annealed on a hot plate at 160 °C for 30 s. A film on a silicon substrate was utilized for the WAXS analysis. Then, the film was fractured, stained with a 0.5% aqueous solution of ruthenium tetroxide (RuO_4), coated with platinum and utilized for the SEM analysis of the cross-section. Another film prepared on a glass substrate was directly utilized for the reflectance measurement.

S2. ^1H and ^{13}C NMR Spectra of Compounds

^1H NMR (CDCl_3 with 0.03 vol% TMS, 400 MHz)

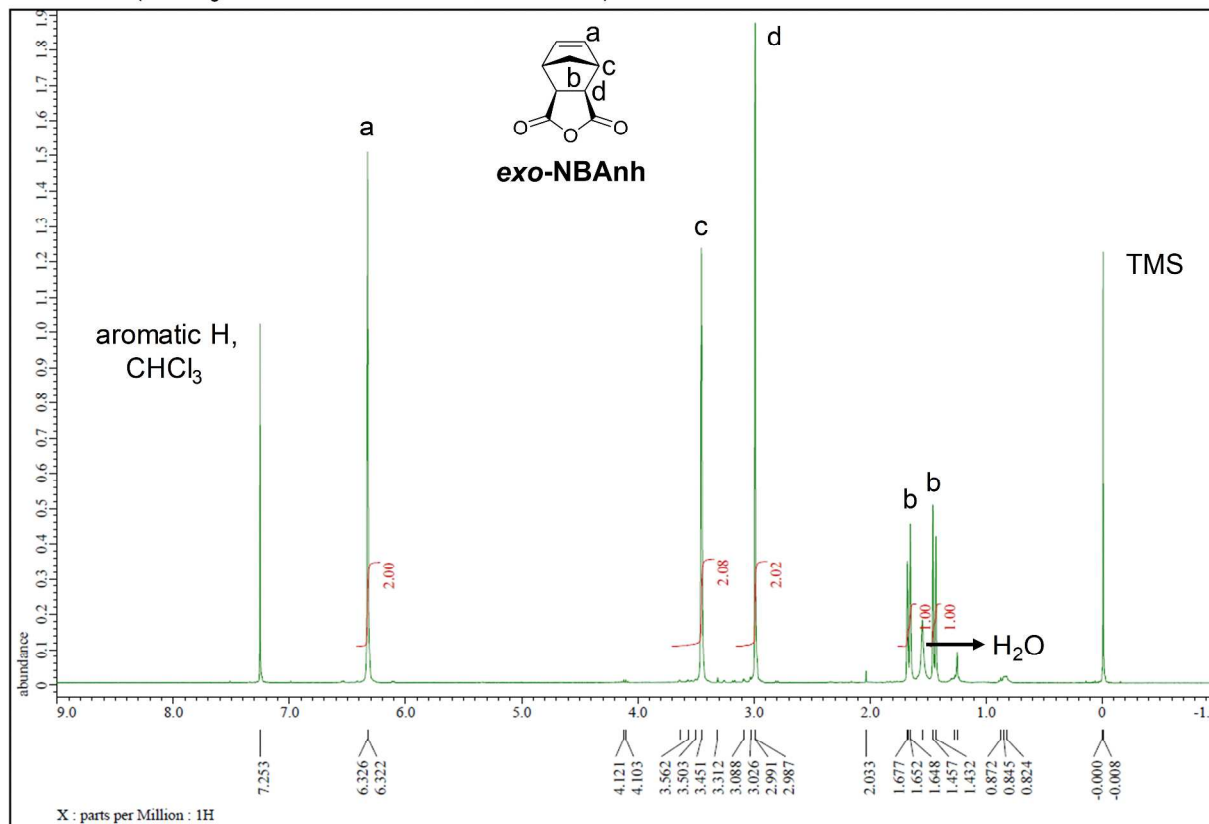


Figure S1. ^1H NMR spectrum of *exo*-NBAnh in CDCl_3 .

^{13}C NMR (CDCl_3 with 0.03 vol% TMS, 100 MHz)

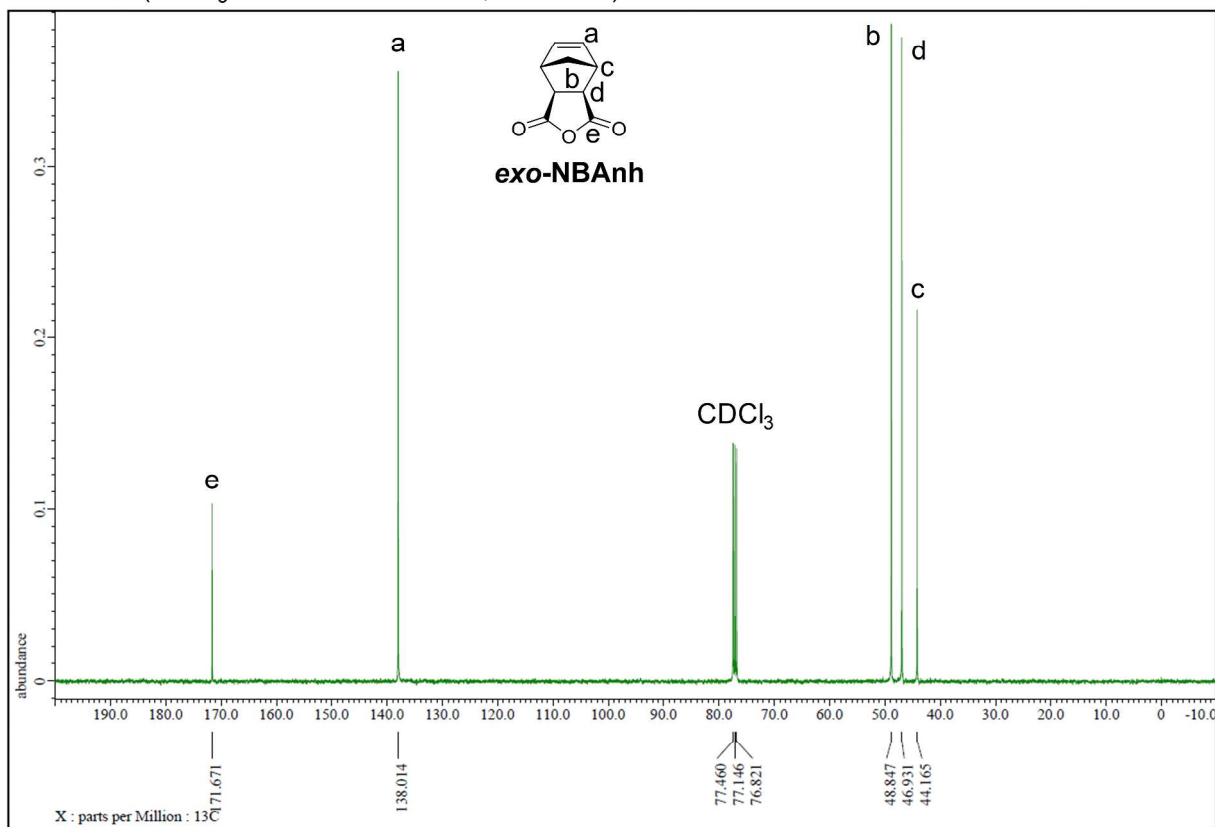


Figure S2. ^{13}C NMR spectrum of *exo*-NBAnh in CDCl_3 .

^1H NMR (CDCl_3 with 0.03 vol% TMS, 400 MHz)

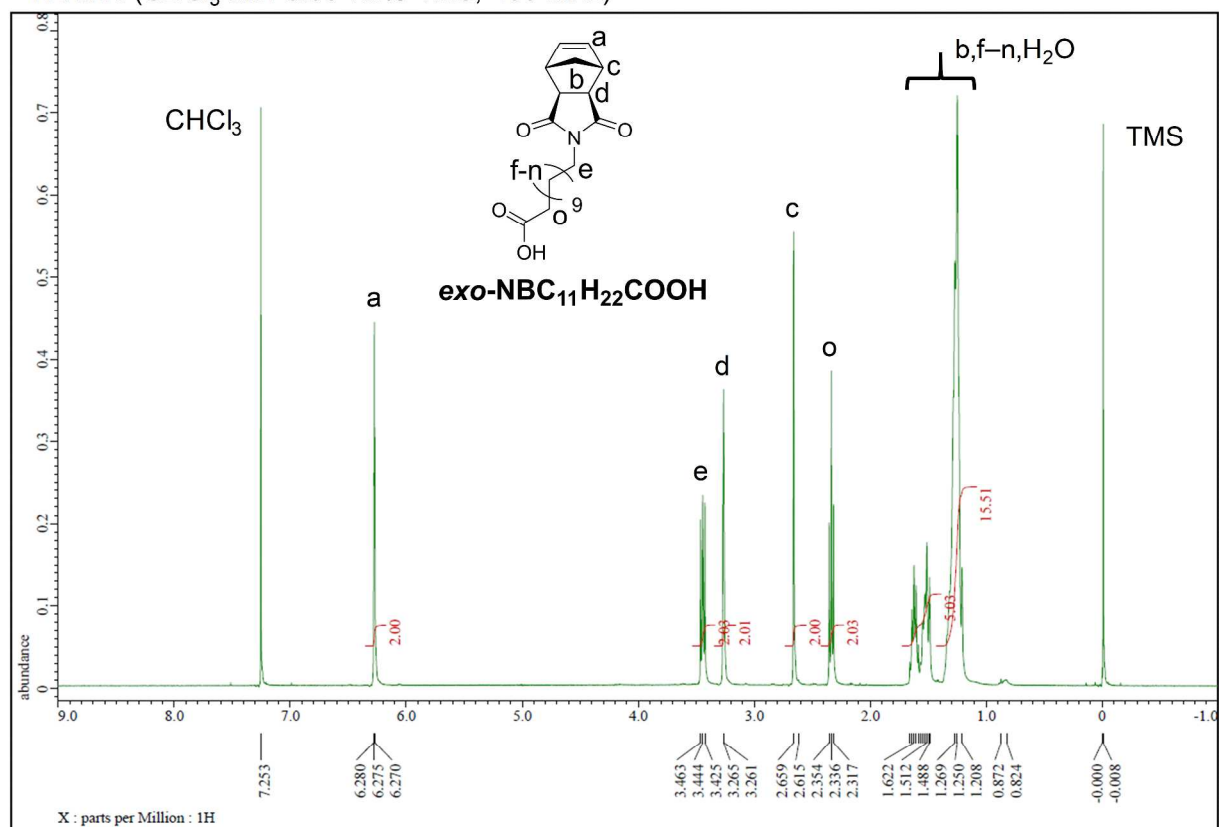


Figure S3. ^1H NMR spectrum of *exo*-NBC₁₁H₂₂COOH in CDCl_3 .

^{13}C NMR (CDCl_3 with 0.03 vol% TMS, 100 MHz)

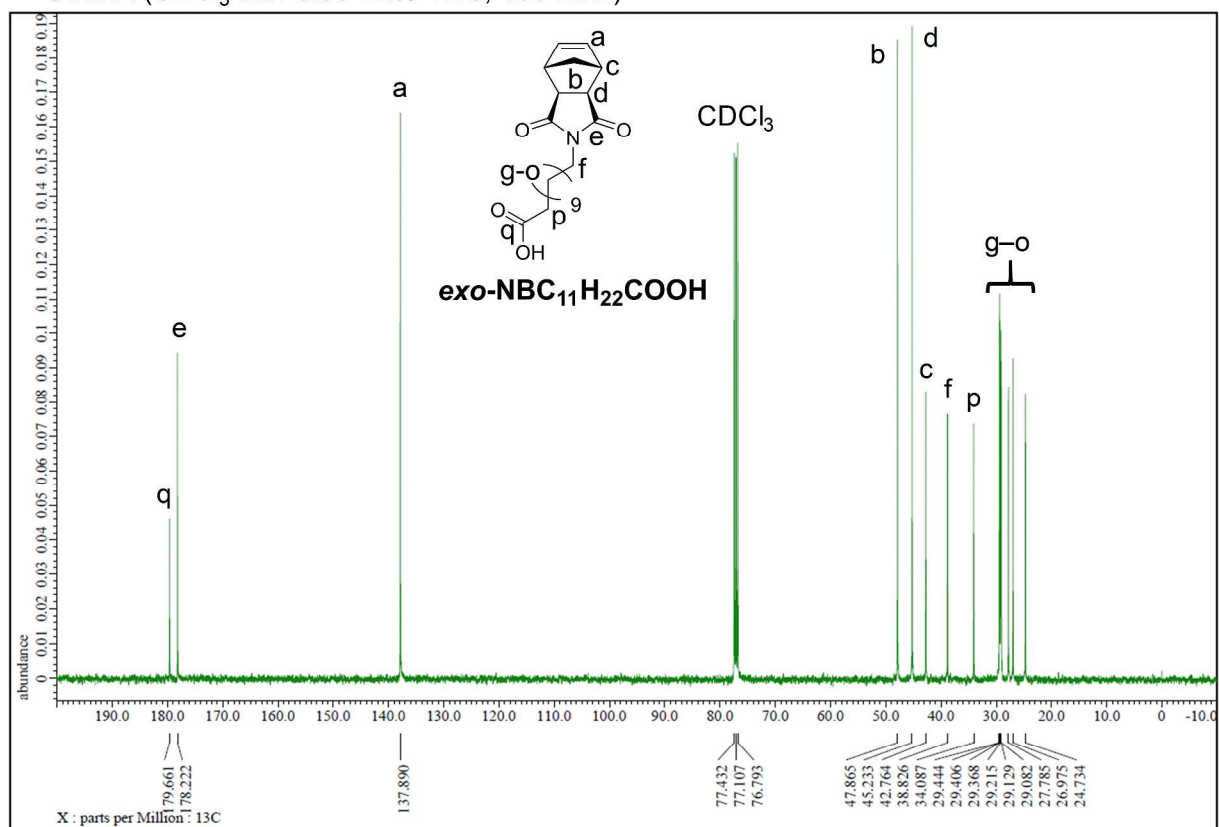


Figure S4. ^{13}C NMR spectrum of *exo*-NBC₁₁H₂₂COOH in CDCl_3 .

^1H NMR (CDCl_3 with 0.03 vol% TMS, 400 MHz)

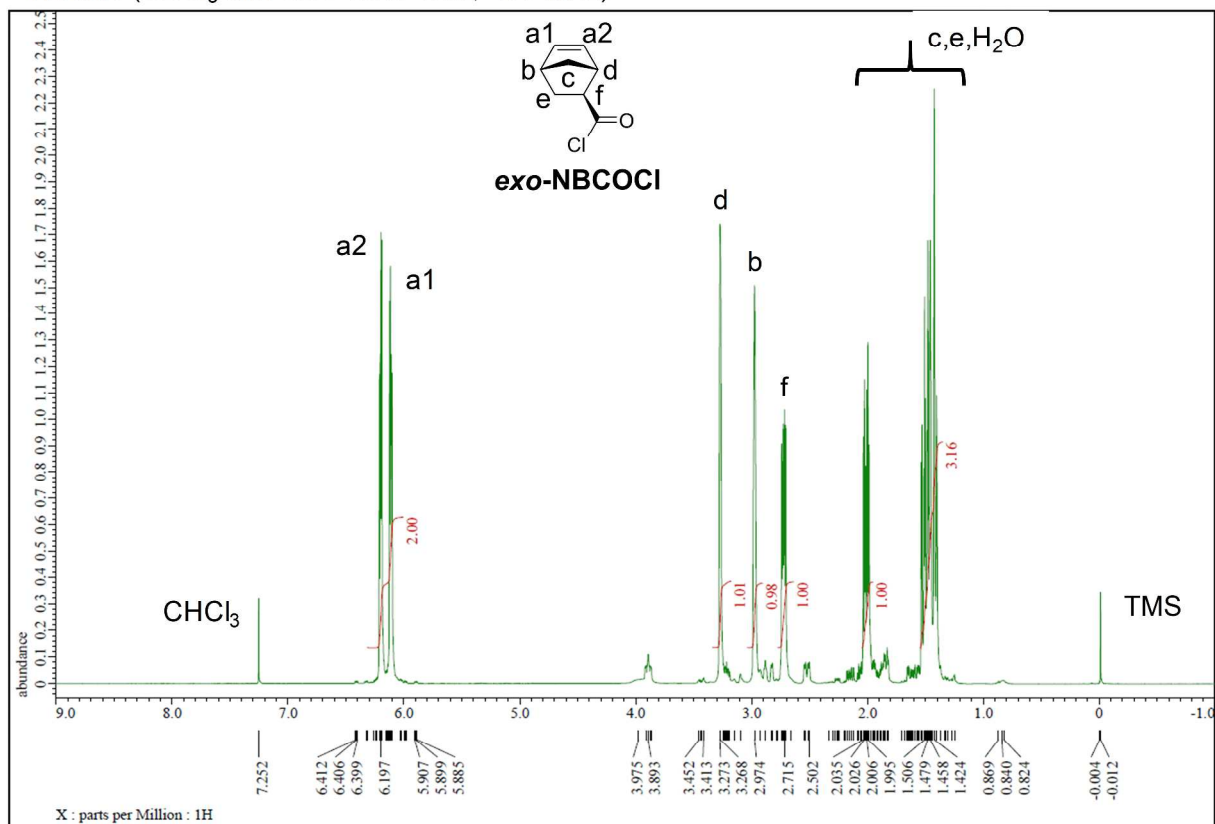


Figure S5. ^1H NMR spectrum of *exo*-NBCOCl in CDCl_3 .

^{13}C NMR (CDCl_3 with 0.03 vol% TMS, 100 MHz)

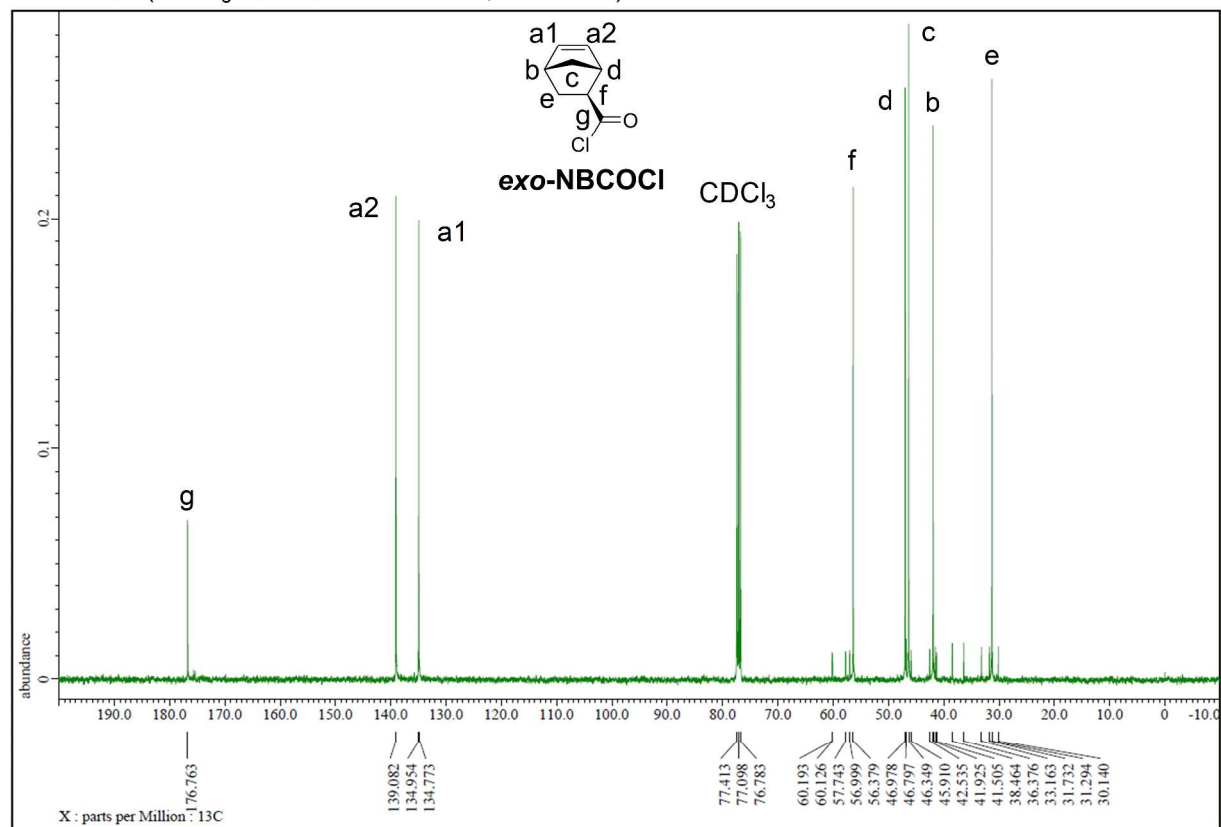


Figure S6. ^{13}C NMR spectrum of *exo*-NBCOCl in CDCl_3 .

^1H NMR (CDCl_3 with 0.03 vol% TMS, 400 MHz)

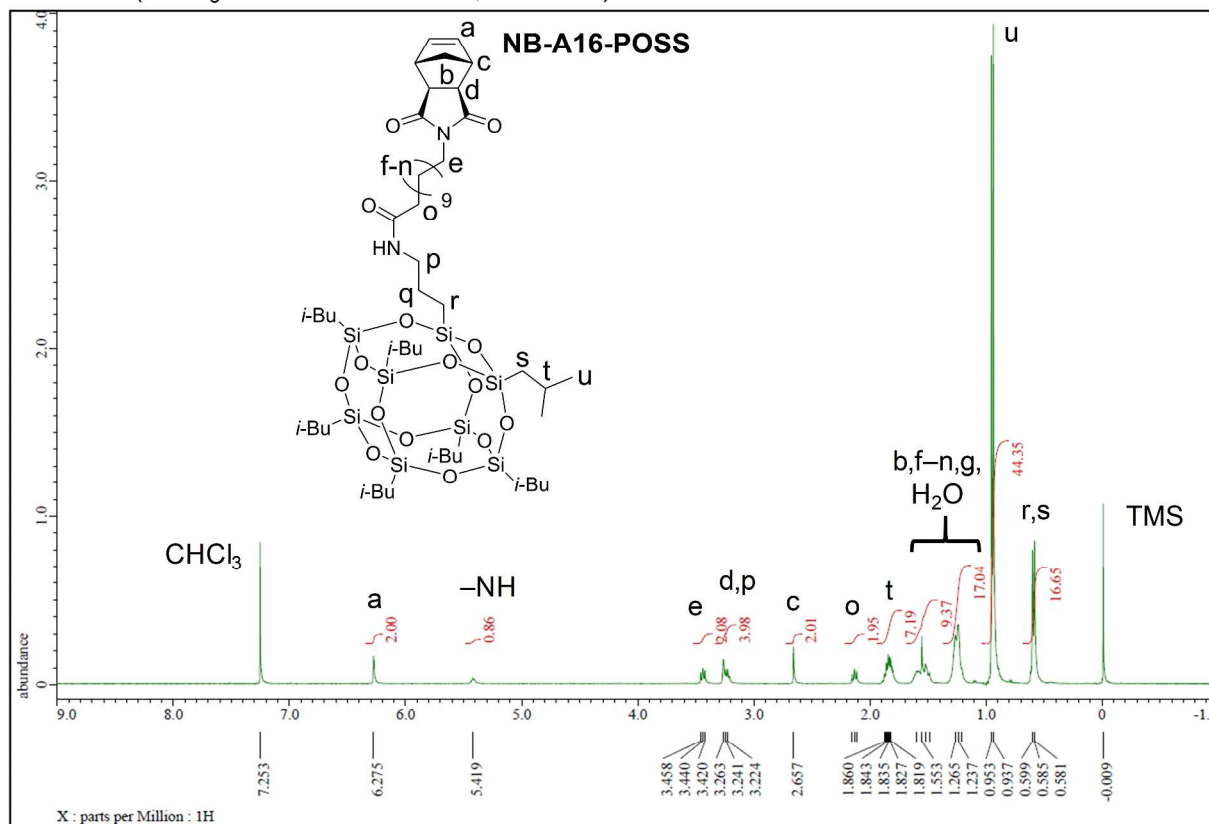


Figure S7. ^1H NMR spectrum of NB-A16-POSS in CDCl_3 .

^{13}C NMR (CDCl_3 with 0.03 vol% TMS, 100 MHz)

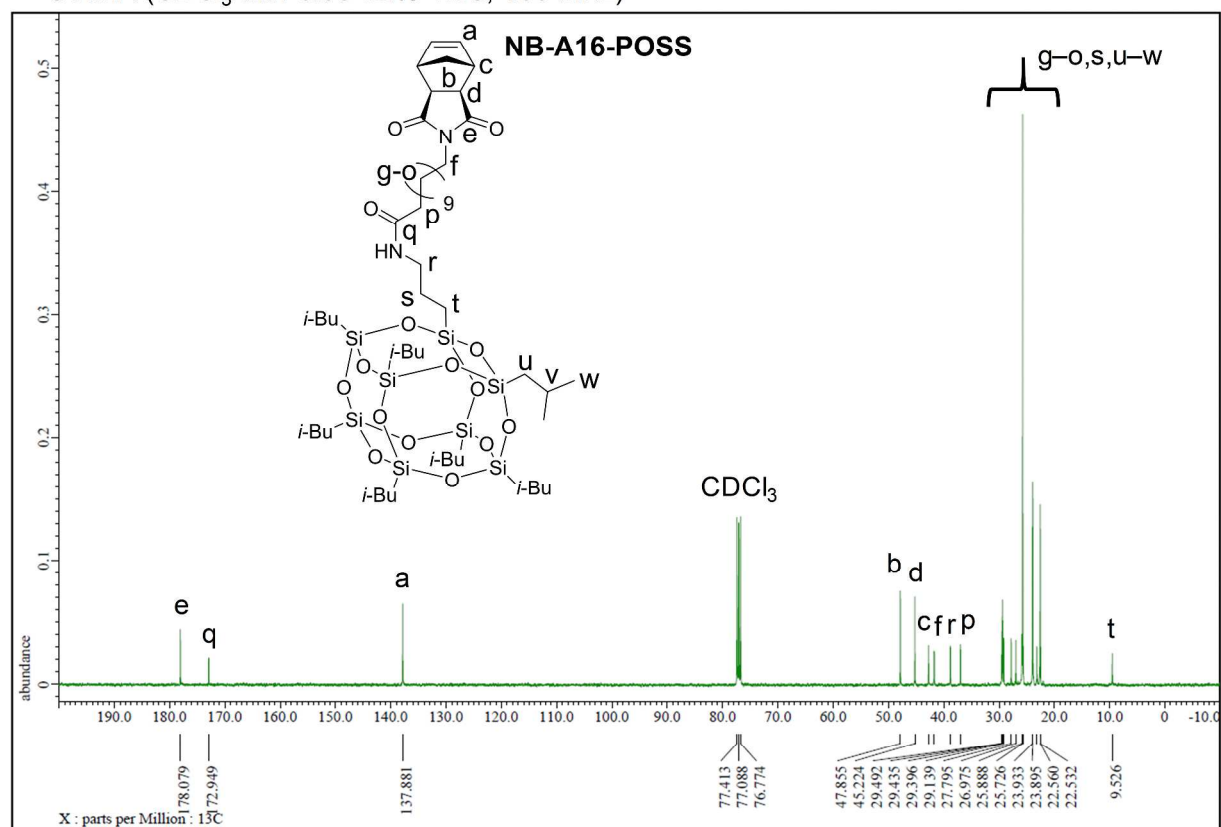


Figure S8. ^{13}C NMR spectrum of NB-A16-POSS in CDCl_3 .

^1H NMR (CDCl_3 with 0.03 vol% TMS, 400 MHz)

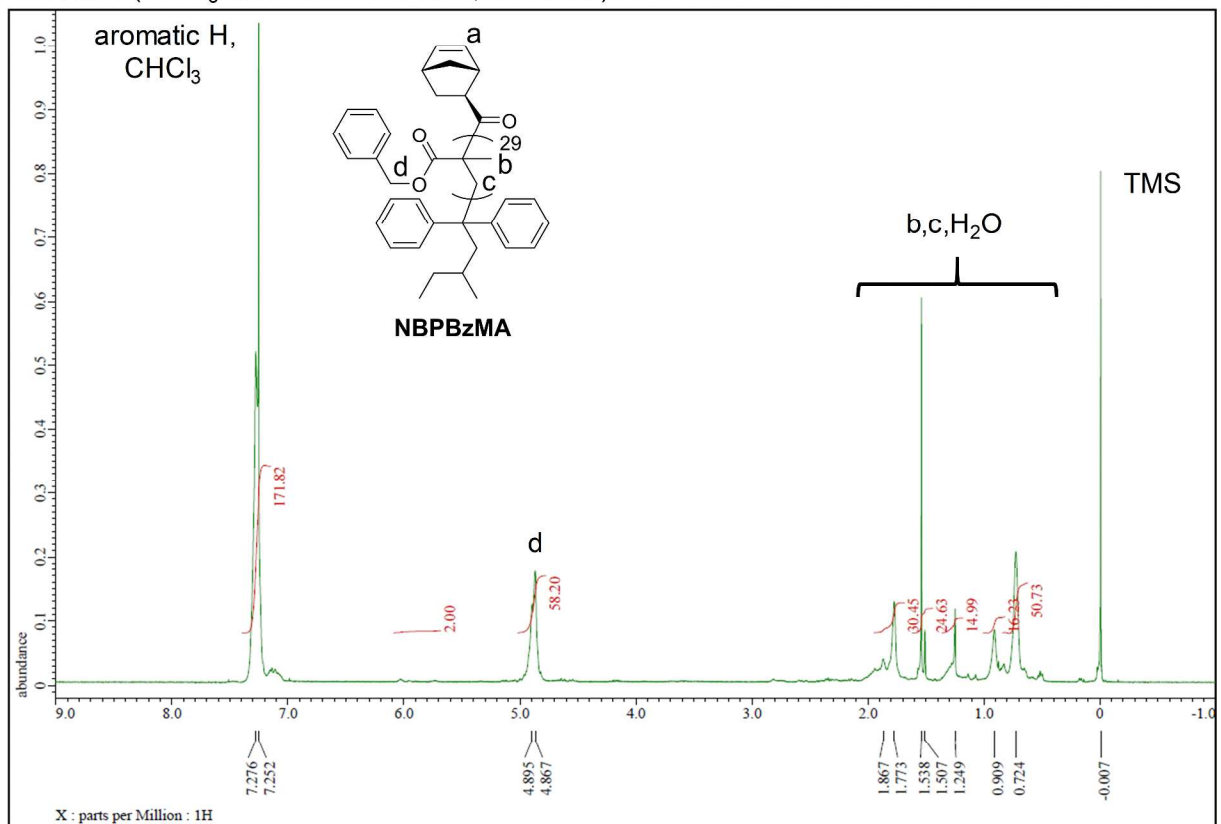


Figure S9. ^1H NMR spectrum of NBPBzMA in CDCl_3 .

^{13}C NMR (CDCl_3 with 0.03 vol% TMS, 100 MHz)

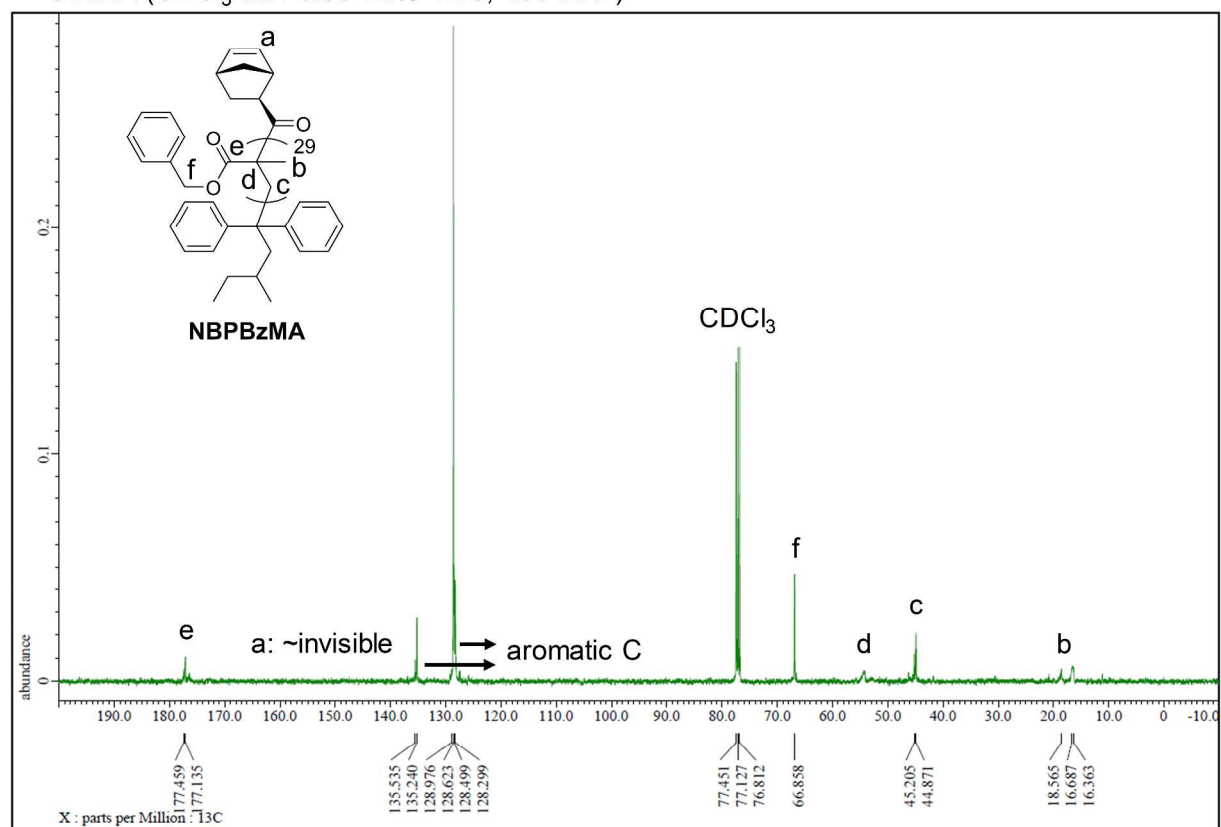


Figure S10. ^{13}C NMR spectrum of NBPBzMA in CDCl_3 .

^1H NMR (CDCl_3 with 0.03 vol% TMS, 400 MHz)

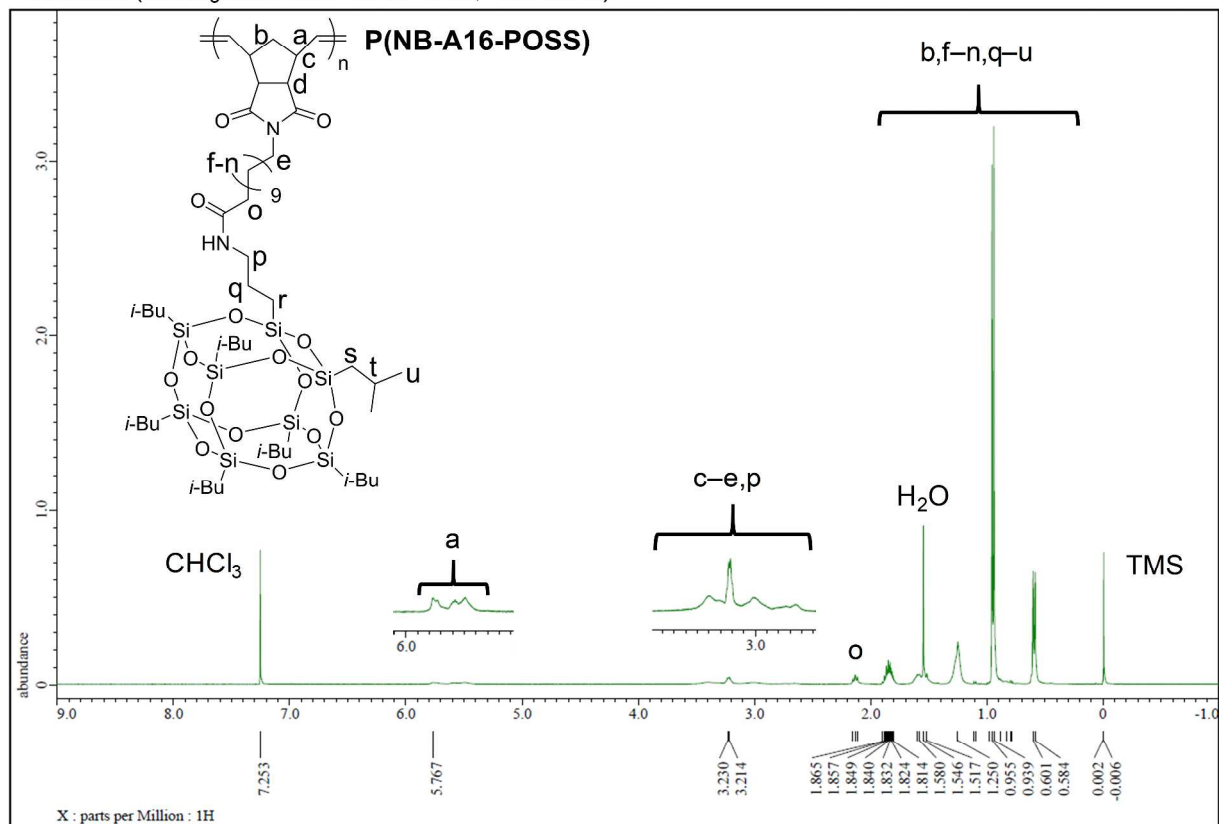


Figure S11. ^1H NMR spectrum of P(NB-A16-POSS) in CDCl_3 .

^{13}C NMR (CDCl_3 with 0.03 vol% TMS, 100 MHz)

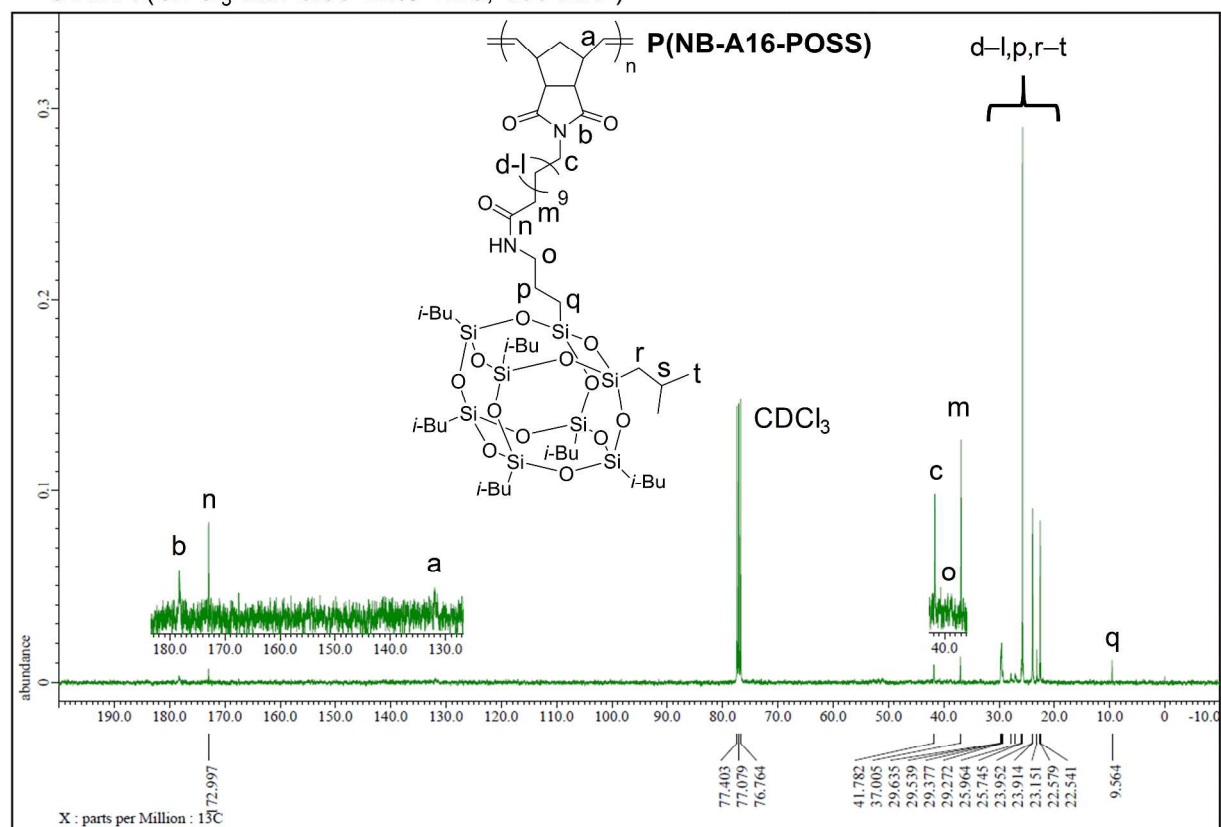


Figure S12. ^{13}C NMR spectrum of **P(NB-A16-POSS)** in CDCl_3 .

^1H NMR (CDCl_3 with 0.03 vol% TMS, 400 MHz)

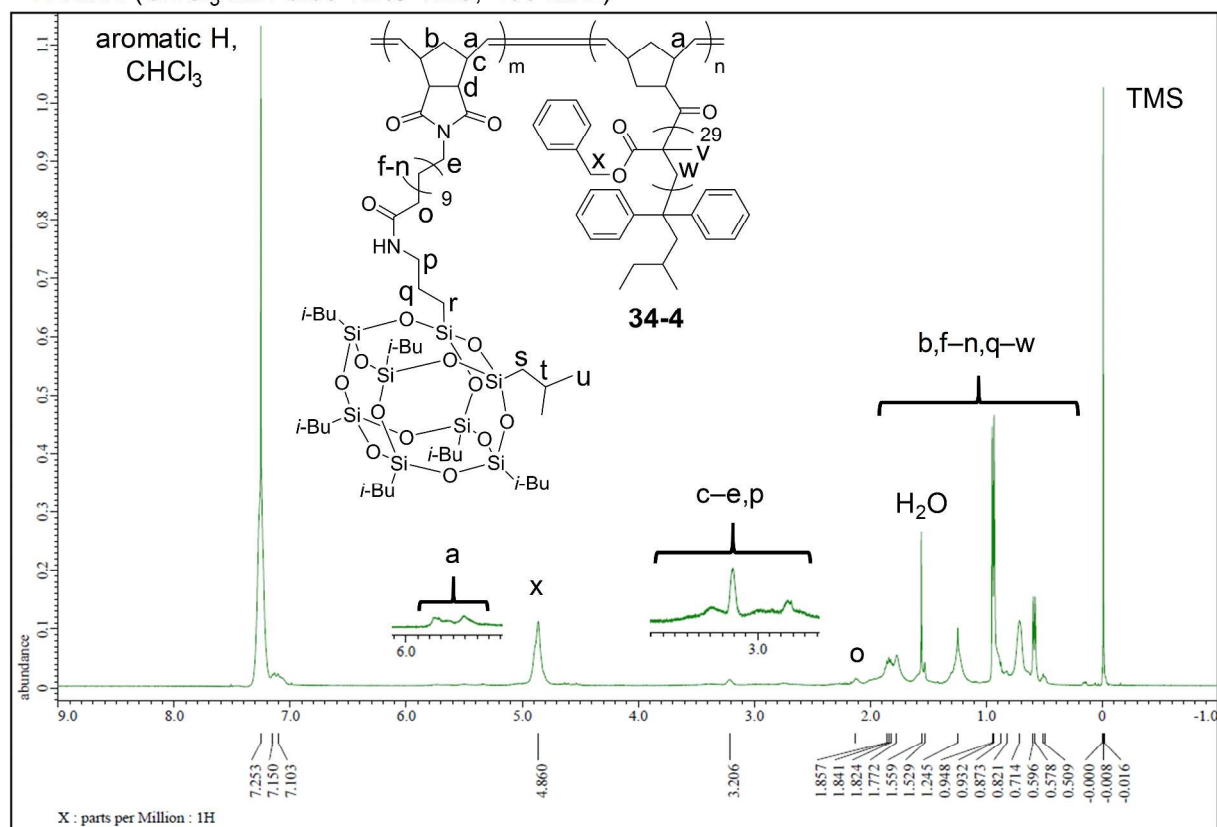


Figure S13. ^1H NMR spectrum of **34-4** ($f_A = 34$ wt%) in CDCl_3 .

^{13}C NMR (CDCl_3 with 0.03 vol% TMS, 100 MHz)

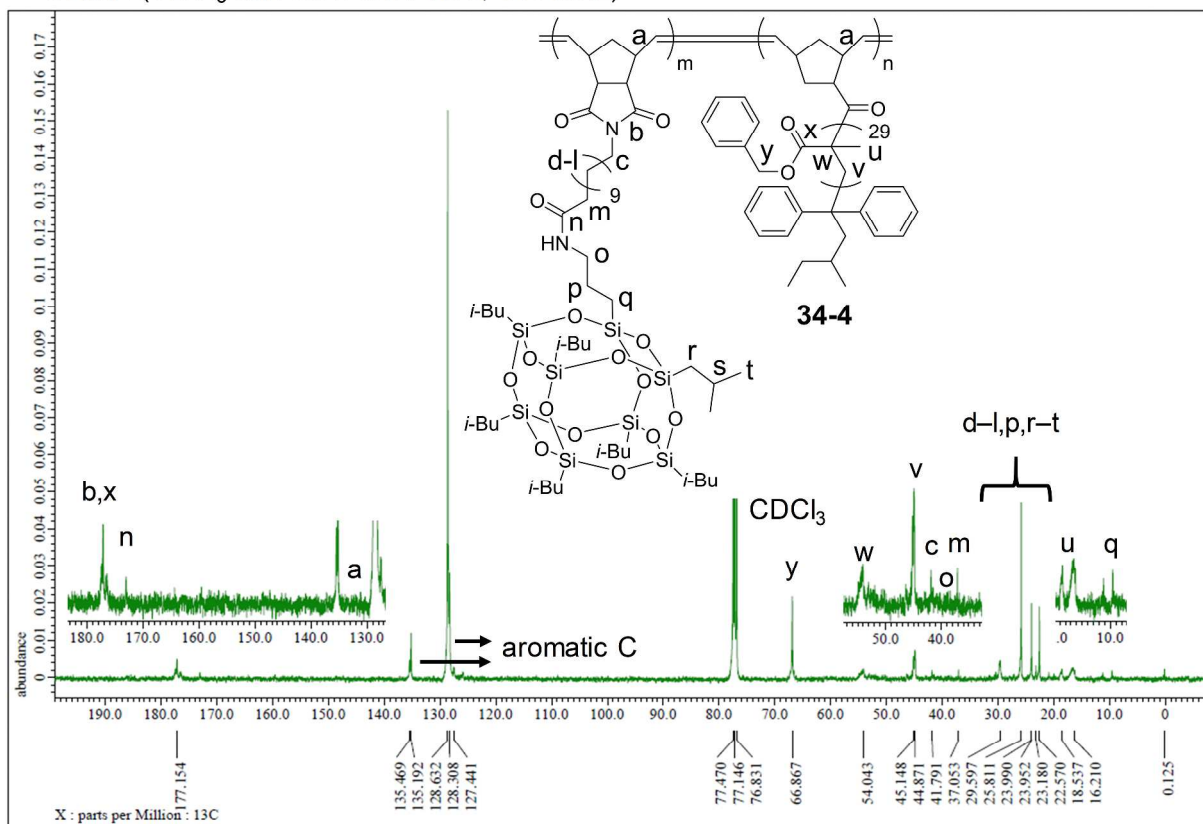


Figure S14. ^{13}C NMR spectrum of **34-4** ($f_A = 34$ wt%) in CDCl_3 .

^1H NMR (CDCl_3 with 0.03 vol% TMS, 400 MHz)

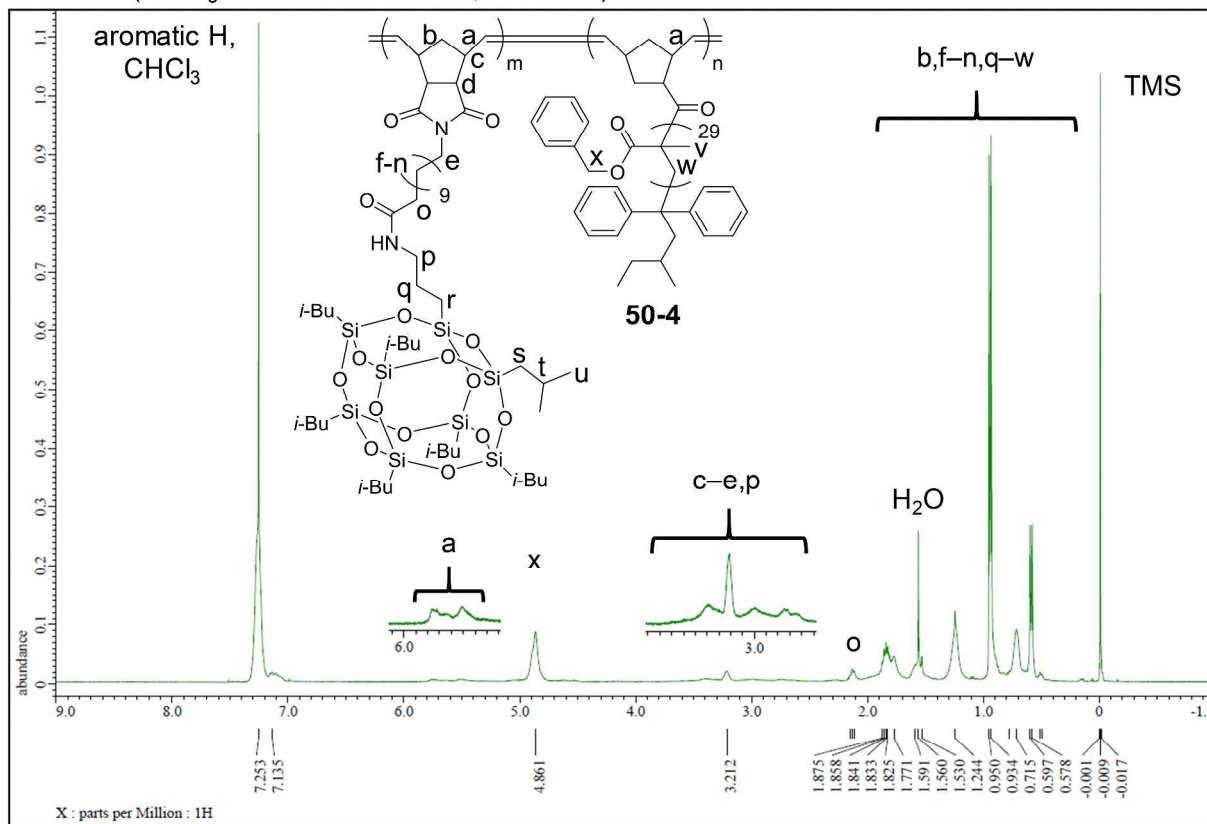


Figure S15. ^1H NMR spectrum of **50-4** ($f_A = 50$ wt%) in CDCl_3 .

^{13}C NMR (CDCl_3 with 0.03 vol% TMS, 100 MHz)

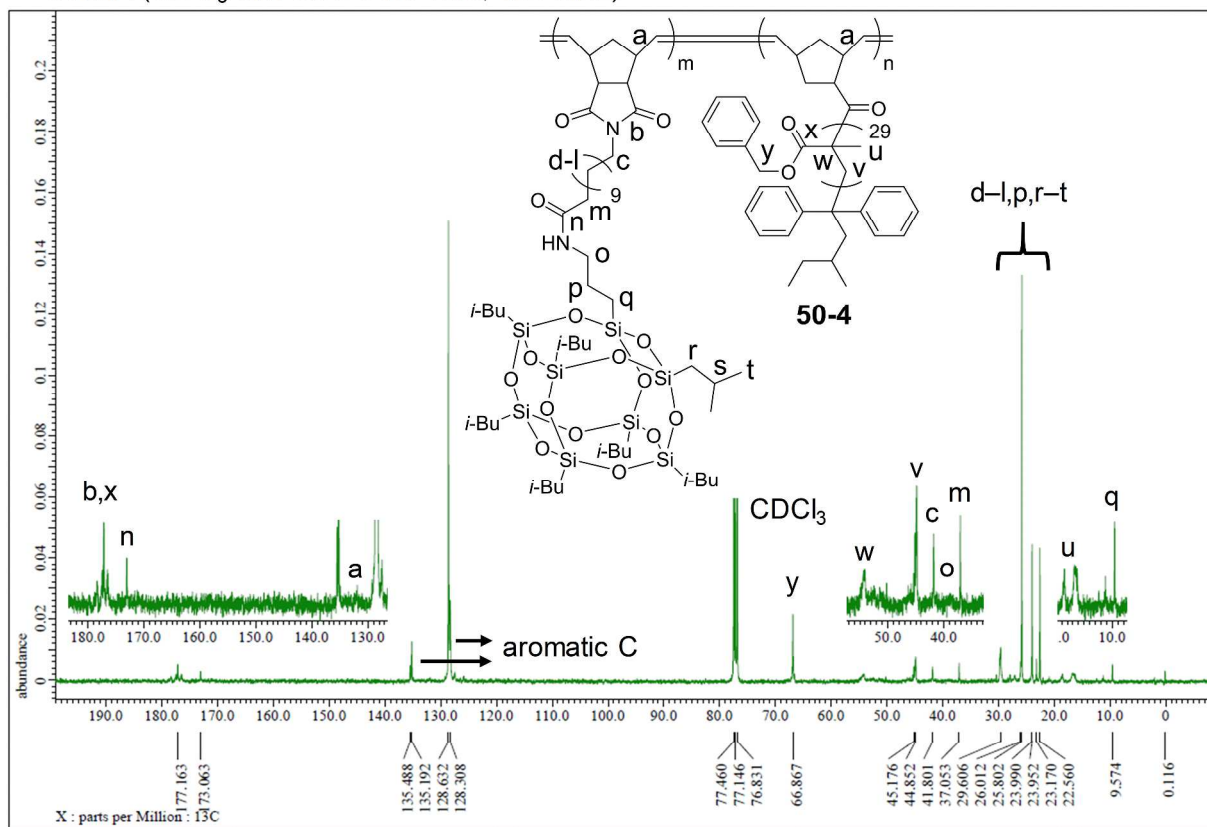


Figure S16. ^{13}C NMR spectrum of **50-4** ($f_A = 50$ wt%) in CDCl_3 .

^1H NMR (CDCl_3 with 0.03 vol% TMS, 400 MHz)

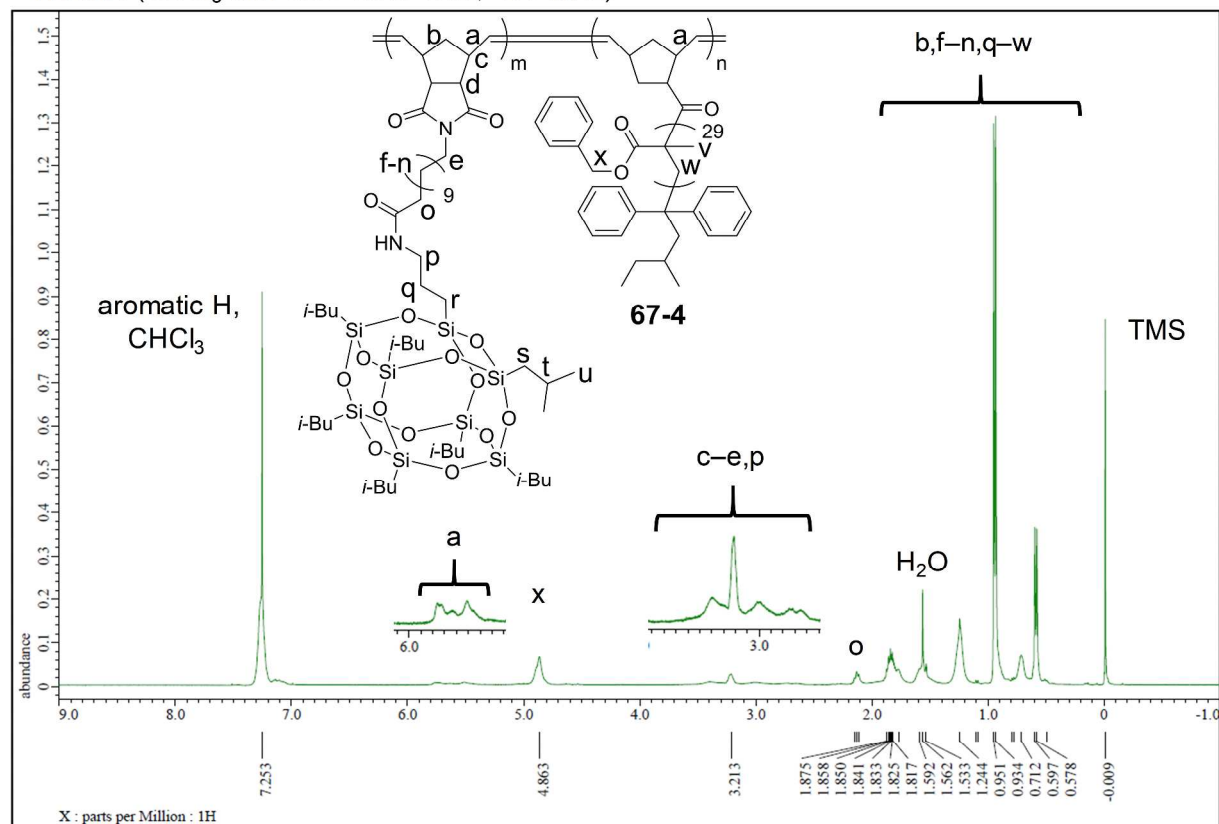


Figure S17. ^1H NMR spectrum of **67-4** ($f_A = 67$ wt%) in CDCl_3 .

^{13}C NMR (CDCl_3 with 0.03 vol% TMS, 400 MHz)

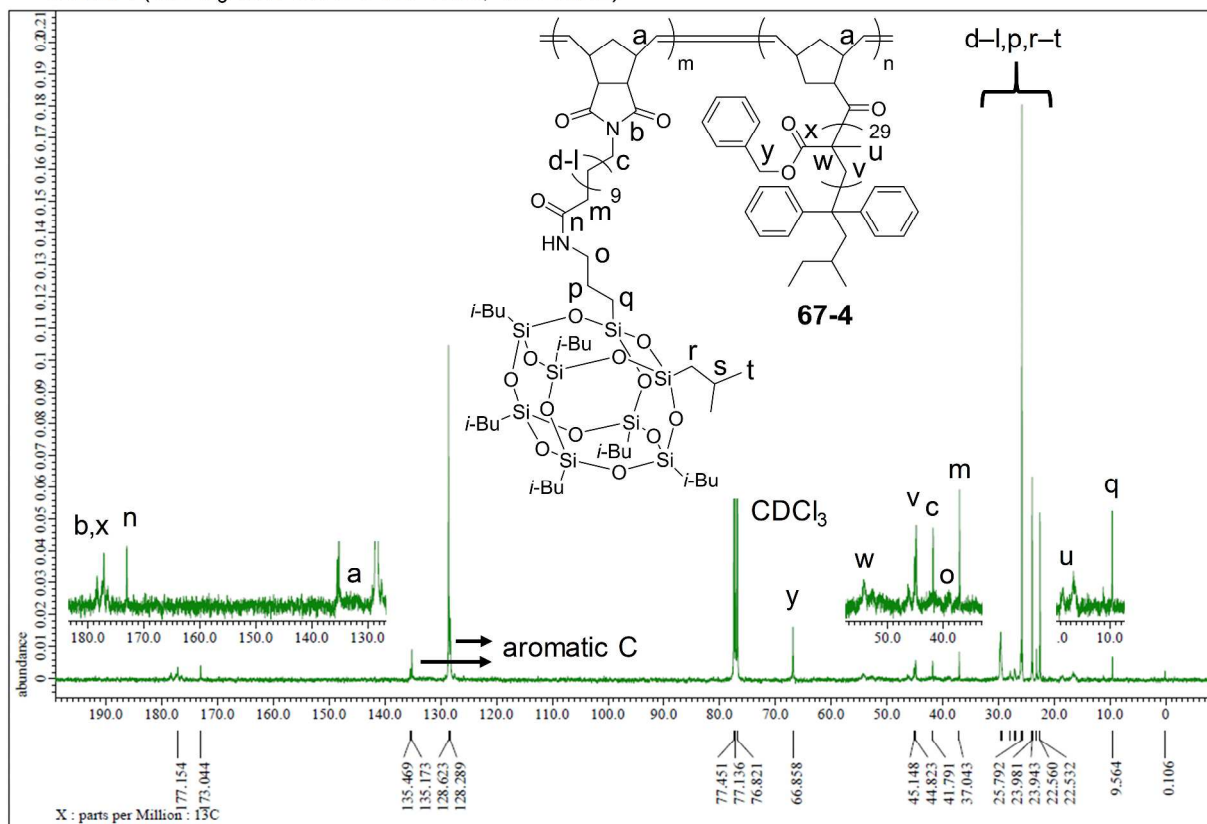


Figure S18. ^{13}C NMR spectrum of **67-4** ($f_A = 67$ wt%) in CDCl_3 .

^{29}Si NMR (CDCl_3 with 0.03 vol% TMS, 97.4 MHz)

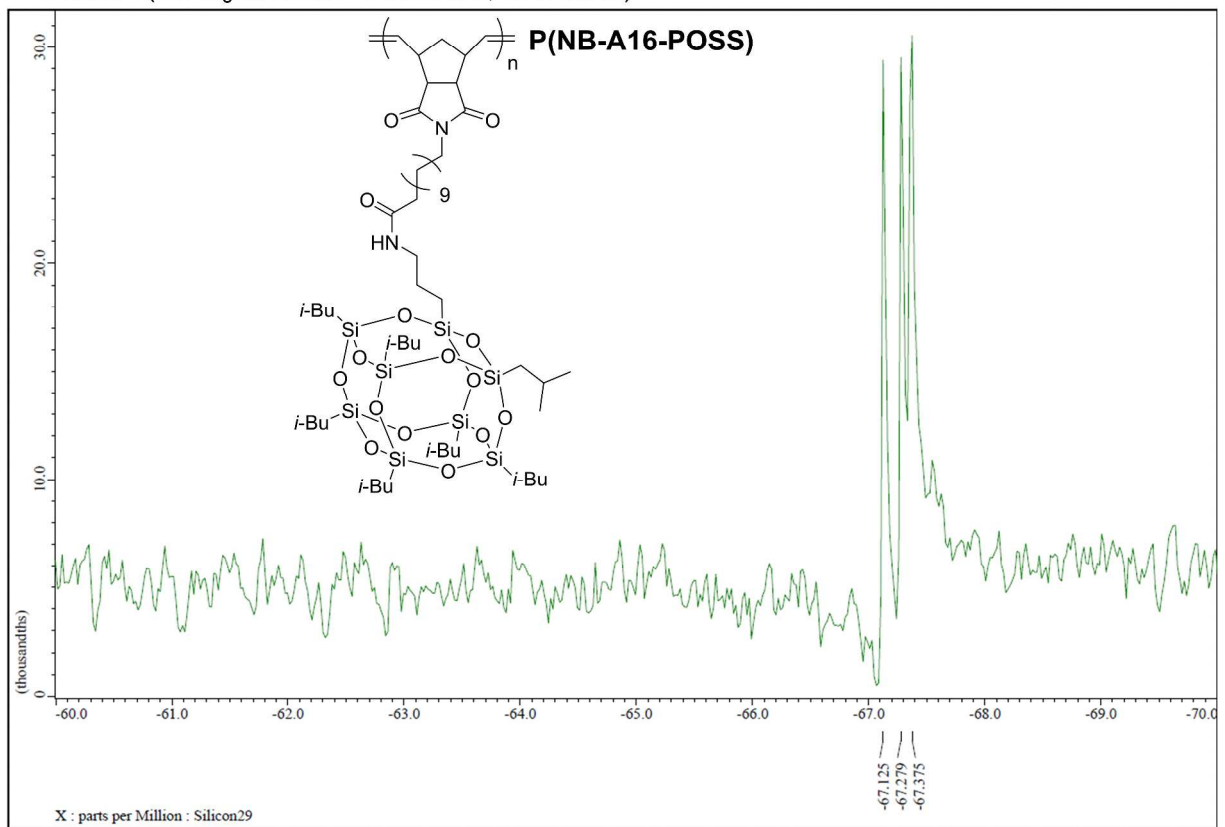


Figure S19. ^{29}Si NMR spectrum of NB-A16-POSS in CDCl_3 .

^{29}Si NMR (CDCl_3 with 0.03 vol% TMS, 97.4 MHz)

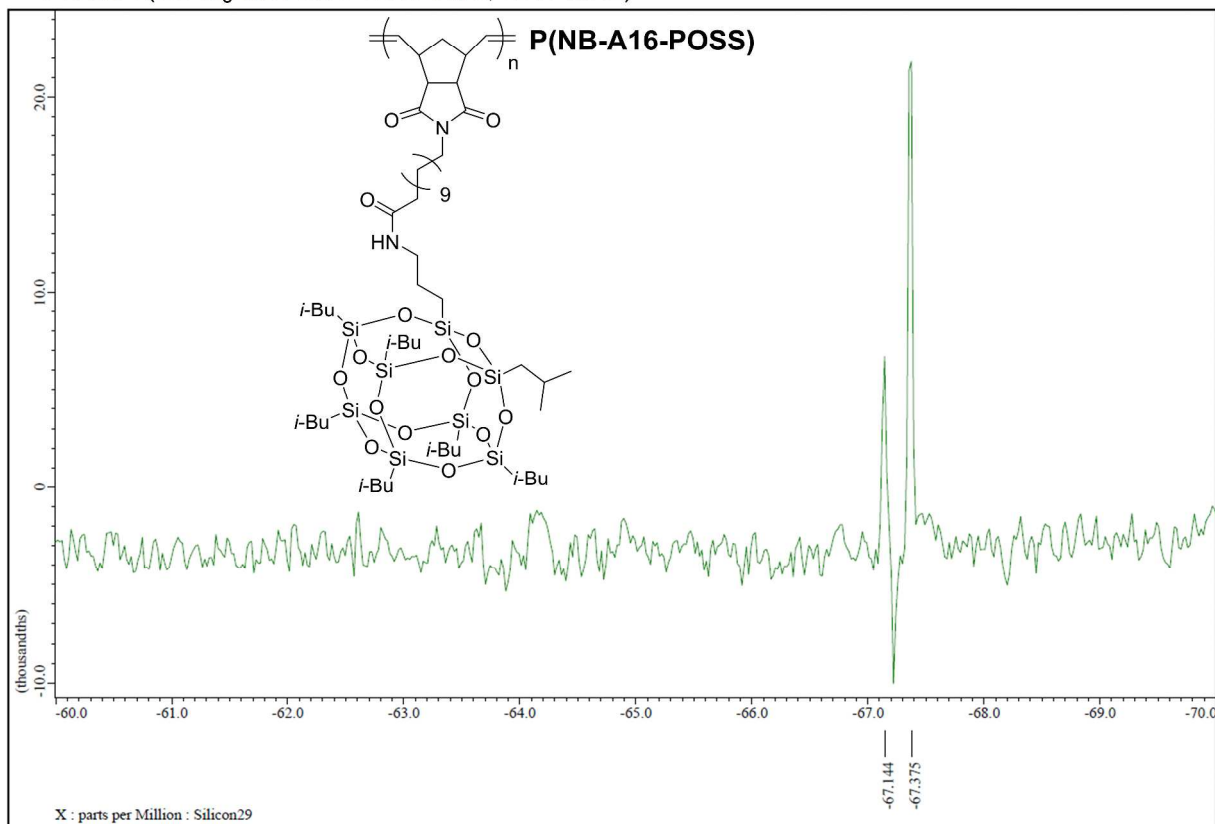


Figure S20. ^{29}Si NMR spectrum of P(NB-A16-POSS) in CDCl_3 .

^{29}Si NMR (CDCl_3 with 0.03 vol% TMS, 97.4 MHz)

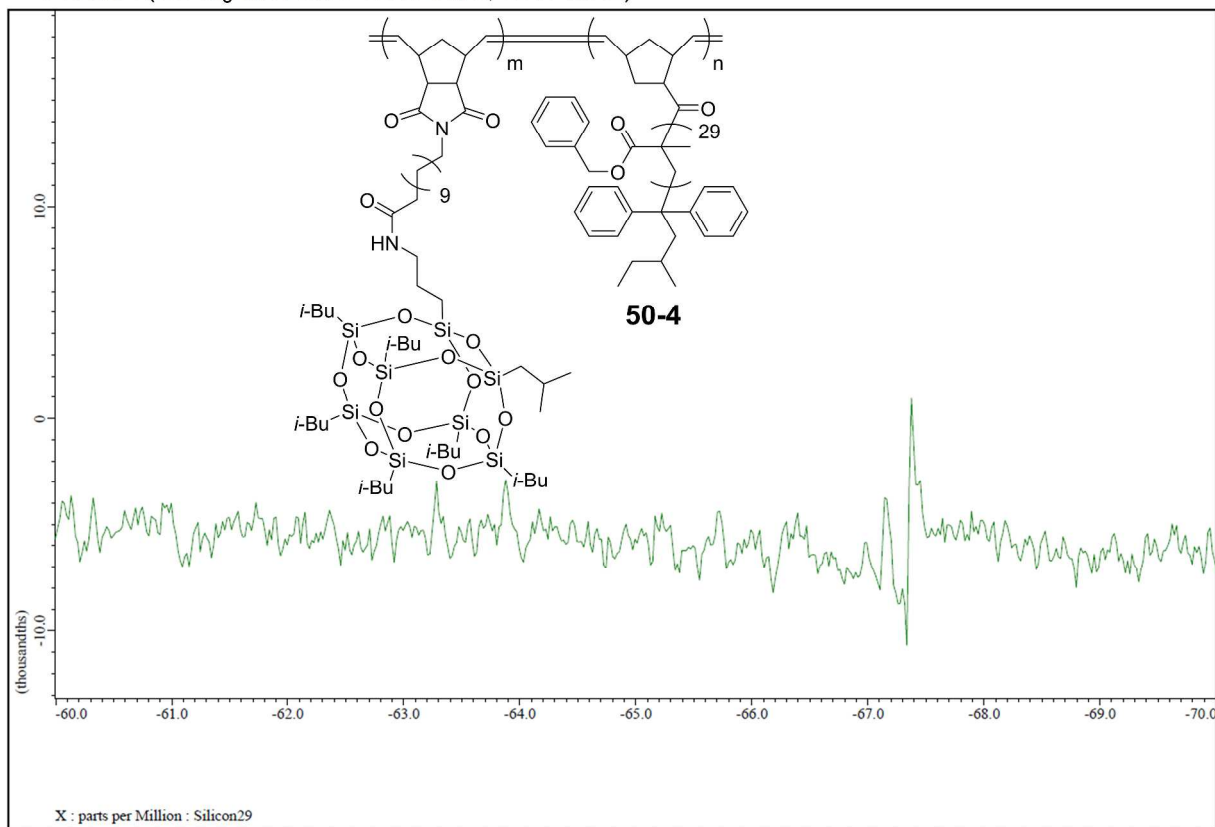


Figure S21. ^{29}Si NMR spectrum of **50-4** ($f_A = 50$ wt%) in CDCl_3 .

S3. TGA Thermograms

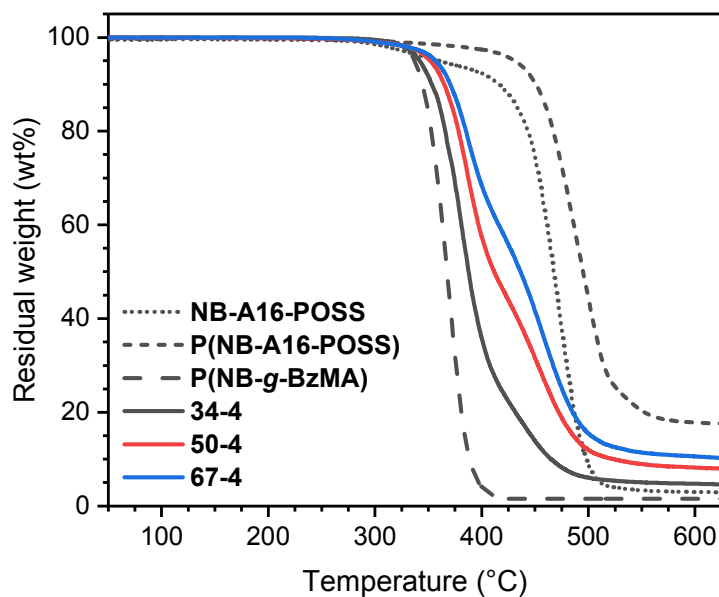


Figure S22. TGA thermograms of **P(NB-A16-POSS)**, **P(NB-g-BzMA)** and **P(NB-A16-POSS)-*b*-P(NB-g-BzMA)s** (**34-4**, **50-4** and **67-4**: $f_A = 34, 50$ and 67 wt%, respectively) recorded at a heating rate of 10 °C/min under a nitrogen atmosphere. Temperatures for 5 wt% loss are 431, 338, 342, 352 and 357 °C for **P(NB-A16-POSS)**, **P(NB-g-BzMA)**, **34-4**, **50-4** and **67-4**, respectively.

S4. References

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