Supporting Information

Fabrication of Hydroxylated Norbornene Foams via Frontal Polymerization for Catalytic Applications.

Andrew Vogler,[a] Tina Dinh,[a] Hanlin M. Wang,[b] Ghaida Aldhahri,[c] Arfa Abrar Malik,[a] and Diego Alzate-Sanchez*[a]

Affiliations: [a.] Chemistry and Chemical Biology Department, Northeastern University, Boston, MA, USA. [b.] Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana−Champaign, Urbana, IL, USA. [c.] Biomedical Engineering Department, Boston University, Boston, MA, USA.
* Corresponding Author E-mail: d.alzatesanchez@northeastern.edu

Table of Contents

Contents

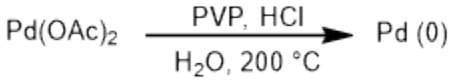
Materials and Instrumentation

Reagents: Dicyclopentadiene, allyl alcohol (≥99%), second generation Grubbs catalyst (≥97%), sodium hydride (95%) and hydroquinone (≥99%) were purchased from Sigma-Aldrich. Methylene chloride (≥99%) 5-ethylidene-2-norbornene (98%), chloroform (>99%), ethanol (99%), ethyl acetate (≥99%), methanol (≥99%), and potassium carbonate (>95%) were purchased from Fisher Scientific. Iodobenzene (99.0%), phenylboronic acid, ethyl vinyl ether (≥98%), biphenyl (99.5%) were purchased from TCI America. Tributyl phosphite (95%), chloroform-d (≥99%), tetrahydrofuran (≥99%), polyvinylpyrrolidone, and palladium (II) acetate (≥99%) were purchased from Thermo Fisher Scientific. All chemicals were used as received.

Instrumentation: X-ray micro-computed tomography (Micro-CT) was done using in a Rigaku CT Lab HX130, operating at 50 kV and a field of view of 30 mm. Transmission electron microscopy was done using a JEOL TEM1010. Scanning electron microscopy and electron dispersive X-ray spectroscopy were done using a S4800 Hitachi Field Emission Scanning Electron Microscope (FE-SEM) equipped with an EDAX energy dispersive spectroscopy system. The specific beam energies were 7.0 kV with a working distance of 10 ± 1 mm that varied for EDS. A 208HR Cressington Sputter Coater with a Pt target was used to coat each polymer for 40 seconds of sputtering time before microscopy analysis. Nuclear magnetic resonance was performed in a 500 MHz Bruker NEO Avance spectrometer and a 400 MHz Bruker Avance NEO spectrometer. Maximum temperature was recorded using an Omega OM-EL-USB-2-LCD thermocouple data logger. Polymerization was recorded using an ELP 2.0 Megapixel USB Camera. An Agilent 6890/5973 GC-MS was paired with an Agilent HP-1 (part number 19091Z-002) 25 m length x 0.200 mm diameter, 0.11 μm thick film column. Frontal velocity was measured using Tracker 6. 1. 5 software.[1] Volume fraction was measured using a BoneJ2 plugin within ImageJ 1.54 software. Contact angle was measured using the LB-ADSA plugin within ImageJ 1.54 software. Images for contact angle were taken using a TAKMLY Wireless Digital Wi-Fi USB Microscope 50X to 1000X Magnification Mini Handheld Endoscope Inspection Camera. Size exclusion chromatography (SEC) was performed on a Tosoh EcoSEC Elite HLC-8420 GPC with a control panel, autosampler, degasser unit, and dual flow pump. Four columns were used within the instrument: a TSKgel SuperH-RC 6.0 mm I.D. x 15 cm, 4 μm; two TSKgel GMH_{HR}-M 7.8 mm I.D. x 30 cm, 5 μm; a TSKgel gaurdcolumn H_{HR}-H 6.0 mm I.D. 4 cm, 7 μm. The instrument contains a refractive index detector, a variable wavelength UV detector, and an independent Tosoh Multi-Angle Light Scattering Detector LenS3.

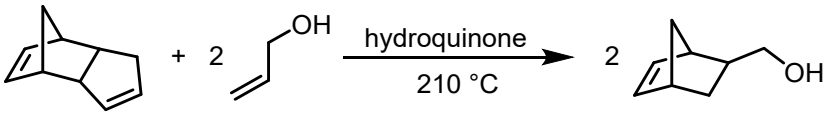
Synthesis and Experimentation

Palladium nanoparticles synthesis:



Polyvinyl pyrrolidine (4.00 g, 0.100 mmol) was dissolved in 40 mL of water until a clear solution was obtained. In a separated container, $Pd(OAc)_2$ (114 mg, 0.508 mmol) was added to HCl (600 µL, 12 M), the suspension was sonicated for 5 min. Afterwards, the palladium solution was added to 20 mL of water and stirred for 10 min. The diluted palladium solution was added dropwise to the polyvinyl pyrrolidine solution under continuous stirring, obtaining a bright orange solution. The combined solution was transferred into a 200 mL Teflon-lined stainless-steel autoclave and placed it in an oven at 200 °C for 19 h. The black suspension obtained was centrifuged at 14 000 rpms for 40 min. Complete decantation of the nanoparticles was not observed, and the upper part of the suspension was removed, leaving 10 % of it in the centrifuge tube. Enough water was added to recover the initial volume, the nanoparticles resuspended, and the suspension centrifugated again. The washing procedure was repeated once with water and twice with methanol. The methanol in the final suspension was removed by rotary evaporation, obtaining a black powder (33.8 mg, 0.318 mmol, 62.3 % yield). Finally, palladium nanoparticles were resuspended in methanol at a concentration of 10 mg mL^{-1}.

HMNB synthesis:



In a 350 mL pressure vessel, allyl alcohol (103 mL, 1.51 mol), dicyclopentadiene (100 g, 0.756 mol), and hydroquinone (155 mg, 1.41 mmol) were stirred under nitrogen until a homogeneous solution was obtained. The vessel was sealed, and the reaction mixture heated to 210 °C for 16 h. The pale-yellow reaction mixture was transferred to a round bottom flask and the excess allyl alcohol was removed by rotary evaporation (70 °C, 20 mbar). The reaction was attached to a short-path distillation head where reduced pressure distillation was performed (120 °C, 10 mbar). Dicyclopentadiene was obtained first (40 °C) followed by HMNB (80 °C). HMNB was isolated as a colorless viscous liquid (101 g, 0.813 mol, 53.6 % yield). ^1H NMR (500 MHz, $CDCl_3$) δ (Major

isomer): 6.14 (dd, J = 5.8, 3.1 Hz, 1H), 5.95 (dd, J = 5.8, 2.9 Hz, 1H), 3.39 (dd, J = 10.4, 6.5 Hz, 1H), 3.25 (dd, J = 10.4, 8.9 Hz, 1H), 2.92 (s, 1H), 2.90-2.70 (m, 1H), 2.34 – 2.27 (m, 1H), 1.81 (ddd, J = 11.6, 9.2, 3.8 Hz, 1H), 1.44 (dq, J = 8.2, 2.2 Hz, 1H), 1.29 – 1.23 (m, 1H), 0.52 (ddd, J = 11.6, 4.5, 2.6 Hz, 1H).). ^{13}C NMR (100 MHz, $CDCl_3$) δ (Major isomer): 137.6, 132.2, 66.6, 49.6, 43.7, 42.3, 41.8, 28.9.

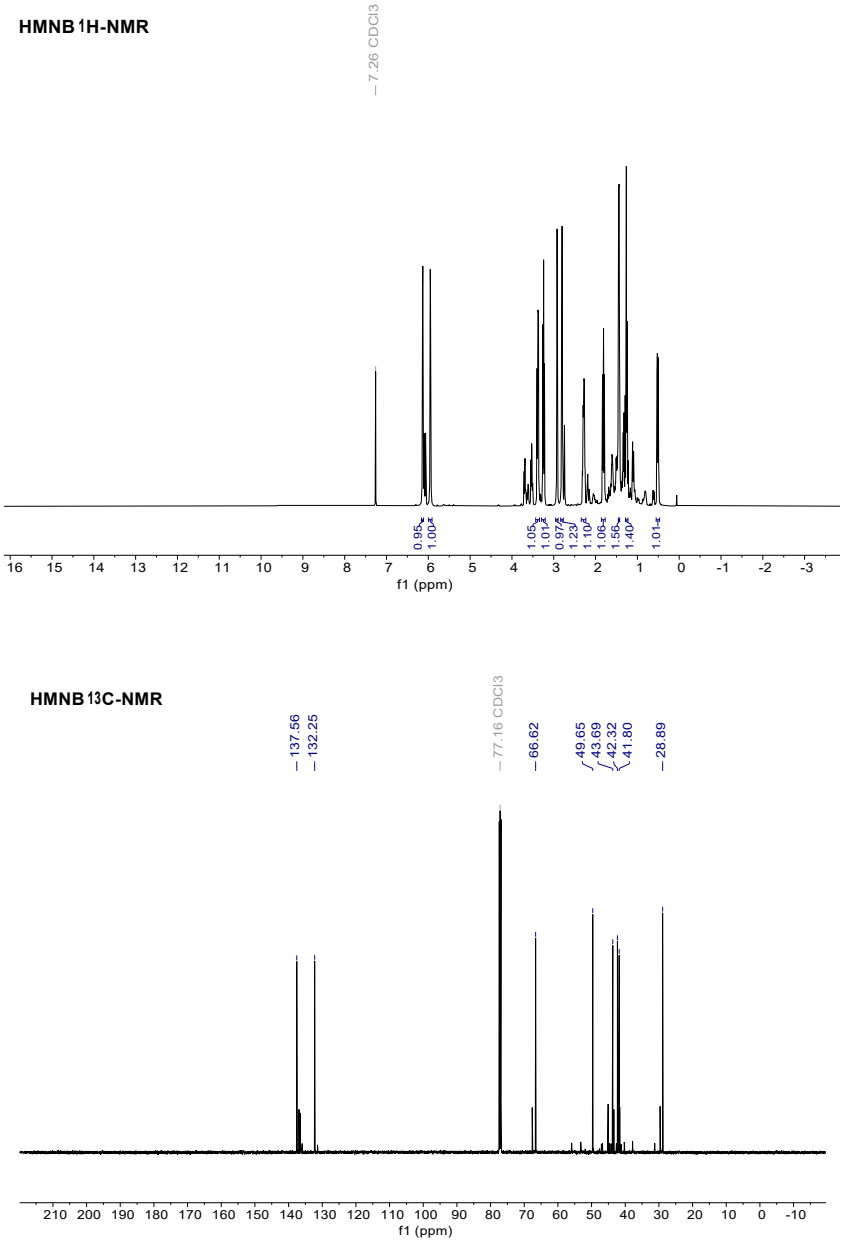
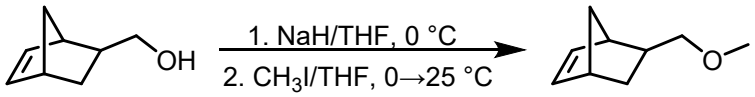


Figure S1. ^{1}H-NMR and ^{13}C-NMR of HMNB

MMNB Synthesis:



This monomer was synthesized following a reported protocol.[2] NaH/oil (3.0 g, 60 wt%, 75 mmol) was suspended in THF (50 mL), centrifugated and the supernatant was removed. This procedure was repeated 3 times to remove the oil. The NaH slurry was transferred into a 3-neck round bottom flask and more THF was added (200 mL). The suspension was cooled down to 0 °C using an ice bath under N_2. HMNB (5.6 g, 45 mmol) was dissolved in THF (20 mL), it was added to the NaH suspension over 30 min, and the solution was stirred at 0 °C for 1h. CH_3I (5.6 mL, 90 mmol) was dissolved in THF (20 mL) and it was added to the reaction mixture over 30 min. The rection was allowed to thaw to 25 °C and react for 5h. The reaction was quenched with HCl (100 mL, 0.01 M) and Et_2O (100 mL) were added. The organic phase was washed with water (100 mL, 3X), dried with $MgSO_4$, and the solvent was removed using rotary evaporation. The yellow liquid in the round bottom flask was attached to a short-path distillation head where reduced pressure distillation was performed (oil bath 90 °C, 75 mbar, boiling point 35 °C). MMNB was isolated as a colorless viscous liquid (3.42 g, 24.7 mmol, 54.6 % yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ (Major isomer): 6.12 (dd, J = 5.8, 3.1 Hz, 1H), 5.93 (dd, J = 5.8, 2.9 Hz, 1H), 3.30 (s, 3H), 3.08 (dd, J = 9.2, 6.6 Hz, 1H), 3.01 (t, J = 9.0 Hz, 1H), 2.89 (s, 1H), 2.79-2.77 (m, 1H), 2.37 – 2.30 (m, 1H), 1.81 (ddd, J = 11.5, 9.2, 3.8 Hz, 1H), 1.44-1.39 (m, 1H), 1.26 – 1.22 (m, 1H), 0.49 (ddd, J = 11.6, 4.5, 2.6 Hz, 1H).). ^{13}C NMR (100 MHz, $CDCl_3$) δ (Major isomer): 137.2, 132.6, 68.1, 58.8, 49.6, 44.1, 42.3, 38.8, 25.7.

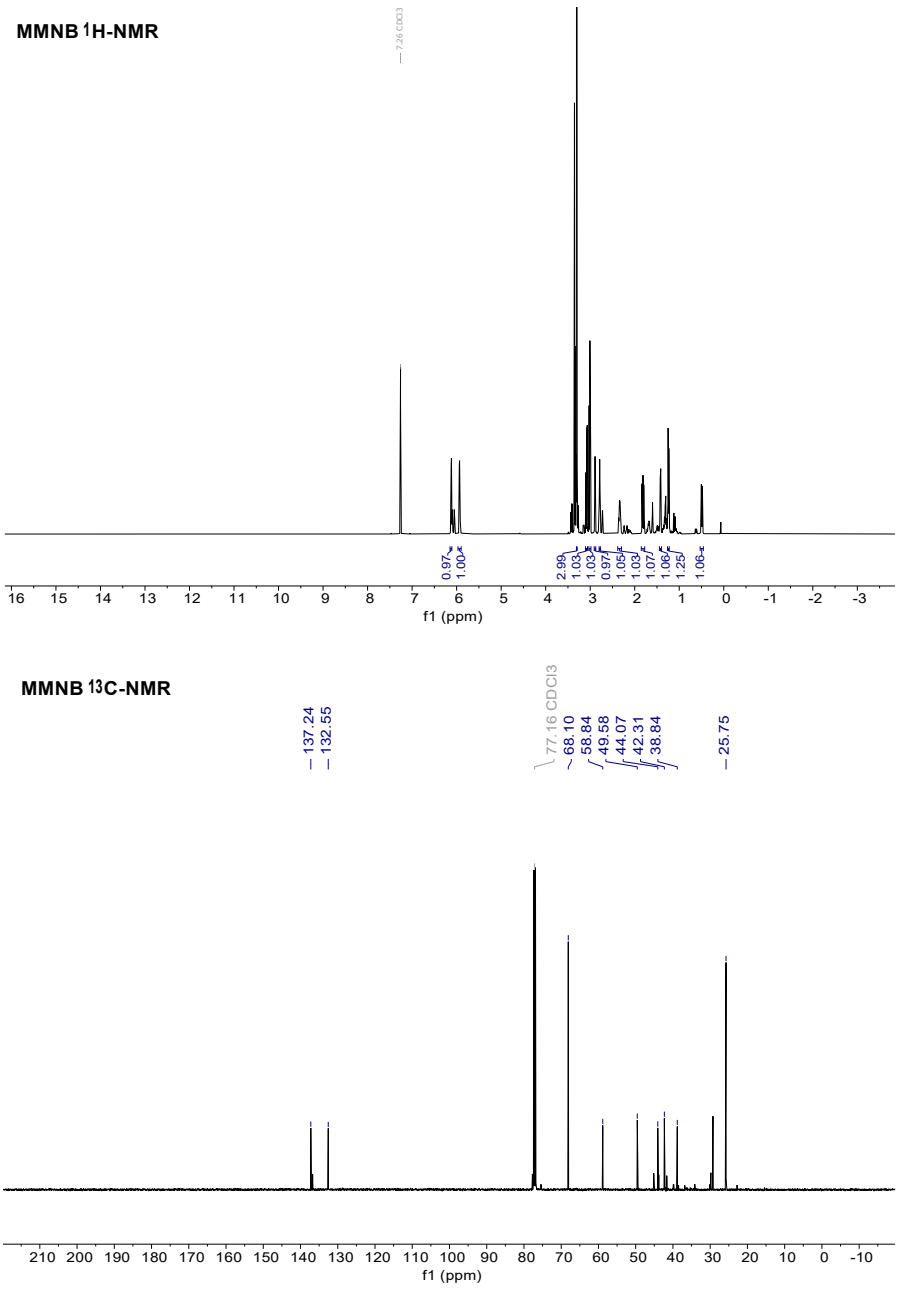


Figure S2. ^{1}H-NMR and ^{13}C-NMR of MMNB

Synthesis of p(HMNB): The procedure for the synthesis of p(HMNB) *via* FROMP was the same for all the formulations. For M/I = 500, HMNB (0.50 g, 4.0 mmol) was mixed with G2 (6.8 mg, 8.0 μmol) in a vial that was sonicated and vortexed. The suspension was pipetted into a test tube where the reaction was initiated by a soldering iron until a propagation front was seen, indicating a self-sustaining reaction.

M/I	HMNB (g)	G2 (mg)
500	1.2	16
1000	1.2	8.2
2500	2.0	5.5
5000	1.5	2.1
10000	1.5	1.0

Synthesis of p(DCPD-*co*-ENB): A solution of 95 wt% DCPD and 5 wt% ENB was generated. For M/I = 10000, DCPD/ENB (2.0 g, total 15 total mmol) and TBP (0.41 μL, 1.5 μmol) were mixed with G2 (1.2 mg, 1.4 μmol) in a vial that was sonicated and vortexed. The suspension was pipetted into a test tube where the reaction was initiated by a soldering iron until a propagation front was seen, indicating a self-sustaining reaction.

M/I	DCPD/ENB (g)	TBP (μL)	G2 (mg)
10000	2.0	0.41	1.2
3500	0.90	0.51	1.6

Synthesis of p(HMNB)-F: Synthesis of the p(HMNB) foams via FROMP was the same for all the formulations. For the foam synthesized with 10 wt % *n*-pentane, HMNB (0.90 g, 7.2 mmol), n-pentane (0.10 g, 1.4 mmol), and G2 (1.8 mg, 2.1 μmol) were mixed in a vial. The reaction mixture was sonicated and vortexed to ensure the absence of gas in the mixture and to aid in mixing. Finally, the reaction was initiated by a soldering iron until a propagation front was seen indicating a self-sustaining reaction.

n-pentane wt%	HMNB (g)	*n*-pentane (g)	G2 (mg)
10	0.90	0.11	1.8
20	0.81	0.20	1.6
30	0.70	0.30	1.4
40	0.60	0.40	1.2

Synthesis of p(DCPD-*co*-ENB)-F: Synthesis of the p(DCPD-*co*-ENB) foams via FROMP were all made using 10 wt% *n*-pentane and a solution of 95 wt% DCPD and 5 wt% ENB. DCPD/ENB (0.90 g, 6.8 total mmol), *n*-pentane (0.10 g, 1.4 mmol), TBP (0.51 µL, 1.9 µmol) and G2 (1.6 mg, 1.9 µmol) were mixed in a vial. The reaction mixture was sonicated and vortexed to ensure the absence of gas in the mixture and to aid in mixing. Finally, the reaction was initiated by a soldering iron until a propagation front was seen indicating a self-sustaining reaction. This experiment was a triplicate.

Protorheology: Into two vials, a 10000/1 HMNB (0.5 g, 4 mmol) and G2 (0.3 mg, 0.4 µmol) solution were made. One vial contained tributyl phosphite inhibitor (0.1 µL, 0.4 µmol). The vials were inverted, a picture taken after 10 seconds of inversion. The solutions were placed in a 30°C water bath and removed periodically for the same inversion photography. This process was repeated until both samples had undergone gelation and did not move position upon inversion**.**

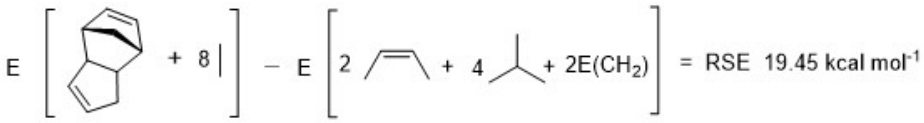
Frontal velocity calculation: A recording of each reaction was opened in the Tracker software.[1] Each recording was calibrated two times at an initial frame where the propagation front was clearly seen. The step size for each measurement was 30 frames and the final frame set to 330 frames after its respective initial frame. The velocity was then calculated as a change in distance over time using point masses. In each video, three total measurements were taken. Each video's frontal velocity was averaged, and standard error calculated for a final frontal velocity.

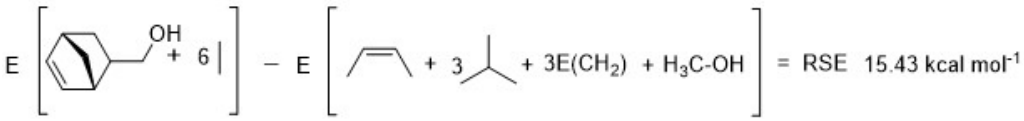
Maximum temperature: A thermal probe was set up to record temperature every second while suspended in the center of the reaction vessel before initiation. Once polymerization began, the probe recorded all changes in temperature and the maximum value was determined. The average maximum temperature and standard error were determined from three independent experiments.

Enthalpy of Polymerization: Three individual M/I=10000 HMNB resins were prepared and placed into a DSC pan before being sealed with a hermetic lid. In one instance, 11.4 mg were used.

The ramp rate was 5 °C/min from 30-200 °C. The enthalpy of polymerization was normalized with respect to mass and determined as the integration of the exotherm peak as 288.41 J g^{-1}. The reported value is the average of three total experiments.

Ring Strain Energies (RSE): Ring strain energies were computed using a homodesmotic approach with Gaussian 16 at the B3LYP/6-31G(d) level of density functional theory.[3-5] The procedure employed an acyclic molecule as the strain-free reference, where the total free enthalpy (E) of each molecule was calculated. E(CH_2) is the energy difference between *n*-pentane and *n*-butane to approximate the incremental CH_2 unit energy.[6]





p(HMNB) solubility: Polymer samples of 500/1 HMNB to G2 ratio were cut and suspended in various solvents including DMF, DMF with 10 wt% NH_4OH, DMF with 10 wt% CH_3COOH, and MeOH in concentrations of 10 mg/mL. After four days, the vials were examined to evaluate the presence of polymer.

ROMP of HMNB: 10 mL of a 20 mM solution of HMNB (25 mg,0.20 mmol) in $CHCl_3$ was generated. To this solution, G2 (1.7 mg, 2.0 µmol) was added, sonicated, and vortexed until a homogenous distribution of initiator was seen. This solution sat for 2 hours total at room temperature before being quenched with and 10 equivalents of ethyl vinyl ether (1.9 µL, 0.020 mmol) with respect to G2. This solution was then poured into a falcon tube where it was centrifuged at 4500 rpm for 5 minutes. Afterwards a dark precipitate was seen floating on top of the solution.

p(HMNB) swelling: Polymer samples of varying HMNB to G2 ratios ranging from 500/1 to 10000/1 were suspended in THF at a concentration of 10 mg/mL for four days. The polymer's masses before and after swelling were recorded. This experiment was done in triplicated.

Glass transition temperature: Discs were cut from polymer samples approximately 10 mg in size and placed into DSC cells with a crimp lid. Each sample underwent the same process independent of polymer type and M/I. For p(HMNB) M/I=500, a 13.3 mg sample was clamped shut within the cell. The experiment ran in three parts starting from 20 °C to 180 °C at 20 °C/min, then 180 °C to -40 °C, and finally -40 °C to 180 °C. The first two parts were implemented to erase the polymers thermal history. In the third cycle, the DSC Glass Transition function was utilized yielding an onset of 74.2 °C, midpoint of 82.3 °C, and ΔCp of 0.238 J g^{-1} K^{-1}.

***In situ f*unctionalization of p(HMNB) and p(DCPD-*co*-ENB) scaffolds:** The deposition of palladium nanoparticles onto the foams was accomplished by performing the palladium nanoparticle synthesis in the presence of either p(HMNB) or p(DCPD-*co*-ENB) scaffolds. Polyvinyl pyrrolidine (2.0 g, 0.050 mmol), $Pd(OAc)_2$ (58 mg, 0.26 mmol), HCl (300 µL, 12 M), water (30 mL), and p(HMNB) (810 mg) were added to a 100 mL Teflon-lined stainless-steel autoclave following the previously described protocol used for the synthesis of the palladium nanoparticles. p(HMNB) was kept immersed in the aqueous solution with the help of a glass fiber mesh. After completion of the reaction, p(HMNB) was isolated, washed with water, methanol and dried under vacuum at 50 °C. The same procedure was done with p(DCPD-*co*-ENB) foams.

***Ex situ* functionalization of p(HMNB) and p(DCPD-*co*-ENB) scaffolds:** Pd NPs were made in the absence of polymer and suspended at a concentration of 10 mg/mL in MeOH. In one instance, p(HMNB) foam (48.6 mg) was suspended in THF (1.08 mL) in a 1.5 mL falcon tube. To this solution, an aliquot of the Pd NPs suspension (24.3 µL) was added. This solution was then oscillated for 24 hours at room temperature before the scaffolds were removed and washed two times with both methanol and water before being dried in a vacuum oven overnight at 50 °C.

Size exclusion chromatography: A blank THF solution was ran through the instrument followed by the solubilized sample. Next, p(MMNB) samples were solubilized in THF at 5 mg mL^{-1}. The solution was pushed through a 13 mm wide, 45 µm syringe filter into SEC vials. The flow rate was set to 1 mL min^{-1} and the experiment was ran for 24 minutes. Refractive index was used to analyze the sample based on a polystyrene calibration curve of 2500, 5000, 9000, 17500, 30000,

and 50000 g mol $^{-1}$. A baseline was set parallel to the base of the signals and the curve integrated from 12.18-15.75 min to yield Mw, Mn, and PDI.

^{1}H NMR Kinetics of HMNB and MMNB: Two separate 222 mM solutions of MMNB (27.6 mg, 0.200 mmol) and HMNB (24.8 mg, 0.200 mmol) were prepared in 900 μL $CDCl_3$. A third solution of G2 (6.8 mg, 8.0 μmol) was made in 400 μL of $CDCl_3$. Right before the ^{1}H NMR experiment began, 100 μL of the G2 solution was added to each monomer solution and the tube inverted several times prior to data acquisition. Mixing lasted about 30 seconds. The first seven scans were done with no delay every 10 seconds including time=0. Scans 8-10 were done every 20 seconds, scans 11-16 done every 30 seconds, and 17-21 done every minute, resulting in a 10-minute experiment.

X-ray microcomputed tomography: HMNB foams were cut using a saw to a final length of 20 mm and polished using a 180-grit sandpaper. Afterwards, they were mounted on a polystyrene support. The mounted foams were located inside of the X-ray microtomography instrument and irradiated for a period of 14 min using a voltage of 70 kV.

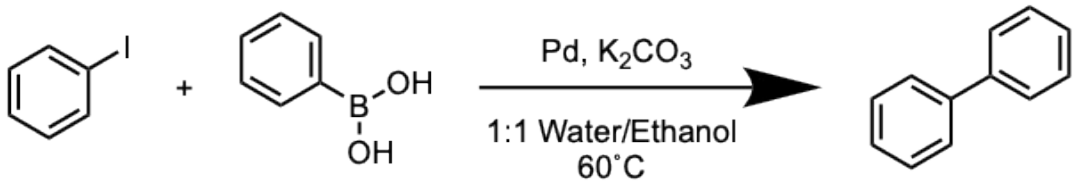
Volume fraction calculations: Calculations were done following the same procedure employed in our previous work.[7] X-ray micro-computed tomography images of the foams were opened and processed using imageJ2 software. After selecting the slices containing the sample, the images were filtered using gaussian blur and the manual threshold function was used to obtain black and white stacks. Then, a region that contains only the sample was drawn and saved using the region of interest (ROI) manager. Interpolation of several ROI images was used to get a ROI for each slide. Afterwards, combination of the ROIs with the clear outside and fill scripts allowed us to access a masked stack of the sample to be analyzed. The volume fraction was calculated using the boneJ2 package for the two images (sample and mask).[8] The bone volume (BV) of the mask was used as the total volume (TV) of the sample to eliminate the blank volume of the image.

Void analysis: X-ray micro-computed tomography images of the foams were opened and processed using imageJ2 software. After selecting the slices containing the sample, the manual threshold function was used to obtain black and white stacks. Then, the images were calibrated using the Micro-CT FOV. The color of the stacks was inverted and the analyze particles function selected. A minimal area of 0.001 cm^2 was used as the lower limit, and an area of 1 cm^2 was used as the upper limit.

Pd suspension in monomer: 100 µL of a 10 mg mL^{-1} solution of Pd in MeOH were added to two vials and MeOH was removed with heat. In one of the vials Pd (1.0 mg, 9.4 µmol) was resuspended in HMNB (1.0 g, 8.1 mmol), and in the other vial Pd (1.0 mg 9.4 µmol) was resuspended in both DCPD (0.95 g, 7.2 mmol) and ENB (0.050 g, 0.42 mmol), the solutions were sonicated/vortexed to help with mixing. An image was taken right after sonication/vortexing and after 20 min.

Contact angle: Contact angle was measured by placing 2.5 µL of DI water onto both p(DCPD-*co*-ENB) and p(HMNB) surfaces which were cut with a saw and polished with 180 grit sandpaper. A picture was taken perpendicular to the surface the water sits on, and the image uploaded into ImageJ where the Drop Analysis LB-ADSA plugin was used to calculate contact angle.[9] The average contact angle and standard error were determined from three independent experiments.

Suzuki-Miyaura coupling:



Iodobenzene (50.8 mg, 0.249 mmol), phenylboronic acid (35.7 mg, 0.293 mmol), and potassium carbonate (68.5 mg, 0.496 mmol) were combined in a 1:1 water/ethanol mixture (5.00 mL). Palladium nanoparticles were then added to the mixture (0.0625 mg, 0.587 µmol, 6.25 µL of a 10 mg/mL suspension) and heated at 60 ˚C. A 300 µL aliquot was taken at eight different time points (10 minutes, 30 minutes, and at each hour up to 6 hours) and diluted 10 times using ethyl acetate. GC-MS was then taken for the eight diluted samples to determine the amount of biphenyl. A control reaction where biphenyl (38.7 mg, 0.251 mmol) and potassium carbonate (68.5 mg, 0.496 mmol) were combined in a 1:1 water/ethanol mixture (5.00 mL) was also run. Quantification was done using the control run assuming that the amount of biphenyl in the control was 100% yield.

The experiments with the palladium scaffolds followed a similar protocol except the quantification of biphenyl was taken after allowing the reaction to run for 4 hours at 60 ˚C. The reaction was diluted 10 times before GC-MS was run. The palladium solution was replaced with either the palladium deposited polymer or foam.

For catalysis recycling, the experiments followed a similar protocol as the palladium scaffolds. Once the reaction was finished, the foam was extracted and washed thoroughly using dichloromethane. The foams were then dried in a vacuum oven at 140 ˚C overnight. Once dried, the foams were reused following the same protocol as the palladium scaffolds.

Additional Figures

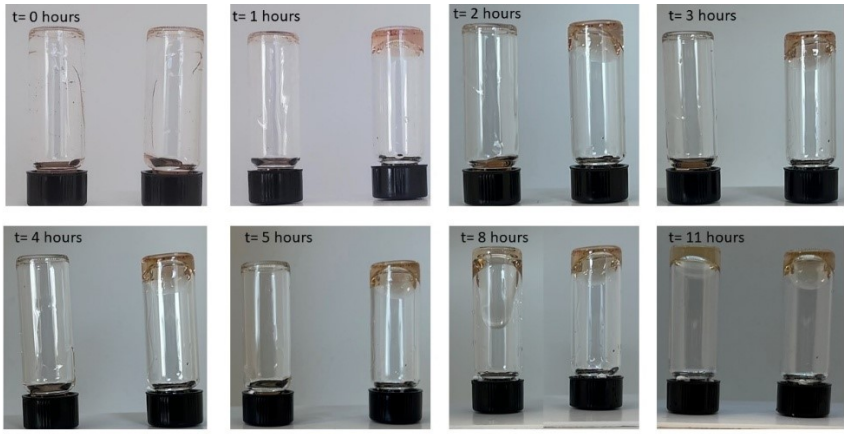


Figure S3. Protorheology experiments of 10000/1 M/I HMNB to G2 with (left) and without (right) tributyl phosphite inhibitor.

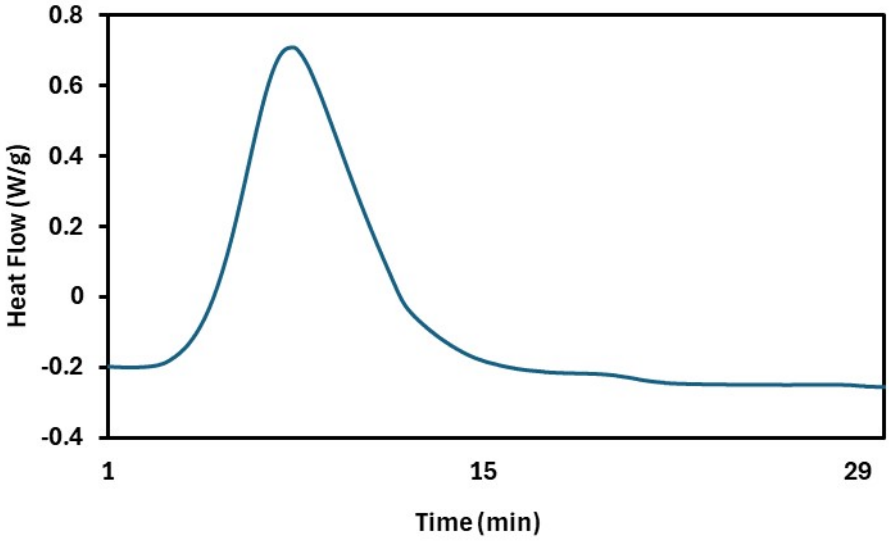


Figure S4. DSC curve from a M/I=10000 HMNB resin.

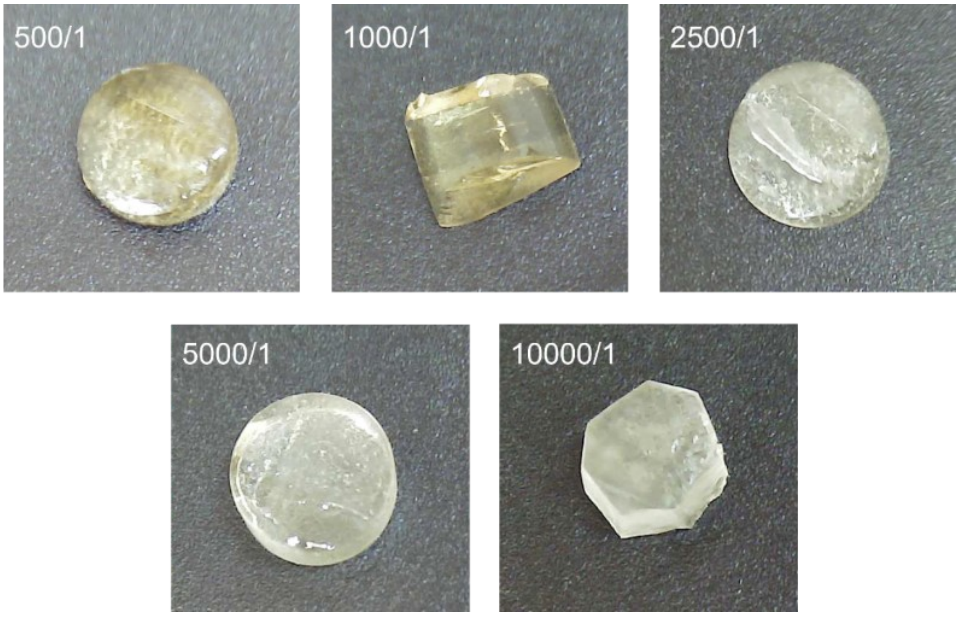


Figure S5. Various M/I p(HMNB) samples submerged in THF for four days.

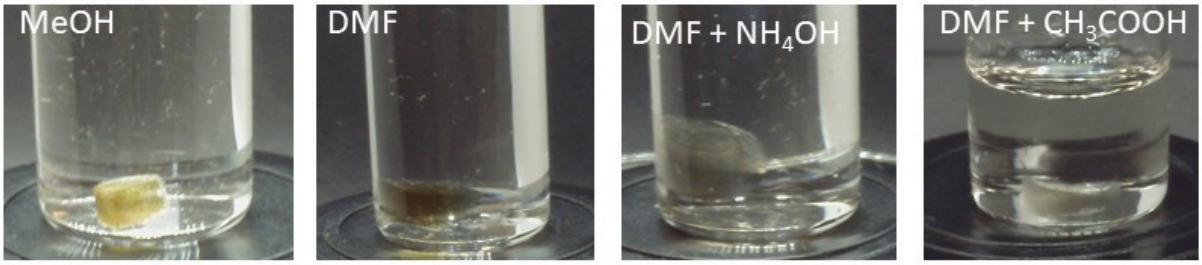


Figure S6. 500/1 M/I HMNB to G2 submerged in various solvents for four days.

Table S1. p(HMNB) swelling experiments**.**

M/I	Initial mass (mg)	Final mass (mg)	Swelling ratio (%)
500A	76.9	173	125
500B	65.3	151	132
500C	63.4	145	129
1000A	85.7	191	123
1000B	90.4	202	123
1000C	93.6	207	121
2500A	93.1	204	120
2500B	96.3	212	120

2500C	78.8	175	122
5000A	96.3	213	121
5000B	99.3	220	122
5000C	121	269	122
10000A	120	263	120
10000B	92.9	202	117
10000C	104	226	118

Table S2. Glass transition temperatures of p(HMNB) sample with various M/I ratios.

M/I	***T*g (°C)**
500	82.3
1000	81.4
2500	80.9
5000	80.5
10000	76.9

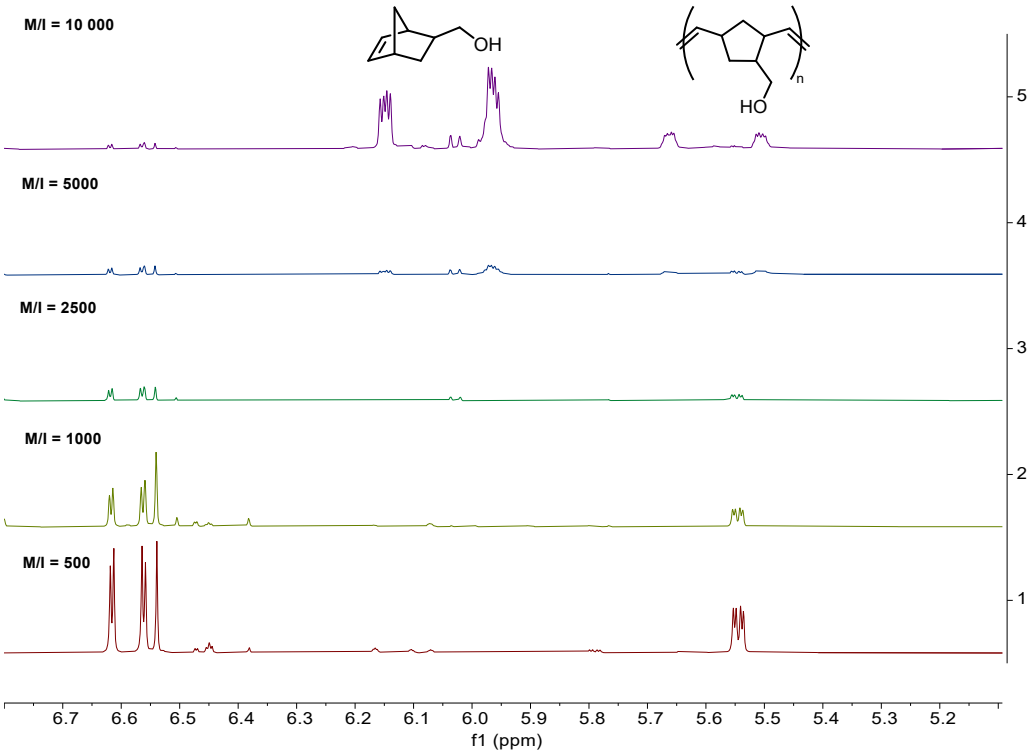


Figure S7. Tetrahydrofuran soluble fraction ^{1}H-NMR spectra of p(HMNB) synthesized with various M/I ratios.

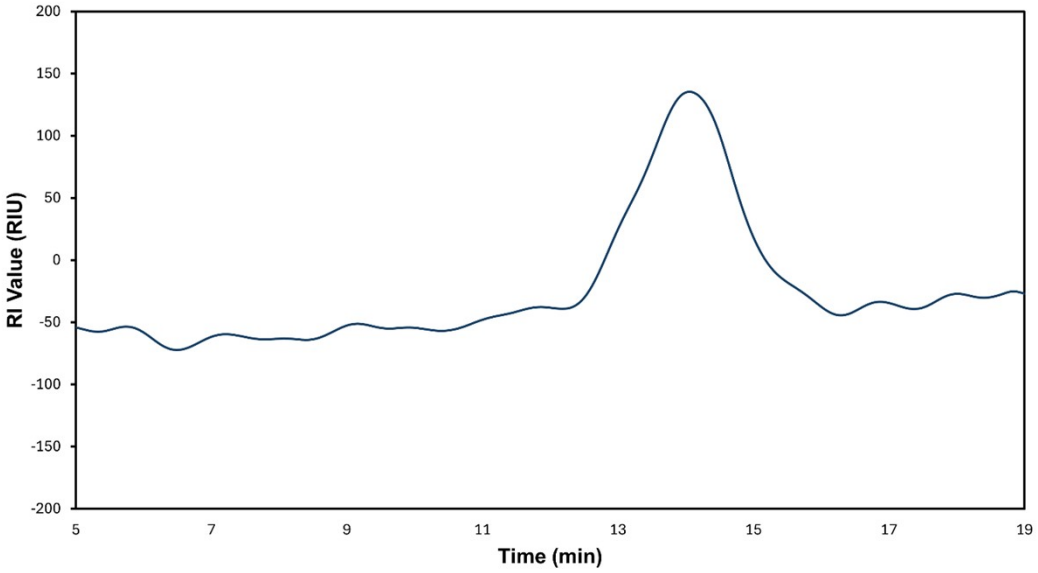


Figure S8. Refractive Index (RI) SEC results of p(MMNB) in THF (5 mg mL^{-1}).

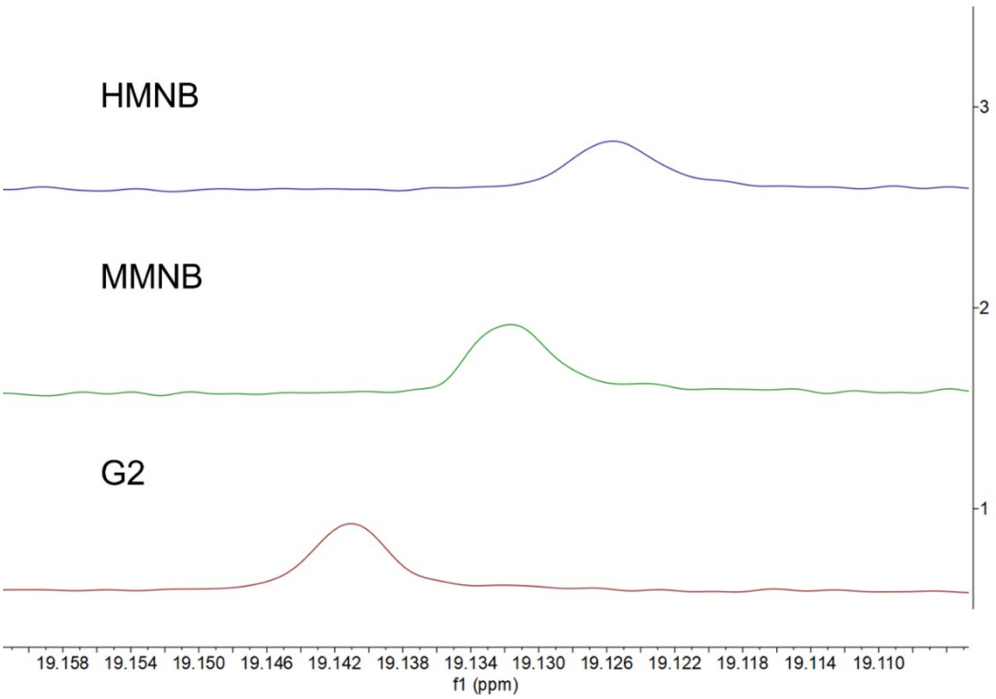


Figure S9. ^{1}H-NMR alkylidene proton peak of G2 with HMNB, MMNB, and G2 alone.

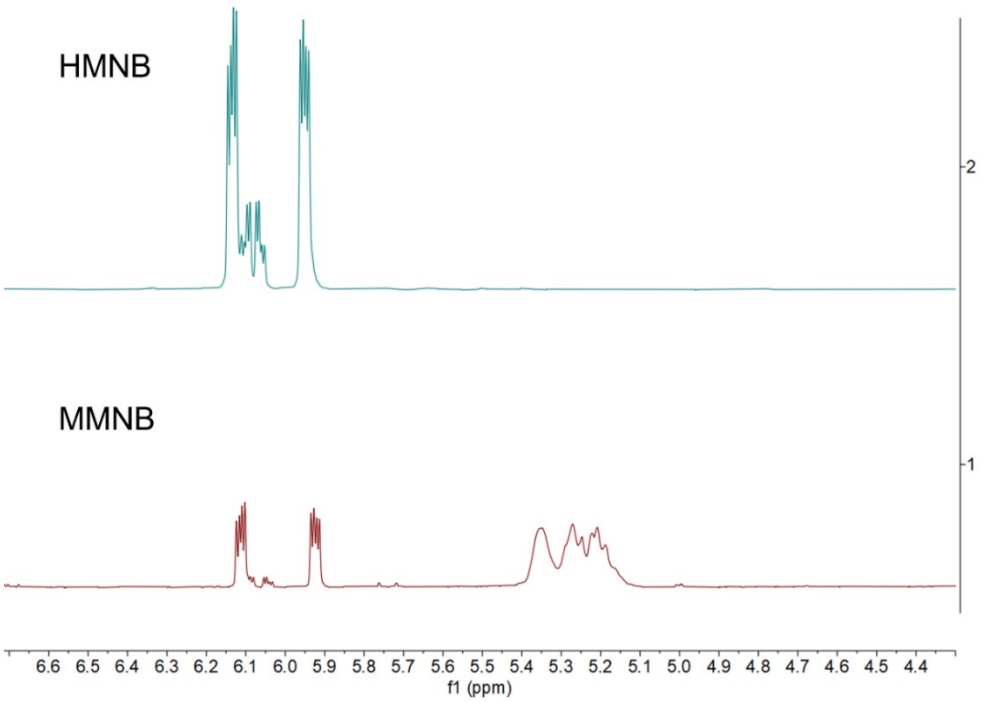


Figure S10. Final ^{1}H-NMR of the MMNB and HMNB kinetic comparison.

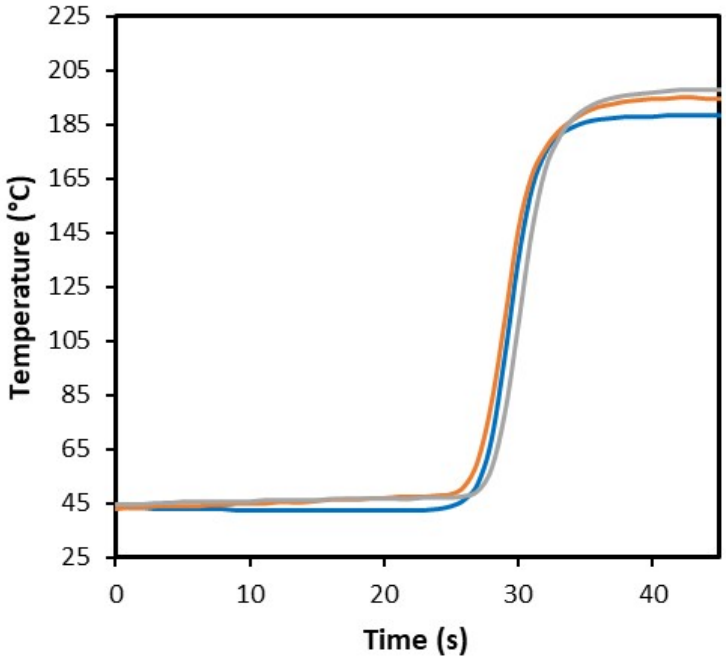


Figure S11. Temperature recordings of three separate HMNB polymerization experiments at M/I=3500.

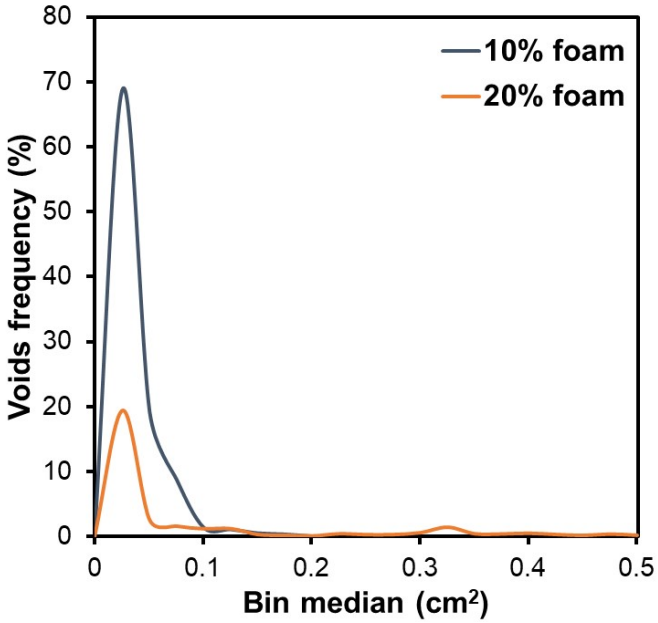


Figure S12. Voids frequency as a function of bin median for the foams synthesized with 10 and 20 wt% *n*-pentane. Voids areas were calculated for each cross section of the Micro-CT reconstructed image. Each bin has a size of 0.025 cm^2.

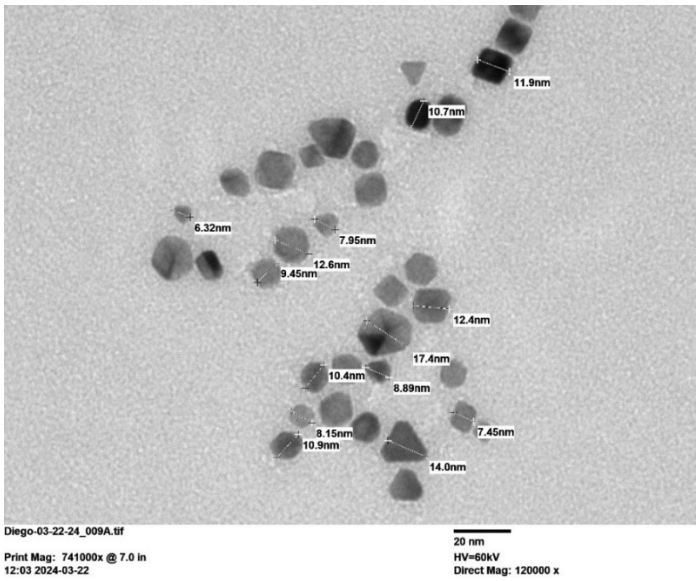


Figure S13. Transmission electron microscopy image of the synthesized palladium nanoparticles.

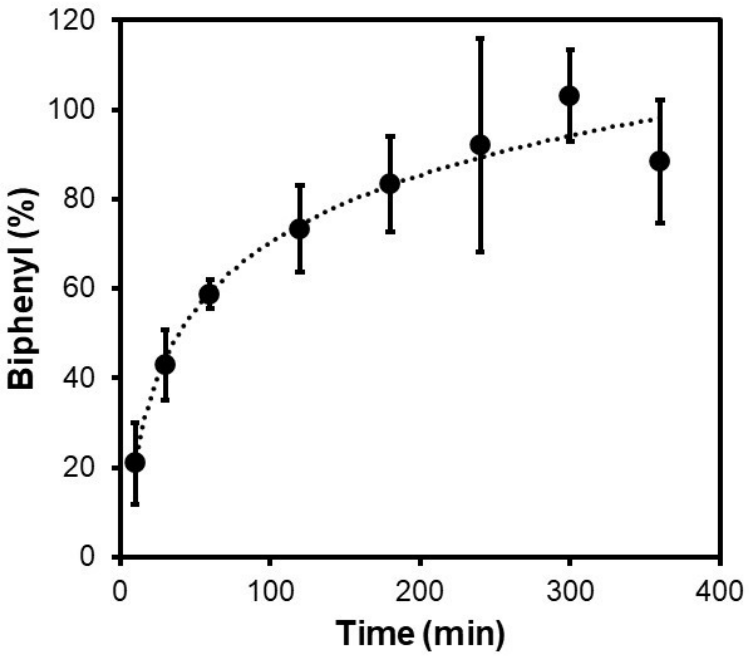


Figure S14. Biphenyl conversion obtained from the Suzuki-Miyaura coupling between iodobenzene and phenylboronic acid using 0.02 mol% palladium nanoparticles.

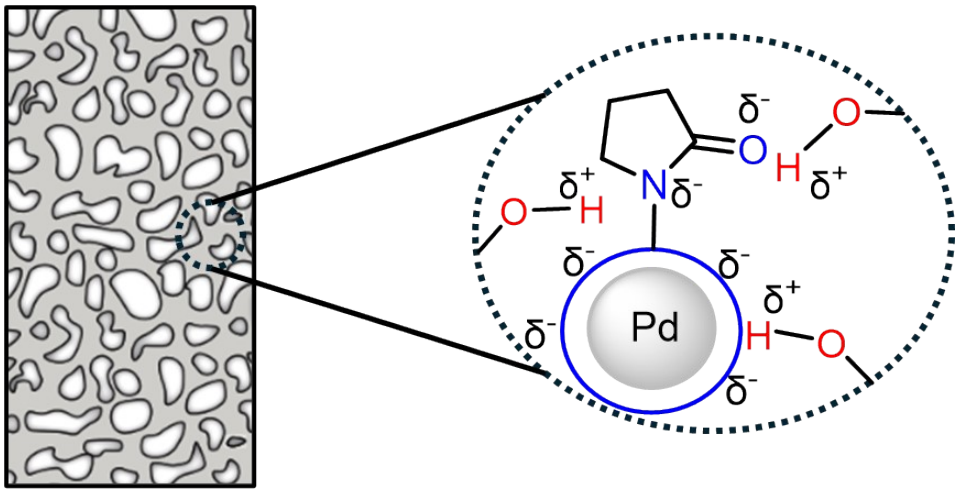


Figure S15. Visual representation of Pd NPs interactions with p(HMNB) foams. Blue represents the polyvinylpyrrolidone coating of the NPs. This interaction is assumed to be the same for both HMNB monomer and p(HMNB) materials.

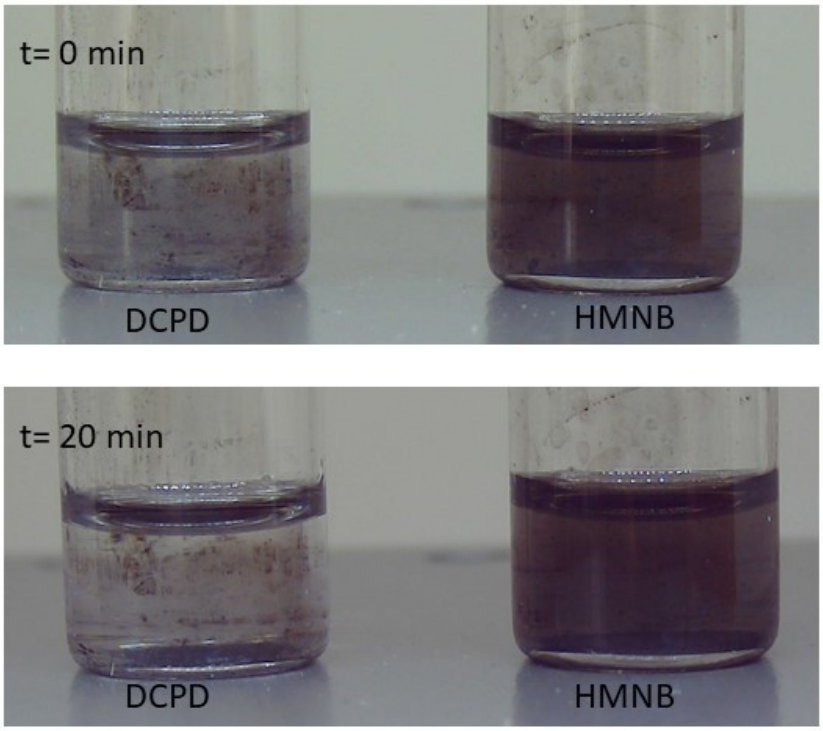


Figure S16. Pd nanoparticle suspension in DCPD/ENB and HMNB solutions.

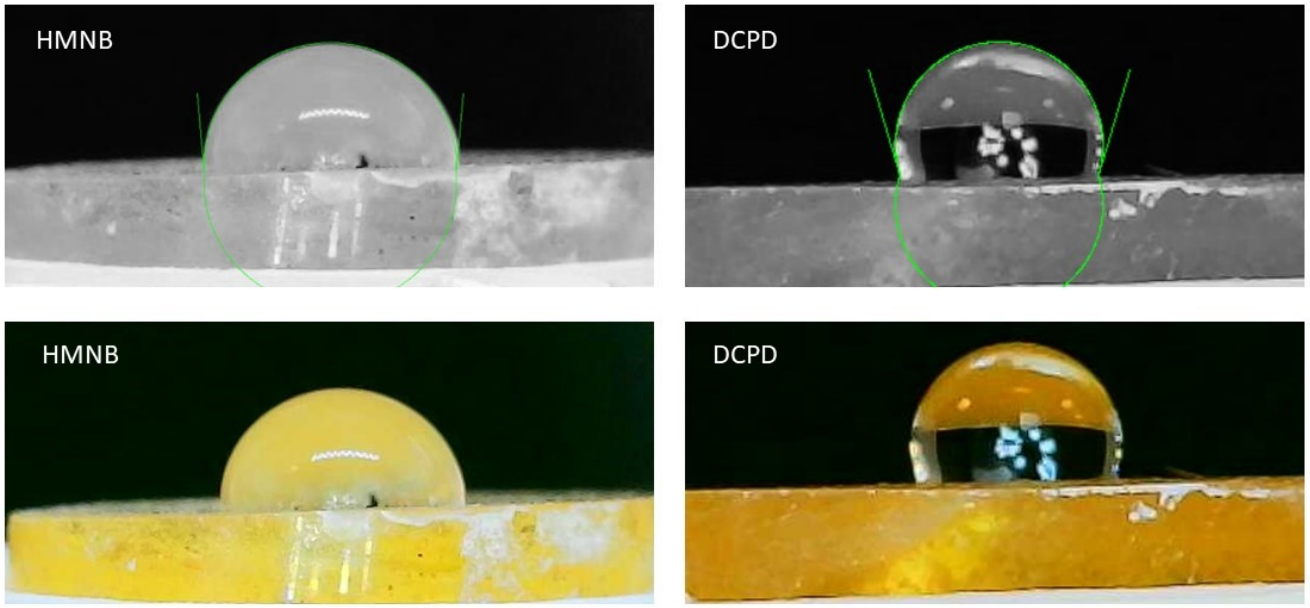


Figure S17. Contact angle with water on p(HMNB) and p(DCPD-*co*-ENB).

Table S3. Comparison of Pd@p(HMNB)-F with reported Pd NP supported materials.

Catalyst	Solvent	Temperature (˚C)	Loading (mol%)	Time (h)	Yield (%)	Reference
Pd@p(HMNB)-F	1:1 Water/Ethanol	60	0.2	4	79	This work
Pd@PUF	1:1 Water/Ethanol	RT	0.2	0.58	95	[10]
Pd@TPU	Ethanol	RT	0.5	3	99	[11]
Pd@Diatomite	1:1 Dimethyl Ether/Water	110	0.1	0.33	95	[12]

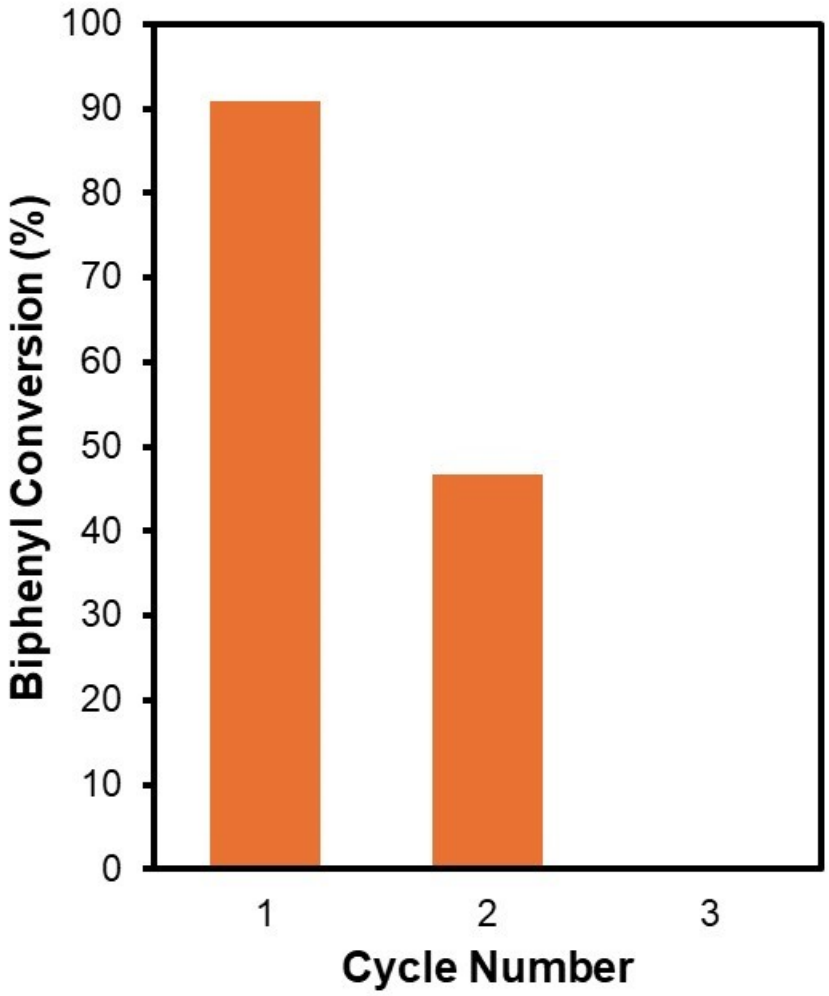


Figure S18. Biphenyl production after three cycles using a Pd@p(DCPD-*co*-ENB)-F scaffold.

References

1. D. Brown, *Journal*, 2024.
2. S. D. Drouin, F. Zamanian and D. E. Fogg, *Organometallics*, 2001, **20**, 5495-5497.
3. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C.

Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Journal*, 2016.
4. A. D. Becke, *The Journal of Chemical Physics*, 1993, **98**, 5648-5652.
5. G. A. Petersson, A. Bennett, T. G. Tensfeldt, M. A. Al-Laham, W. A. Shirley and J. Mantzaris, *The Journal of Chemical Physics*, 1988, **89**, 2193-2218.
6. P. R. Khoury, J. D. Goddard and W. Tam, *Tetrahedron*, 2004, **60**, 8103-8112.
7. D. M. Alzate-Sanchez, M. M. Cencer, M. Rogalski, M. E. Kersh, N. Sottos and J. S. Moore, *Advanced Materials*, 2022, **34**, 2105821.
8. R. Domander, A. Felder and M. Doube, *Wellcome Open Research*, 2021, **6**.
9. A. F. Stalder, G. Kulik, D. Sage, L. Barbieri and P. Hoffmann, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2006, **286**, 92-103.
10. L. Sahoo, S. Mondal, N. C. Beena, A. Gloskovskii, U. Manju, D. Topwal and U. K. Gautam, *ACS Applied Materials & Interfaces*, 2021, **13**, 10120-10130.
11. S. K. Dey, D. Dietrich, S. Wegner, B. Gil-Hernández, S. S. Harmalkar, N. de Sousa Amadeu and C. Janiak, *ChemistrySelect*, 2018, **3**, 1365-1370.
12. Z. Zhang and Z. Wang, *The Journal of Organic Chemistry*, 2006, **71**, 7485-7487.