Electronic Supplementary Material (ESI) for ChemComm.

A Plug and Socket Approach For Tightening Polyelectrolyte Multilayers

Cen Lin, Erwin R. Stedronsky, Luke Jordan, Nathan Wittenberg and Steven L. Regen

Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania 18015

email: slr0@lehigh.edu

Electronic Supplementary Information

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1. Materials and Methods

β-Cyclodextrin, *p*-toluenesulfonyl chloride, dimethylamine solution (2 M in methanol), potassium iodide, poly(4-styrenesulfonic acid) (PSS, sodium salt, Mw ~ 70 kDa), *n*-octadecyltrichlorosilane (OTS), sephadex CM-25 (Da exclusion ~ 30,000, NH_4^+ form) and ammonium chloride were obtained from Sigma-Aldrich and used without further purification. Poly(*p*-vinylbenzyl chloride) (PVBC, Mw 60 kDa) (Polymer Sources Inc., QC, Canada), poly[1-(trimethylsilyl)-1-propyne] (PTMSP, Gelest, Inc., Morrisville, PA) and branched poly(ethyleneimine) (*b*-PEI, Mw=70 kDa, Polysciences Inc., Warrington, PA) were also used as received. Ellipsometry measurements were made using VASE ellipsometer (J.A. Woollam Co., Lincoln, NE), equipped with variable wavelength (250-1700 nm) and variable angle of incidence (15°-90°) system. The refractive indices that were used to estimate the thickness of the *n*-octadecyltrichlorosilane (OTS)-modified layer, the branched poly(ethyleneimine) layer, and the polyelectrolyte multilayers were 1.46, 1.41 and 1.41, respectively. All ^{1}H-NMR spectra were recorded on a Bruker 500-MHz instrument. Chemical shifts are reported in ppm and were referenced with respect to residual solvents.

2. Preparation of Membranes

Procedures that were used to prepare PTMSP casting membranes, OTS-modified silicon wafers and polyelectrolyte multilayers were the same as those previously reported.[1, 2]

3. Gas Permeation Measurements

Gas permeation measurements were made with a home-built stainless steel permeation apparatus. The gases studied were H_2 (Ultra High Purity, water < 3 ppm, Messer Griesheim Industries, Inc., Malvern, PA), CO_2 (Ultra Pure, water < 3 ppm, Praxair, Inc., Danbury, CT) and N_2 (prepurified grade, water < 3 ppm, Praxair, Inc., Danbury, CT). Prior to gas permeation measurements, all membranes were allowed to dry in a desiccator for 48 h after layer-by-layer deposition. During such time, the approximate room temperature was 22 ± 2 °C. Typically, a membrane to be measured was placed in the permeation cell between two Viton rubber O-rings (3.45 cm i.d., Scientific Instrument Services, Inc.) with a support screen (4.70 cm, Millipore Corp.) and held securely with a quick flange clamp (Scientific Instrument Services, Inc.). Membranes were always placed in the cell such that the polyelectrolyte multilayers faced the high pressure side of the pressure gradient. All permeant gases travelled from gas cylinders through an elastomer diaphragm regulator (Brooks Instrument, 8601D), which was connected to a Heise gauge port. A plastic tubing line connected from the Heise gauge outlet to the permeation cell. The pressure gradient that was applied across each membrane was 40 psi. After passing through the membrane, the gaseous permeant was directed into a 40 cm long glass U-tube flowmeter (2 mm i.d.). The volumetric flow rate of the gas was then measured by recording the time (t_f - t_i) that was required for a methyl isobutyl ketone solution containing crystal violet to travel a set distance (d_f - d_i), thereby sweeping out a defined volume. Measurements were taken using this constant pressure-variable volume apparatus until steady-state values were achieved (0.5 h for H_2 and 1 h for N_2). At least four volumetric flow rates were recorded for each membrane, and the mean and standard deviations were determined. The normalized flux was calculated with the use of the mean volumetric flow rate, the area that was available for flow (9.36 cm^2), and the pressure gradient (2.7 atm) that was employed. This procedure was repeated for the next permeant gas. In general, the permeation properties were first measured for H_2, CO_2 and then for N_2. To ensure that no damage to the membrane had occurred while these measurements were being made, after the last permeant was investigated, the H_2 permeances were measured again and found to be unchanged.

4. Membrane Thicknesses Measured by Ellipsometry

A silicon wafer bearing an appropriate PEM was fixed within the ellipsometer and exposed to a humid N_2 stream. This was performed by first passing a dry N_2 stream through an airstone that was submerged in deionized water contained in a Buchner flask, and then blowing this humid stream directly onto the PEM. The change of the optical thickness of PEMs was then monitored as a function of time. A λ value of 632.8 nm and an incident angle of 70° were chose for all measurements. The refractive index was assumed to be constant upon swelling and have a value of 1.41. All other membrane thicknesses that were measured by ellipsometry were determined in the laboratory ambient environment.

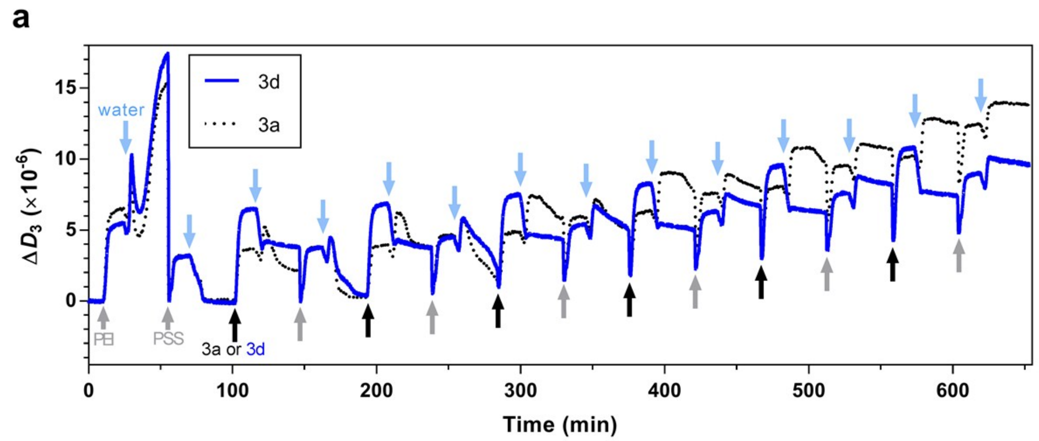
5. Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D)

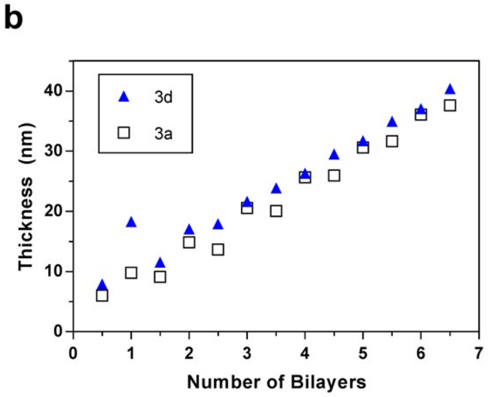
A quartz crystal microbalance with dissipation (QCM-D) instrument (Explorer E1, Q-Sense, Gothenberg, Sweden) was used to grow PEM films and calculate their mechanical properties. Films were formed on quartz crystals pre-coated with silicon dioxide (QSX 303, Q-Sense) and a self-assembled monolayer (SAM) of octadecyltrichlorosilane (OTS). To form the SAM, sensors were cleaned by 20 minutes of sonication in 2% (w/v) sodium dodecyl sulfate (SDS) solution, rinsed extensively with 18.2 MOhm·cm type I ultrapure water (PureLab Classic UV, ELGA LabWater, High Wycombe, UK), dried under a stream of nitrogen gas, then plasma cleaned (PDC-001, Harrick Plasma, Ithaca, NY) for 5 minutes on the highest setting at ~270 mTorr air gas. The sensors were then soaked in OTS in hexane for 20 min, rinsed with hexane and dichloromethane, and dried with a stream of nitrogen gas. The sensor was then mounted in the QCM flow cell, and ultrapure water was injected over it with a peristaltic pump with Tygon tubing (inner diameter 0.76 mm) at a flowrate of 53.3 μL/min. After a stable baseline in water was reached, a solution of polyethyleneimide (PEI) was injected over it, followed by washing with water for 30 minutes. Next, alternating solutions of PSS and PSTAC (**3a** or **3d**) were injected, each followed by 30 min washing, until a total of 14 polymer layers had been added to the surface (i.e. 6.5 bilayers of PSS/PSTAC, ending with PSS). Films were grown at 23 ± 0.002°C. A resonant fundamental excitation frequency of 5 MHz and resonant odd harmonics (3^{rd} through 13^{th}) were collected ~2× per second, along with stopping excitation to measure ringdown of the sensors, which gives the dissipation of the material.

Analysis to determine thickness and mechanical properties of the PEM films was performed using software provided by the instrument manufacturer (Dfind v1.1, Q-Sense). This software models the films as a viscoelastic material, which can be mechanically modeled as a Voigt element, which is a spring (which represents the elasticity of the film) and a dashpot (which represents the viscosity of the film) in parallel.[3] These films were modeled as viscoelastic films and not rigid films because the ratios of the dissipation shifts to frequency shifts (ΔD_n / ($-\Delta f_n$ /n)) were not << 4×10^{-7} s, a rule of thumb indicated by Reviakine.[3] The ratios for film **3a** were 2.1×10^{-7} s (3rd harmonic), 3.0×10^{-7} s (5th harmonic), and for film **3d** were 1.3×10^{-7} s (3rd harmonic), and 1.8×10^{-7} s (5th harmonic).

Fixed parameters included the density and viscosity of water (997.54 g/L and 0.93 mPa·s) and polymer in 0.1 M NaCl solutions (1001.66 g/L and 0.93 mPa·s), and the density of the film, which was assumed to be 1100 kg/m^3.

Calculated parameters included the hydrated thickness of the film, shear elastic modulus and viscosity. All harmonics except the first were used for modeling. The "smartfit" option was used, along with the following advanced options: not modeling bare periods , extrapolating fit curves with 1D thickness modeling, weighting of a moving average of the noise of the harmonics, a maximum relative parameter jump of 30%, and not selecting power law frequency dependency of the fitted parameters.





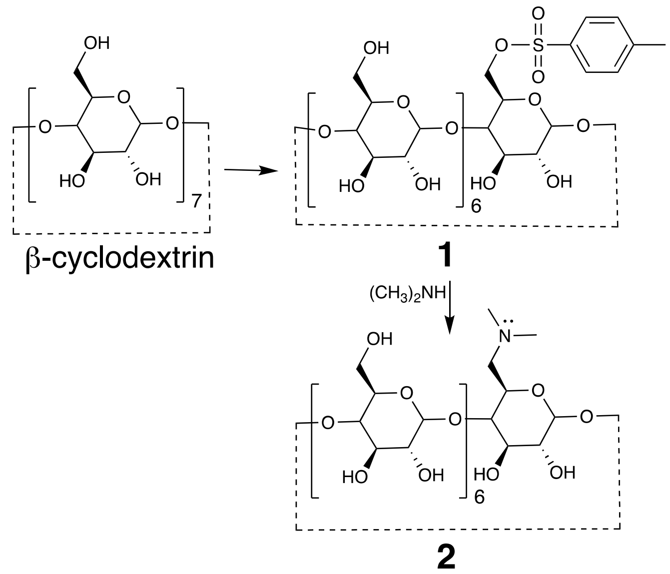
c

PEM	Shear Modulus (kPa)	Viscosity (mPa*s)	Thickness (nm)
(PSS/**3a**)$_{6.5}$	258.5 ± 0.6	5.189 ± 0.005	37.63 ± 0.01
(PSS/**3d**)$_{6.5}$	441.3 ± 1.4	8.473 ± 0.011	40.41 ± 0.01

Figure S-1. Additional plots of PEM films grown in a QCM-D flowcell. (**a**) Measured dissipation shift (3rd harmonic) over time for PEMs with either **3a** (black dotted line) or **3d** (blue solid line). Arrows indicate start of injections (gray = PEI, then followed by PSS injections, black = PSTAC injections, and blue = water washes). (**b**) Modeled hydrodynamic thickness of the PEMs with either **3a** (black, open squares) or **3d** (blue, filled triangles). Bilayer counting starts after the PEI layer: half numbers are after PSS layers, whole number are after PSTAC layers, all values are after washing. (**c**) Table of the mechanical properties after forming and washing 6.5 bilayers.

6. Synthetic Procedures

Scheme S-1



Synthesis of 1 (6-O-Monotosyl-*β*-cyclodextrin)[4]

The synthetic procedure that was used to prepare **1** was similar to that previously reported.[4] Briefly, to 60 mL of an aqueous solution containing a suspension of β-cyclodextrin (10 g, 8.82 mmol) was slowly added 11 mL of 2.5 N NaOH aqueous solution. A solution that was prepared from *p*-toluenesulfonyl chloride (2.52 g, 13.2 mmol) and 5 mL of acetonitrile was then added, dropwise to the resulting homogeneous solution. The reaction mixture was stirred in a sealed flask for 3 h at 25 °C. After removal of unreacted *p*-toluenesulfonyl chloride by filtration, ammonium chloride (1.3 g, 24 mmol) was added to adjust the pH to ca. 8. Cooling at 4 °C overnight led to a white precipitate, which was collected by filtration and washed with 2 × 5 mL cold deionized water. Subsequent lyophilization afforded a white solid (3.1 g, yield 30%) having ^{1}H NMR (500 MHz, DMSO): δ 7.75 (d, 2H), 7.44 (d, 2H), 5.81-5.63 4 (m, 14H), 4.87-4.76 (m, 7H), 4.49-4.35 (m, 8H), 4.20 (m, 1H), 3.71-3.20 (m, 39H, overlapping signal with H_2O), 2.43 (s, 3H).

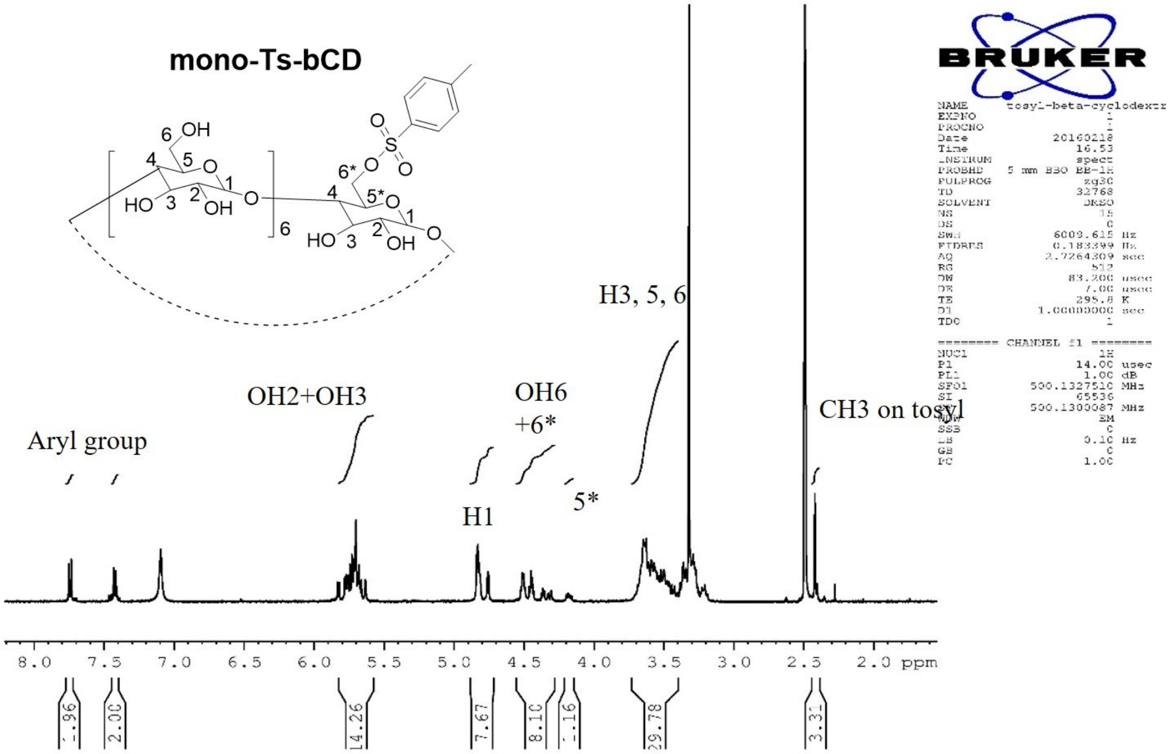


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Figure S-2. ^{1}H NMR spectrum of **1** in d_6-DMSO.

Synthesis of 2 (6-dimethylamine-*β*-cyclodextrin)

To 15 mL of a DMF solution containing **1** (2 g, 1.54 mmol) was added 15 mL (30.8 mmol, 20 eq) of a dimethylamine solution (2 M in methanol) and KI (2.56 mg, 1%). The reaction mixture was heated at 70 °C for 24 h and poured into 60 mL of ether to precipitate the crude product. The crude product was then dissolved in 10 mL of a mixture of methanol/water (1/3, v/v) and the pH adjusted to ca. 2. Further purification was performed *via* ion-exchange chromatography on Sephadex CM-25 (Sigma-Aldrich, Da exclusion ~ 30,000, NH_4+ form). The product was first bound to the column and impurities removed by flushing the column with deionized H_2O. In a second step, the desired product **2** was removed using a 0.1 M ammonium hydroxide aqueous solution. The eluent was monitored by TLC (the desired product appearing as a single spot at R_f 0.1 with eluent [methanol/ethyl acetate/H_2O; (2/2/1, v/v/v)]. Subsequent lyophilization afforded 1.3 g (60%) of **2** as a white solid having ^{1}H NMR (500 MHz, d_6-DMSO): 5.95-5.55 (m, 14H, OH2+OH3), 4.89-4.76 (m, 7H, H1), 4.39-4.35 (m, 6H, 6*OH6), 3.76-3.50 (m, 26H, H3, 5, 6), 2.20-2.19 (s, 6H, $N(CH_3)_2$). HRMS (ESI): m/z calculated 1162.4243, $[M+H]^+$; found 1162.4259.

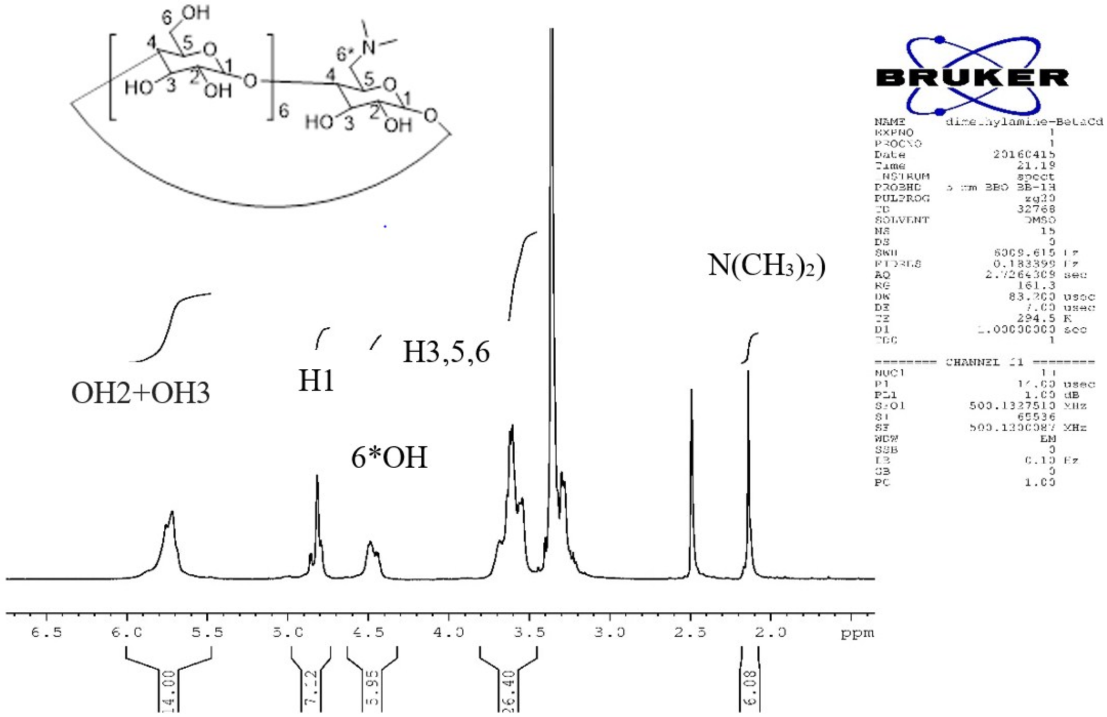

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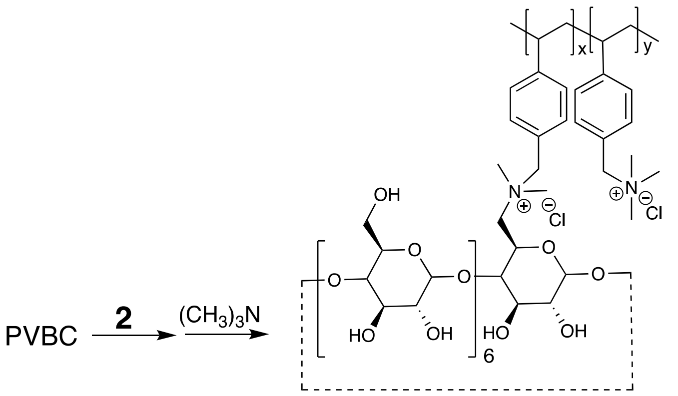
Figure S-3. ^{1}H NMR spectrum of **2** in d_6-DMSO.

Synthesis of Polyelectrolytes with Various Loadings of β-Cyclodextrin

Scheme S-2



Polycations (x,y = mol fraction)

3a, x= 0; y=1
b, x= 0.06; y= 0.94
c, x= 0.16; y=0.84
d, x= 0.32; y=0.68

Synthesis of 3a

The procedure used to prepare **3a** was the same as that previously reported.[5]

Synthesis of 3b

To 3 mL of a *N,N*-dimethylformamide solution containing poly(*p*-vinylbenzyl chloride) (PVBC, Mw 60 kDa, Polymer Source Inc., Dorval, Canada) (200 mg, 1.31 mmol repeat units) was added 2 mL of a *N,N*-dimethylformamide solution containing **2** (0.152 g, 0.131 mmol, 0.1 eq). The reaction mixture was stirred in a sealed flask under nitrogen atmosphere for 24 h at room temperature. To this mixture was then added 0.624 mL of a trimethylamine solution (4.2 M in EtOH, 2 eq). A white precipitate formed after stirring for only a few minutes. Addition of 2 mL of H_2O resulted in the return of a homogeneous solution. After 24 h, the product mixture was poured into 40 mL of diethyl ether to precipitate the polymer. The crude product was then dissolved in 10 mL of deionized water and dialyzed against deionized water for 48 h (changing the dialysate every 12 h, using a Float-A-Lyzer dialysis tube, MWCO 3.5-5KD). Subsequent lyophilization afforded 0.33 g (yield: 91%) of product as a pale yellow solid having ^{1}H NMR (500 MHz, D_2O): δ 6.30-7.51 (brm, 4H), 5.25-4.90 (br, 0.42H), 4.65-4.15 (br, 2H), 4.15-3.15

(brm, 2.52H), 3.10-2.63 (br, 8.82), 2.15-0.95 (brm, 3H). Anl. Calcd for $C_{14.05}H_{21.96}NClO_{2.04}\cdot 1.6\ H_2O$ (repeat unit): C, 56.62; H, 8.27; N, 4.57. Found: C, 56.37; H, 7.69; N, 4.11. The degree of β-cyclodextrin loading was estimated by the integration value of the signal in the range of 4.15-3.15 ppm (H 2, 3, 4, 5, 6 in βCD) and was confirmed by the signal in the range of 5.25-4.90 (H 1 in βCD). Here, the mole percentage of β-cyclodextrin for **3b** is equal to the ratio between 2.41 and 39, approximately 6%, where 2.41 is the integration value of signal in the range of 4.15-3.15 ppm corresponding to H 2, 3, 4, 5, 6 of β-cyclodextrin (as labeled in Figure 6.3) and 39 is the total number of protons corresponding to H 2, 3, 4, 5, 6 for one molecule of β-cyclodextrin.

Similar procedures were adopted for other polymers (**3c** and **3d**) except that the number of equivalents of **2** was increased, *i.e.*, 0.25 eq (0.38 g) for **3c** and 0.5 eq (0.76 g) for **3d**, respectively, with respect to 200 mg of poly(*p*-vinylbenzyl chloride). Anal. Calcd for **3c** ($C_{18.56}H_{28.56}NClO_{5.44}\cdot 1.7\ H_2O$) (repeat unit): C, 53.16; H, 7.68; N, 3.34. Found: C, 52.84; H, 7.08; N, 2.92. Anal. Calcd for **3d** ($C_{18.56}H_{28.56}NClO_{5.44}\cdot 1.7H_2O$) (repeat unit): C, 53.16; H, 7.68; N, 3.34. Found: C, 52.84; H, 7.08; N, 2.92.

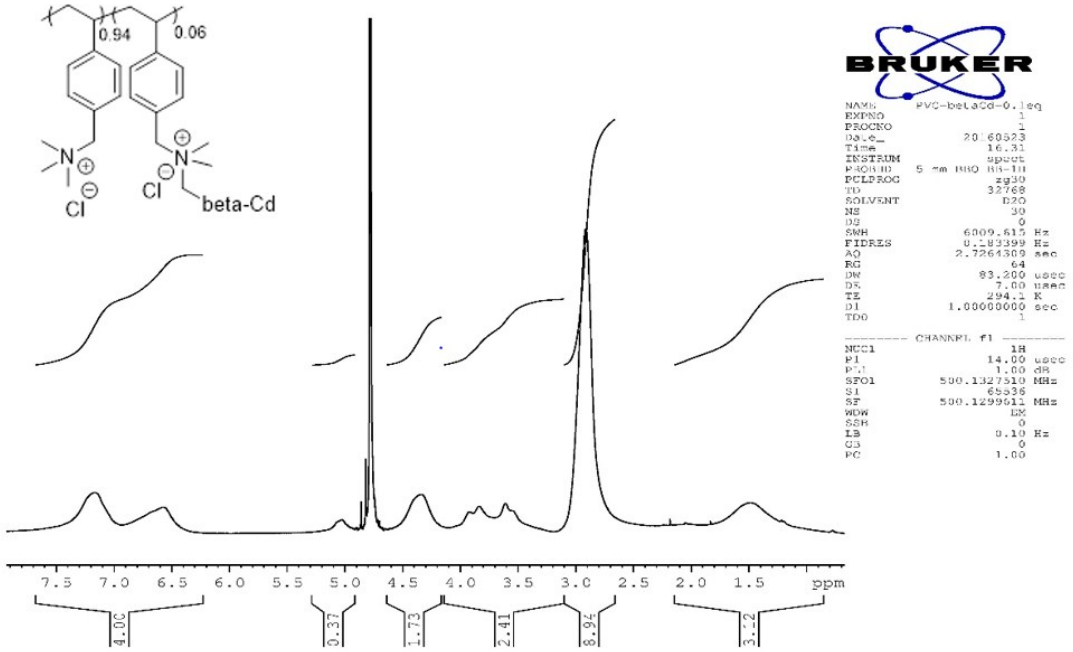


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Figure S-4. ^{1}H NMR spectrum of **3b** in D_2O.

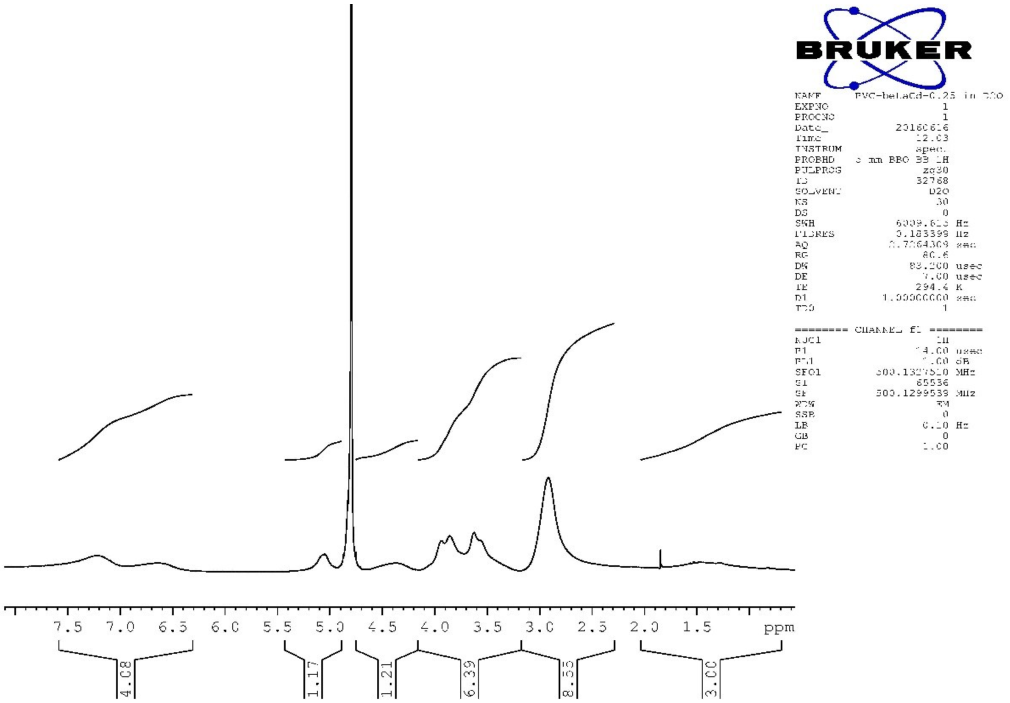

Figure S-5. ^{1}H NMR spectrum of **3c** in D_2O.

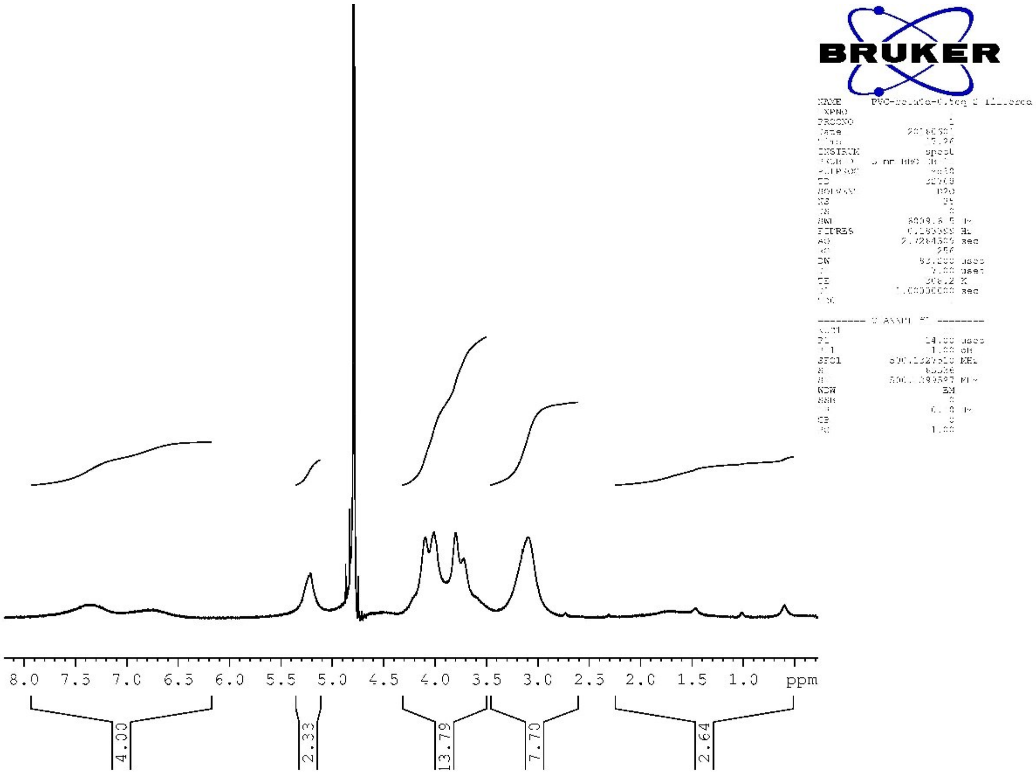

Figure S-6. ^{1}H NMR spectrum of **3d** in D_2O.

7. References

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