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Structure-Property Relationships of Amine-Rich and Membrane-Disruptive Poly(oxonorbornene)-Coated Gold Nanoparticles

Supporting Information

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Instrumentation

Gel permeation chromatography (GPC, in chloroform, calibrated with poly (methyl methacrylate) standards) was performed on a PSS SDV column (PSS, Mainz, Germany). NMR spectra were recorded on a Bruker 250 MHz spectrometer (Bruker, Madison, WI, USA) using MeOD and CDCl₃ as solvent and tetramethylsilane (TMS) as internal reference.

PONs Synthesis and Characterization

To obtain **P(D-B)**, oxanorbornene monomers **B** (oxanorbornene monomer with **Butyl** and amine side chains) and **D** (oxanorbornene monomer with **Diamine** side chains) were copolymerized (Scheme S1) following literature procedures.^[1] Amine functional groups of the oxanorbornene monomers were protected by tert-butyloxycarbonyl protecting group (BOC). Grubbs' third generation catalyst was synthesized as described by Love.^[2] Dichloromethane (DCM) was freshly distilled prior to polymerization. The amount of each reagent used, and the molecular weight of the resulting polymers as determined by GPC, can be found in Table S1. A typical polymerization was performed under nitrogen atmosphere using standard Schlenk techniques. Monomers **B** and/or **D** were dissolved in dry DCM (20 mL) and stirred for 30 min. Grubbs' third generation catalyst **G3** was dissolved in dry DCM (1 mg mL⁻¹) in a second flask and added to the monomer solution. The reaction mixture was allowed to react for 30 min. Subsequently, an excess of ethyl vinyl ether (1 mL) was added to terminate the reaction. After precipitation in ice-cold *n*-hexane (600 mL), the product was dried under reduced pressure. The isolated yields were roughly 90%. ¹H-NMR (250 MHz, CDCl₃) δ = 5.85 - 5.93 (br m, C=CH, trans), 5.55 - 5.66 (br m, C=CH, cis), 5.32 - 5.46 (br s, NH), 5.07 - 5.19 (br m, C=CH-CH, cis), 4.65 - 4.76 (br m,

C=CH-CH, trans), 4.04 - 4.26 (m, O-CH), 3.27 - 3.45 (br m, N-CH₂), 3.05 - 3.21 (br m, CH), 1.55 - 1.63 (m, CH₂), 1.23 - 1.49 (m, B-CH₂ & 3 × boc-CH₃), 0.93 (t, B-CH₃).

For removal of the Boc protecting groups, the polymers were dissolved in dry chloroform and the same amount of HCl in dioxane (4 M) was added. When the deprotected polymer started to precipitate, dry MeOH was added until it was dissolved again. The crude product was precipitated in ice-cold Et₂O (600 mL) and dried under reduced pressure. The isolated yield was roughly 90%. ¹H-NMR (250 MHz, MeOD-d₄, peaks corresponding to C=CH-CH (trans) and CH overlapped with the solvent signals) δ = 8.05 - 8.20 (br. m, NH₃⁺), 5.89 - 6.05 (br m, C=CH, trans), 5.63 - 5.84 (br m, C=CH, cis), 5.01 - 5.29 (br m, C=CH-CH, cis), 4.01 - 4.53 (m, O-CH), 3.30 - 3.70 (m, N-CH₂), 1.55 - 1.73 (m, CH₂), 1.30 - 1.50 (m, B-CH₂), 0.97 (t, B-CH₃).

Scheme S1: Copolymerization of the oxanorbornene derivatives **B** and **D** via ring-opening metathesis polymerization. The monomers were initiated with Grubbs' third generation catalyst **G3**. The living chain end was then quenched with ethyl vinyl ether to yield the copolymers **P(D-B)**.

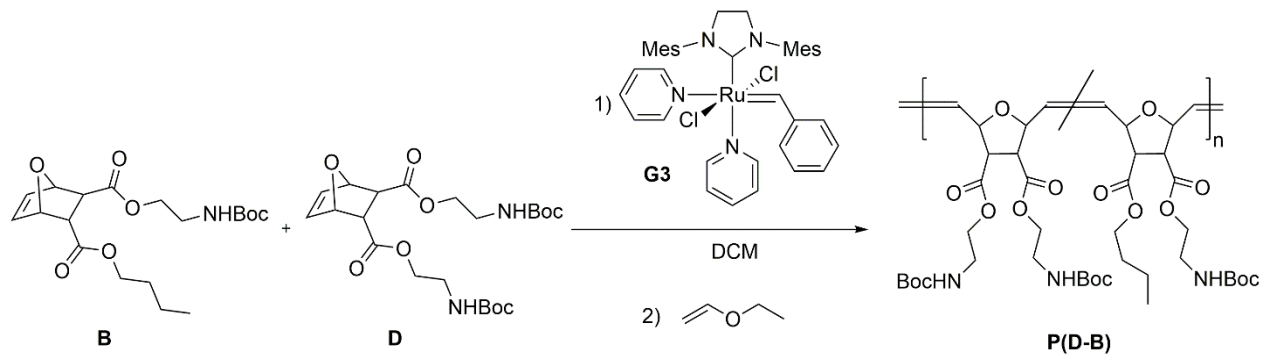


Table S1: Experimental parameters for the ring-opening metatheses polymerization of the oxanorbornene monomers **B** and **D**. The subscript refers to the molar fraction of each repeat unit. For example, **P(D₁-B₉)** refers to a poly (oxanorbornene) (PON) made from 90 mol% **B** and 10 mol% **D**.

<i>Copolymer</i>	<i>n_D:n_{Bu}</i>	<i>Amine content (%)</i>	<i>M_{n Target} (g·mol⁻¹)</i>	<i>m_B (mg)</i>	<i>n_B (mmol)</i>	<i>m_D (mg)</i>	<i>n_D (mmol)</i>	<i>Av.MW_{Monomer} (g·mol⁻¹)</i>	<i>N(Repeating Unit)</i>	<i>n_{Catalyst} (mmol)</i>	<i>m_{Catalyst} (mg)</i>	<i>M_n^a (g·mol⁻¹)</i>	<i>Đ^a</i>
P(D₁₀-B₀)	10:0	100	4702	0.00	0.00	1000	2.61	470.23	10	0.261	189.72	4700	1.14
P(D₉-B₁)	9:1	95	4615	100	0.26	1104	2.35	461.53	10	0.261	189.72	4700	1.14
P(D₅-B₅)	5:5	75	4267	500	1.30	614	1.35	426.71	10	0.261	189.72	4000	1.12
P(D₁-B₉)	1:9	55	3919	900	2.35	123	0.26	391.89	10	0.261	189.72	3900	1.13
P(D₀-B₁₀)	0:10	50	3832	1000	2.61	0.00	0.00	383.19	10	0.261	189.72	3500	1.13

^a Determined using GPC in chloroform relative to PMMA standards.

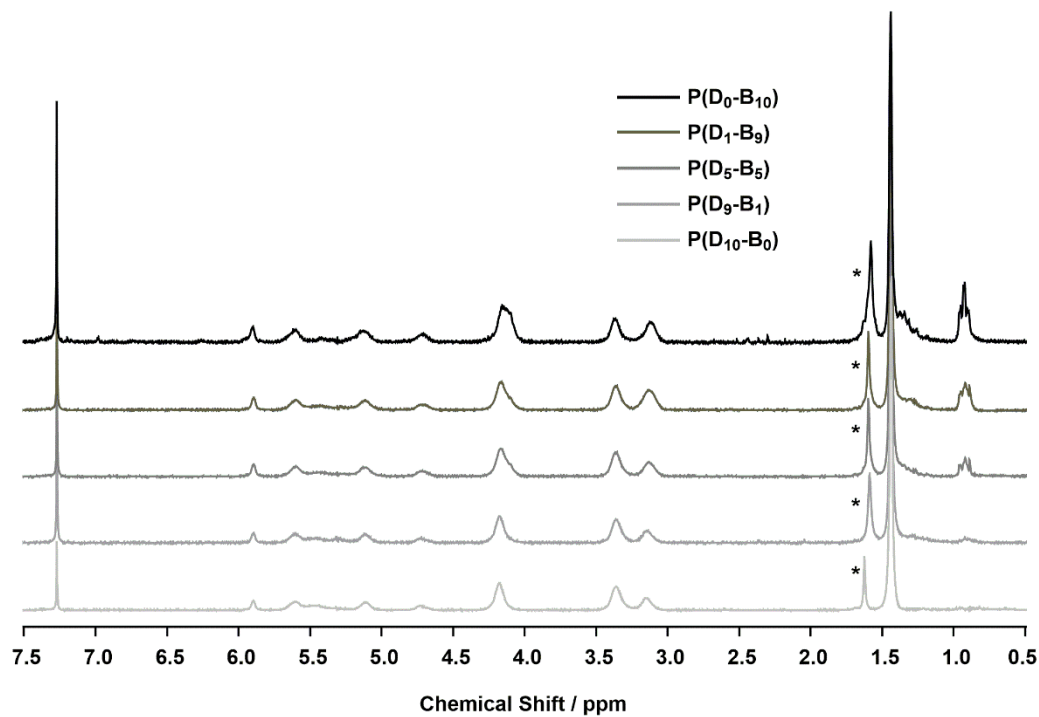


Figure S1: ^1H -NMR spectra of the BOC protected copolymers **P(D-B)**. The water peak of the solvent is marked with an asterisk (*).

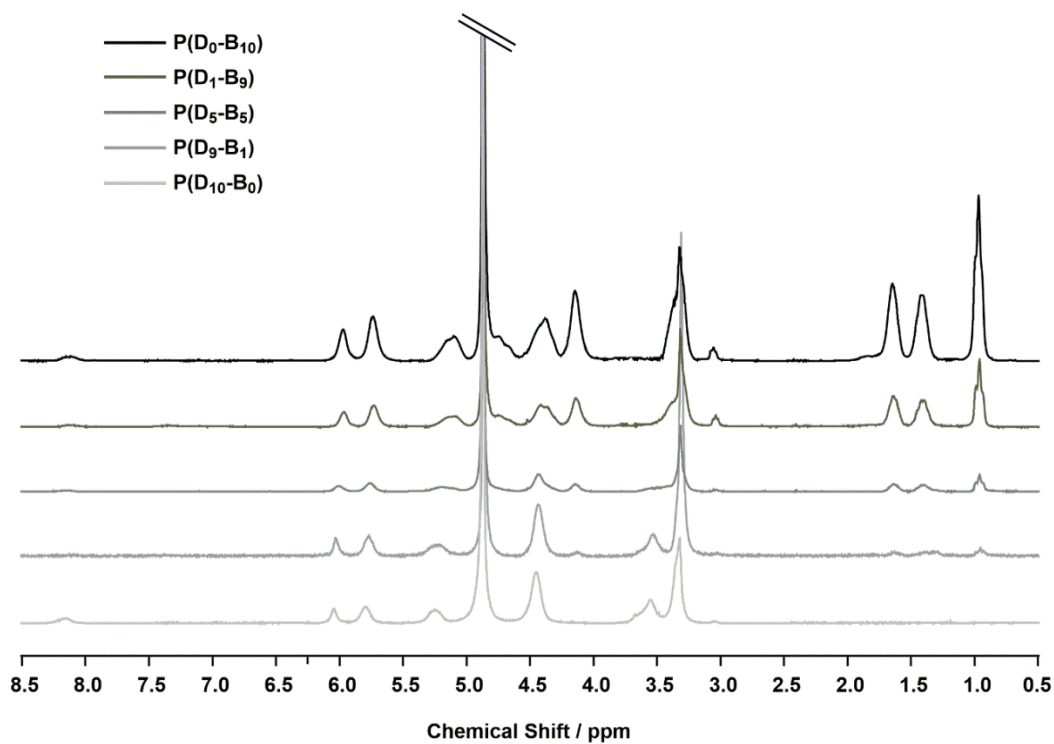


Figure S2: ^1H -NMR spectra of the deprotected copolymers **P(D-B)**.

The GPC data is given in Table S1. The elugrams are showing the refractive index (RI) signal as a function of the elution time for PONs with varying amine content (see Figure S3).

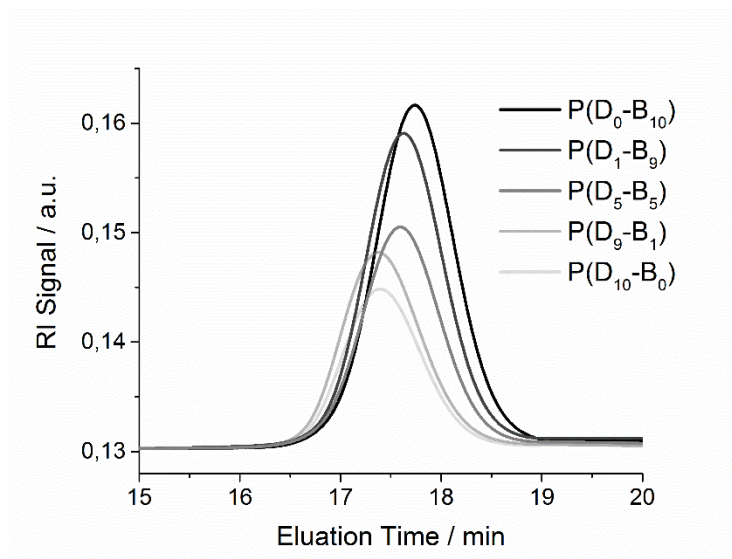


Figure S3: GPC elugrams of the copolymers **P(D-B)** used to determine the molecular weight and chain length of poly (oxonorbornenes) (PONs).

References

- [1] Lienkamp, K.; Madkour, A. E.; Musante, A.; Nelson, C. F.; Nüsslein, K.; Tew, G. N., *Journal of the American Chemical Society*, (2008) **130**, 9836.
- [2] Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H., *Angewandte Chemie International Edition*, (2002) **41**, 4035.