Electronic Supplementary Material (ESI) for Polymer Chemistry.

The formation and study of Poly(ethylene oxide)-Poly(norbornene) block-copolymers on the surface of titanium-dioxide particles – A Novel approach towards transposing si-ROMP to larger surface modification

Edgar Cao, Loïc Pichavant, Eric Prouzet and Valérie Héroguez*

Electronic Supplementary Information

Synthesis and Characterization of α-norbornenyl-ω-carboxylic acid poly(ethylene oxide) (NB-PEO-COOH

1. Materials

Ethylene Oxide (EO) (>99.5%, Aldrich), NaH (60% in mineral oil, Aldrich), 5-norbornene-2-methanol (98%; mixture of both endo and exo; Aldrich), 2-bromoethyl acetate (97%, Aldrich), Sodium Sulphate (99%, Sigma Aldrich), and Bicyclo[2,2,1] hept-2-ene (99%, also known as Norbornene, Aldrich) were ordered from Aldrich and used as received. Sodium (99.9% trace metal in mineral oil, Sigma Aldrich), heptane (99%, Sigma Aldrich), dichloromethane (>99.8%, Sigma Aldrich), 1,4-dioxane (99.8%, Sigma Aldrich), hydrochloric acid (HCl; 37%; Sigma Aldrich), diethylether (99.7%, Sigma Aldrich) were used without further processing. DMF (anhydrous 99.8%, Sigma-Aldrich) and Ethanol (96% purissimum grade pur; Xilab) was used as received. THF (J.T. Baker) was distilled on CaH_2, stored on sodium/benzophenone and cryodistilled before use. Acidic methanol was obtained by mixing 5 drops of HCl (37%; Sigma Aldrich) in 10 mL methanol (Xilab). Diphenyl methyl potassium (DPMK, 0.61 mol/L in THF) was synthesized following a well-known method[1] and stored in a graduated burette. NaOH (98%, Fisher Scientific) was used to create the 0.1 M NaOH solution (4 g in 1 L DI Water). Celite (Prolab) was used for filtration to remove any unreacted DPMK. The water used in these experiments was 18 MΩ Ultra pure DI water (Millipore system).

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[1] Raju Francis et al., “Synthesis and Surface Properties of Amphiphilic Star-Shaped andDendrimer-Like Copolymers Based on Polystyrene Core and Poly(Ethylene Oxide) Corona,” *Macromolecules*, 36, no. 22 (2003): 8253–59.

2. Step 1: Synthesis of NB-PEO-OH

The synthesis of NB-PEO-COOH proceeds in a similar fashion as which was described by Pichavant *et al.* (2011).[2] In this procedure, anionic polymerization was performed in order to synthesize the poly(ethylene oxide) chain of the macromonomer. To start, gaseous ethylene oxide (EO) is condensed into a fully sealed glass apparatus (500mL round bottom flask) that has been previously flamed-dried 3 times with a stir bar and then added with freshly cut sodium (about a total volume of 3 cm^3 cut into small pieces).

In a dewar container, ethanol is cool down to -30˚C (using liquid nitrogen) and used to cool the round bottom flask. The EO gas is condensed into the round bottom flask until the liquid EO just reaches above the stir bar.

WARNING: Ethylene Oxide (EO) is a flammable, compressed gas that can sterilize you! Always wear protective gear (face shield, gloves), ensure fumehood is in working order (shield is down) and that the EO canister is in a good distance inside the fumehood (i.e. not near the front of the fumehood).

After the EO canister is closed and disconnected from the round bottom flask (Note: leave the connection tube inside the fumehood for at least 20 minutes before removal), the mixture of EO with sodium was left to stir for 2 hours (temperature: -30˚C - -15˚C). The EO + sodium mixture was then cyrodistilled into a burette cooled with an ethanol bath at -80°C in order to recover the pure EO (roughly 27 mL was collected; 0.541 mol).

In a separate round bottom flask, 300 mL of THF was cyrodistilled and 5-norbornene-2-methanol (1 mL; 8.323×10^{-3} mol) was injected under nitrogen flow (note that all conditions are under anhydrous, inert atmosphere). This mixture was left to stir for 20 minutes before DPMK (anionic initiator; 10.9 mL or 6.658×10^{-3} mol) was added.

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[2] Pichavant L, Bourget C, Durrieu M-C, Héroguez V. Synthesis of pH-Sensitive Particles for Local Delivery of an Antibiotic via Dispersion ROMP. *Macromolecules*, 44, no. 20 (2011): 7879-87.

All the collected, purified EO was then added into this mixture after waiting another 20 minutes, and then left to react over 72 hours.

The anionic living chains were then deactivated with the addition of acidic methanol (5 mL) and left to stir for 20 minutes. Mixture was then precipitated in diethylether (dropwise) at room temperature, filtered and vacuumed for 2 hours. The sample was dissolved in DCM and filtrated over Celite (to remove DPMK). The collected eluent was then rotovaped to remove most of the DCM, then redissolved in THF to be re-preciptated in diethylether (0˚C). The collected perciptate was filtrated, collected, vacuumed for another 2 hours before redissolving in 1,4-dioxane (10 mL) and lyophilized overnight. The product (NB-PEO-OH; approx. 20 g) was then collected and stored in an argon glovebox until use.

3. Step 2: Synthesis of NB-PEO-COOH

Sodium hydride (0.85 g; determined with the final molar ratio of 10:1 of NaH to NB-PEO-OH) was weighted in a disposable vial and dispersed in heptane (10 mL). The mixture was then filtered and washed with more heptane until a white powder is obtained. The powder is quickly transferred to a round bottom flask connected to a condenser. Cyrodistilled THF (15 mL) is then added to dissolve/disperse the NaH white powder. Continuous nitrogen flow is then added into the system while a solution of NB-PEO-OH (7.04 g) is mixed with cyrodistilled THF (40 mL) and added dropwise into the stirring NaH+THF. After the bubbling has subsided, the nitrogen flow was stopped and left to stir for another 90 minutes. 2-bromoethyl acetate (1 mL) was then syringed into the round bottom flask (via septum) and the mixture was heated (60˚C, refluxed) and left to react overnight (approx. 15 hours).

The mixture was then cooled down to room temperature, and excess NaH was deactivated by adding 1 M HCl solution in a dropwise manner. THF was then removed using the rotovap and then dissolved in DCM (20 mL), dried with sodium sulfate and filtrated. The collected eluent solution of DCM + macromonomer is then rotovaped again, precipitated in diethylether (0˚C) and filtrated. The collected powder (or macromonomer) is dissolved in 1,4-dioxane and lyophilized overnight.

The collected powder/macromonomer (5.25 g) is redissolved into 60 mL of 0.1 M NaOH and mixed with another 235 mL of 0.1 M NaOH. The mixture is then left to stir for 24 hours at 55˚C under reflux. 3 M HCl (10 mL) was then added to the mixture upon cooling to room temperature, and adjusted to pH = 7. Afterwards, water was removed using a rotovap. The new fully functionalized NB-PEO-COOH is dissolved in DCM (stirred for 2 hours) and sodium sulphate was added to remove any remaining water. The mixture is then filtered and the collected eluent is concentrated to 20 mL. Cold diethylether (0˚C) is then used to precipitate the mixture, and the collected powder is dried under vacuum for 1 hour. 1,4-dioxane (~40 mL) is then added to the round bottom flask, frozen and left to lyophilize overnight. The final collected powder (NB-PEO-COOH, 4.8 g) was then stored in the glovebox until used.

4. Characterization by ^{1}H NMR

The structure of the molecules were checked using ^{1}H NMR (Bruker AVANCE, 400MHz). In each case, about 10 mg of the compound was mixed with 450 µL of $CDCL_3$ (or deuterated chloroform) to be measured. During the analysis of functionalizing the NB-PEO derived compounds (i.e. NB-PEO-COOH, NB-PEO-OH etc…), the relaxation time was set to 2 seconds with 32 scans.

^{1}H NMR was the ideal method of characterizing the growth and functionalization of the macromonomer. Note that the macromonomer is composed of 3 portions – the ROMP capable functionality provided by the norbornenyl group, the PEG chain for CO_2 selectivity, and the carboxylic acid group that can form the amide bond with the surface. The measurement after reacting 5-norbornene-2-methanol with ethylene oxide through anionic ring-opening polymerization can be seen in Figure S1. Although the reaction occurs with a variety of different steps, we can note that the subsequent groups highlighted from the figure show how each hydrogen component is linked to those found within the spectra (i.e. the faint blue rectangles found on the norbornenyl group double bonds correspond to the region found on the ^{1}H NMR spectra with the same colour).

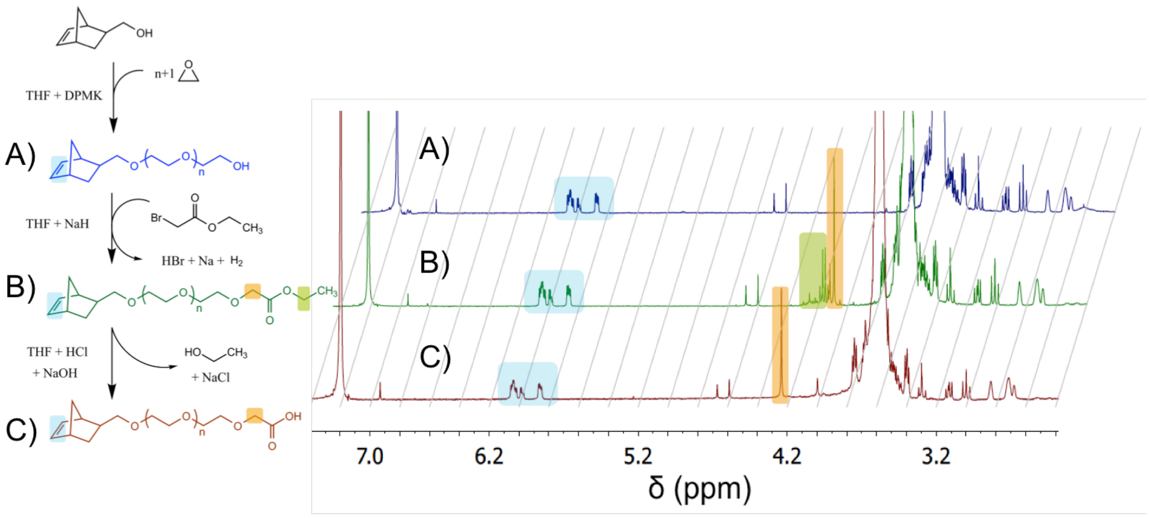

Figure S1: ^{1}H NMR spectra on the evolution of anionic polymerization of 2-norbornene-5-methanol to A) α-norbornenyl-poly(ethylene oxide) (or NB-PEO-OH) and subsequent 2-step functionalization to form B) α-norbornenyl-ω-ester poly(ethylene oxide) (or NB-PEO-COOCH$_2$CH$_3$), and finally C) α-norbornenyl-ω-carboxylic acid poly(ethylene oxide) (or NB-PEO-COOH)

NB-PEO-OH: ^{1}H NMR data in CDCl$_3$: δ (ppm) = 1.08-1.79 (m, 4H, -CH$_{2}$-$_{cycle}$); 2.72-3.45 (m, 3H, -CH-$_{cycle}$); 3.63 (m, 298H, -CH$_2$-O-); 5.91-6.09 (m, 2H, -CH=CH-$_{cycle}$)

NB-PEO-COOCH$_2$CH$_3$: ^{1}H NMR data in CDCl$_3$: δ (ppm) = 1.27 (t, J = 7Hz, 2.6H, CH$_3$-); 1.08-1.79 (m, 4H, -CH$_2$-$_{cycle}$); 2.72-3.45 (m, 3H, -CH-$_{cycle}$); 3.63 (m, 302H, -CH$_2$-O-); 4.13 (s, 1.7H, -O-CH$_2$-COOEt); 4.21 (q, J=7Hz, 2.6H, O-CH$_2$-CH$_3$); 5.91-6.09 (m, 2H, -CH=CH-$_{cycle}$)

NB-PEO-COOH: ^{1}H NMR data in CDCl$_3$: δ (ppm) = 1.08-1.79 (m, 4H, -CH$_2$-$_{cycle}$); 2.72-3.45 (m, 3H, -CH-$_{cycle}$); 3.63 (m, 323H, -CH$_2$-O-); 4.08 (s, 1.5H, -O-CH$_2$-COOH); 5.91-6.09 (m, 2H, -CH=CH-$_{cycle}$)

From the ^{1}H NMR spectra, we can conclude that the reaction has been achieved. In this case, the target molecular weight for the macromonomer was roughly 3500 g/mol. In order to determine this point, we can compare the different integration values for the peaks for each group (with the norbornenyl group set at a value of 2.0). The values can be found in Table S1 below.

Table S1: Integration values found for the synthesized macromonomer. Similar to Figure S1, the components are: A) NB-PEO-OH B) NB-PEO-COCH$_2$CH$_3$ and C) NB-PEO-COOH. The target values are the ideal values for ~75 repeating units.

Sample	Target	A	B	C
Norbornenyl Group: Double Bond - 5.9-6.1 ppm	2.0	2.0	2.0	2.0
PEG Group - ~3.6 ppm	300	298	301.7	323.3
Between Carboxylic Acid and Ester Group- 4.1 ppm	2.0*	-	-	1.48

* The values here are meant for the final product C). in order to calculate the final yield of functionalized macromonomer. Dividing the integrated value of 1.48 by the ideal/target value of 2.0 yielded the percent of functionalization of 74%.

As each group (norbornenyl group at 5.8-6.1 ppm, PEG groups around 3.57 ppm and the hydrogen atoms found between the final ethylene oxide group and the carboxylic acid group around 4.24 ppm) were good markers for following the functionalization of the macromonomer, these key peaks were integrated to determine the overall functionalization and the subsequent molecular mass. The functionalization of NB-PEO-OH to NB-PEO-COOH yielded about 74%, or 74% of the final product had a carboxylic acid group for use. In the case of molecular mass, we can easily calculate each macromonomer by following some rules:

- Taking the PEG Group integration value, divide this value by 4 (representing 4 hydrogen atoms per repeating unit) and multiplying this value by 44 g/mol
- Adding the end group molecular weight (i.e. NB-PEO-OH ends in –OH, thus would be 17 g/mol, NB-PEO-COOCH$_2$CH$_3$ ends in CH$_2$-COOCH$_2$-CH$_3$ (71.07 g/mol) and NB-PEO-COOH ends in -COOH (59.03 g/mol)
- Adding the norbornenyl group up to the first oxygen unit, or 124 g/mol

These rules ultimately resulted in calculating the macromonomers to be in the range of 3500 g/mol to 4000 g/mol (specifically, NB-PEO-OH = 3422 g/mol, NB-PEO-COOCH$_2$CH$_3$ = 3517 g/mol, and NB-PEO-COOH = 3743 g/mol). In this case, the final product NB-PEO-COOH can be roughly taken as 3750 g/mol (and used for future calculations as such), and has a degree of polymerization of 81 (note ~324/4 = 81).

TGA Calculations

5. Calculation of APTES grafting density

Based off the assumptions presented in the article, alongside the fact to take the mass difference between the pre/post heated TiO_2 samples, we can perform the following calculations:

1) Determining the total number of APTES molecules:

$$Total\ Molecules_{APTES} = \left[\frac{Mass\ Loss_{TiO_2-g-APTES} - \ Mass\ Loss_{TiO_2}}{Molar\ Mass_{degraded\ APTES\ group}}\right] x\ N_A$$

where:

- $Molecules_{APTES}$ is in the units “molecules”
- $Mass\ Loss_{TiO_2-g-APTES}$ is in the units “g”
- $Mass\ Loss_{TiO_2}$ is in the units “g”
- $Molar\ Mass_{degraded\ APTES}$ is in the units “g/mol” (or 58 g/mol)
- N_A is Avogadro’s Number, which is $6.022x10^{23}$ molecules/mol

2) Determining the volume of Evonik particles:

$$Total\ Volume_{TiO_2} = \left[\frac{Mass_{TiO_2\ Initial} - Mass\ Loss_{TiO_2}}{\rho_{TiO_2}}\right]$$

where:

- $Mass_{TiO_2\ Initial}$ and $Mass\ Loss_{TiO_2}$are in units of “g”
- $\rho_{TiO_2}$is the density of TiO_2, which is $4.23g/cm^3$
- $Total\ Volume_{TiO_2}$is in units of “cm^3”

3) Determining the volume of each Evonik particle:

$$Volume_{each\ TiO_2} = \left[\frac{4\pi r^3}{3}\right]$$

where:

- r is the radius of the TiO_2 particle, in units of “cm”
- $Volume_{each\ TiO_2}$ is the volume of each TiO_2 particle, in units of “cm^3”

4) Determining the total surface area of each Evonik particle:

$$Surface\ Area_{\ each\ TiO_2} = \ 4\pi r^2$$

where:

- r is the radius of the TiO_2 particle, in units of “cm”
- $Surface\ Area_{each\ TiO_2}$ is the surface area of each TiO_2 particle, in units of “cm^2”

5) Number of TiO_2 particles:

$$Number\ of\ TiO_2\ Particles = \frac{Total\ Volume_{TiO_2}}{Volume_{each\ TiO_2}}$$

where:

- $Number\ of\ TiO_2\ Particles$ is in units of “particles”

6) Dividing the Molecules of APTES by the Number of TiO_2 Particles:

$$\frac{Molecules_{APTES}}{TiO_2\ Particle} = \frac{Total\ Molecules_{APTES}}{Number\ of\ TiO_2\ Particles}$$

where:

- $\frac{Molecules_{APTES}}{TiO_2\ Particle}$ is in units of “molecules/particle”

7) To determine grafting density

$$Grafting\ Density_{APTES} = \frac{Total\ Molecules_{APTES}}{(Surface\ Area_{each\ TiO_2}\ x\ Number\ of\ TiO_2\ Particles) x\ 10^{14}}$$

where:

- $\frac{Molecules_{APTES}}{TiO_2\ Particle}$ is in units of “molecules/particle”
- $Grafting\ Density_{APTES}$ is in units of “molecules/nm^2”
- 10^{14} is used to convert cm^2 into nm^2

The resulting calculations result in the values found in Table S2:

Table S2: TGA calculations for TiO_2 vs TiO_2-g-APTES

Step	Values	Units
Total Molecules of APTES	$8.41x10^{18}$	molecules
Total Volume of TiO_2	$8.63x10^{-3}$	cm^3
Volume of each TiO_2	$5.24x10^{-16}$	cm^3/particle
Surface Area of each TiO_2	$3.14x10^{-10}$	cm^2
Number of TiO_2 Particles	$1.65x10^{13}$	particle
Molecules of APTES/Particle	$5.10x10^{5}$	molecules/particle
Grafting density	16.25	molecules/nm^2

6. Calculation of NB-PEO-COOH grafting density

The mass loss due to the NB-PEO-COOH can be made separately. In this case, the assumptions made in the article still hold true, but additional calculations can be made, including:

8) Determining the total number NB-PEO-COOH

$$Total\ Molecules_{NB-PEO-COOH} = \left[\frac{Mass\ Loss_{TiO_2-g-APTES-PEO-NB} - Mass\ Loss_{TiO_2-g-APTES}}{Molar\ Mass_{NB-PEO-CO*}}\right] x\ N_A$$

where:

- $Molecules_{NB-PEO-COOH}$ is in the units "molecules"
- $Mass\ Loss_{TiO_2-g-APTES-PEO-NB}$ is in the units "g"
- $Mass\ Loss_{TiO_2-g-APTES}$ is in the units "g"
- $Molar\ Mass_{NB-PEO-CO*}$ is in the units "g/mol" (or 3733 g/mol)
- N_A is Avogadro's Number, which is $6.022x10^{23}$ molecules/mol

9) Determining the number of NB-PEO-COOH per Evonik Particle

$$Molecules\ Per\ Particle_{TiO_2} = \left[\frac{Total\ Molecules_{NB-PEO-COOH}}{Number\ of\ TiO_2\ Particles}\right]$$

where:

- $Total\ Molecules_{NB-PEO-COOH}$ is in units "molecules"
- $Number\ of\ TiO_2\ Particles$ is in units of "Particles"
- $Molecules\ Per\ Particle_{TiO_2}$ is in units of "molecules/particle"

10) To determine the NB-PEO-COOH grafting density

$$Grafting\ Density_{NB-PEO-COOH} = \frac{Total\ Molecules_{NB-PEO-COOH}}{(Surface\ Area_{\ each\ TiO_2}\ x\ Number\ of\ TiO_2\ Particles) x\ 10^{14}}$$

where:

- $Surface\ Area_{\ each\ TiO_2}$ is in units "cm^2" (is $3.14x10^{-10}$ cm^2)
- $Grafting\ Density_{NB-PEO-COOH}$ is in units of "molecules/nm^2"
- 10^{14} is used to convert cm^2 into nm^2

Using this method, the resulting calculated values are found in Table S3.

Table S3: Calculated values extracted from TGA to calculate the grafting density of the number of norbornenyl grafted initiator sites possible. Bolded regions represent the newly calculated values.

Step	Values	Units
Total Volume of TiO_2	$8.63x10^{-3}$	cm^3
Volume of each TiO_2	$5.24x10^{-16}$	cm^3/particle
Surface Area of each TiO_2	$3.14x10^{-10}$	cm^2
Number of TiO_2 Particles	$1.65x10^{13}$	particle
Total Molecules of NB-PEO*	**$1.41x10^{18}$**	**molecules**
Molecules of NB-PEO*/Particle	**$8.58x10^{4}$**	**molecules/particle**
Grafting Density of NB-PEO*	**2.73**	**molecules/nm^2**

*NB-PEO represents the number of α-norbornenyl-ω-carboxylic acid poly(ethylene oxide) attached to the surface, or NB-PEO-COOH that was attached to the surface.

7. Degree of Polymerization (for polynorbornene)

To determine the DP of the polynorbornene chain formed after the NB-PEO-COOH grafting and activation with the Grubbs 1st Generation Initiator, we can perform the following calculations (in unison with the presented assumptions in the article):

1). Total Surface Area Calculation:

$$Total\ Surface\ Area = \left(\frac{3.14x10^{-10} \left(\frac{Mass\ Remaining_{TiO_2}}{\rho_{TiO_2}} \right)}{5.24x10^{-16}\ Total\ Volume_{TiO_2}} \right) x10^{14}$$

Where the total surface area is in units of nm^2

- Note that the $3.14x10^{-10}$is the surface area of each particle
- Note that the $5.24x10^{-16}$is the total volume of each TiO_2

2). Total Moles of Initiators Calculation:

$$Total\ Moles\ of\ Initiators = \frac{Total\ Surface\ Area\ x\ Initiator\ Density}{6.022x10^{23}\ (which\ is\ N_A)}$$

- Total Surface Area (in nm^2)
- Initiator Density (of 2.73 initiators/nm^2)

3). Moles of Monomers:

$$Moles\ of\ Monomers = \frac{Mass\ loss\ of\ Polymer}{Molecular\ Weight\ (Norbornene)}$$

- Molecular Weight of Norbornene is 94.15 g/mol

4). Degree of Polymerization:

$$Degree\ of\ Polymerization = \frac{Moles\ of\ Monomer}{Total\ Moles\ of\ Initiators}$$

This calculation would lead us to obtain the resulting values in Table S4.

Table S4: Calculated degree of polymerization for the resulting film of polynorbornene initiated by si-ROMP from Evonik particles.

Step	Values	Units
Original Mass of TiO_2-g-APTES-PEO-NB Film	3.58	mg
Mass Loss of Polynorbornene (pNB)	0.00353346	g
Mass Remaining of TiO_2	0.00004654	g
Total Surface Area	$6.60x10^{14}$	nm^2
Total Moles of Initiators	$2.99x10^{-9}$	mole
Moles of Monomer (NB)	$3.75301x10^{-5}$	mole
Degree of Polymerization	12534.77	

Thus, we have determined that the sample had a DP of roughly 12500 for polynorbornene from these functionalized Evonik particles.

8. Calculation of estimated polymer layer thickness

From the calculated DP of each unit (as mentioned, 12500 for the PNB section, while the PEO had a DP of 81we can take the knowledge of bond lengths to calculate a rough estimate of the maximum length these copolymers make on the surface. It has been reported in literature that C-O bonds are about 1.42 Å, C-C bonds are 153 Å and C=C bonds are 134 Å.[3] Thus, assuming that each single bond is roughly at an angle of 120˚, while double bonds are assumed to be "linear" in this respect, we obtain a value of approximately 8.3 microns in length, as shown in Figure S2.

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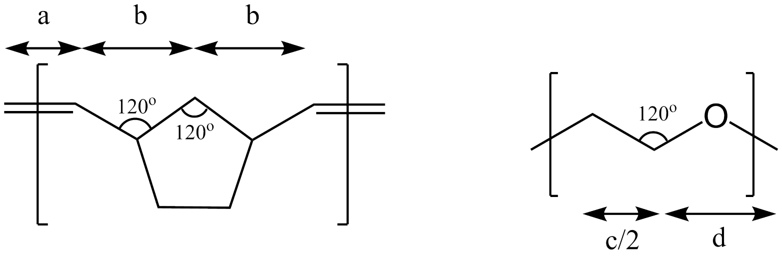
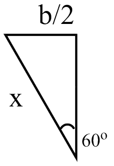
[3] David R Lide, *CRC Handbook of Chemistry and Physics, 85th Edition*, (CRC Press, 2004).



*NOTE: b, c/2 and d is one edge of an equilateral triange

We can calculate equilateral triangles by dividing in half:



Thus using trigonometry:

$b/2 = x\sin(60^{o})$

$b = 2x\sin(60^{o})$

Thus:

$a = 0.134$ nm

$b = 2(0.153)\sin(60^{o}) = 0.265$ nm

$c/2 = 0.153\sin(60^{o}) = 0.132$ nm

$d = 2(0.142)\sin(60^{o}) = 0.246$ nm

each PNB unit = $a + b + b = 0.664$ nm
each PEO unit = $c/2 + d = 0.378$ nm

Overall Lenth of Polymeric Chain:

DP (PNB) * 0.664 nm + DP (PEO) * 0.378 nm = 12500*0.664 nm + 81*0.378 nm = **8.3 microns**

Figure S2: Calculation of length of polymeric chain