

# Hydrophobic and antifouling modification of graphene oxide with functionalized polynorbornene by surface-initiated ring-opening metathesis polymerization

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## Synthesis of fluorinated substituted norbornenes (NBF<sub>n</sub>)

5-(perfluoro-*n*-alkyl) norbornenes (NBF<sub>n</sub>, *n*=4, 6, 8, 10) with long fluorinated chains were synthesized by the literature method utilizing a Diels-Alder reaction<sup>[1-2]</sup>. Briefly, the corresponding 1H,1H,2H-perfluoro-1-alkene reacted with freshly distilled cyclopentadiene (molar ratios=1: 1) in a Parr Instruments high-pressure reaction vessel. The reaction was maintained at 170°C in an autoclave for 72 h. The reaction was completed in the presence of hydroquinone (0.03 mole fraction) as a quenching agent. Then, the crude product was filtrated and purified by distillation. The yield of compound was about 30-50%, and the ratio between *endo*-isomer and *exo*-isomer was about 4:1 determined by GC characterization analysis.

## Preparation of macromonomer Nb-PEG

Four monomers with different chain length of polyethylene glycol pendent (Nb-PEG550, Nb-PEG1000, Nb-PEG1200, Nb-PEG2000) were synthesized by the pegylation of 5-norbornyl acid chloride. A 10mL flask was charged with 5-norbornene-2-carboxylic-acid (5mmol) and dichlorosulfoxide (3 mL, 40 mmol), and the reaction mixture was refluxed under nitrogen atmosphere with stirring for 12h. After the excess dichlorosulfoxide was evaporated under reduced pressure, bright orange-yellow chloride liquid was obtained. Polyethylene glycol monoethylether (0.5 mmol) with molecular weight of 2000 was added into a 25 mL single-necked round-bottom flask and 10 mL of tetrahydrofuran was added to dissolve. Then an excess of sodium was added and reaction mixture was refluxed under nitrogen atmosphere for 12 h. The solution of sodium polyethylene glycol was added dropwise to the previously obtained chloride liquid using a syringe, and was stirred under N<sub>2</sub> at reflux for 12 hours. The reaction mixture was cooled down to room temperature and precipitated with an excess cold ether. The product was dissolved in THF and precipitated with cold ether two or three times, then dried over under vacuum at room temperature. A pale yellow, ester-flavored solid powder was obtained in the yield of 92%, and the structure was characterized by NMR spectroscopy.

## Typical procedures for ring opening metathesis polymerization of fluorinated substituted norbornenes (pNBF<sub>n</sub>)

The glassware was flame-dried. To a solution of NBF<sub>n</sub> monomers (0.12 mmol) in anhydrous THF (1.0 mL) was added Grubbs catalyst 2<sup>nd</sup> generation in THF (1.0 mL) via syringe at room temperature under nitrogen atmosphere. The reaction mixture was stirred for 6 hours at room temperature, quenched with ethyl vinyl ether (1.4 × 10<sup>-2</sup> mL, 0.14 mmol), and stirred for overnight. The reaction mixture was slowly added to 100 mL of vigorously stirred cold hexane. The polymer thus obtained was separated by filtration, dried under reduced pressure.

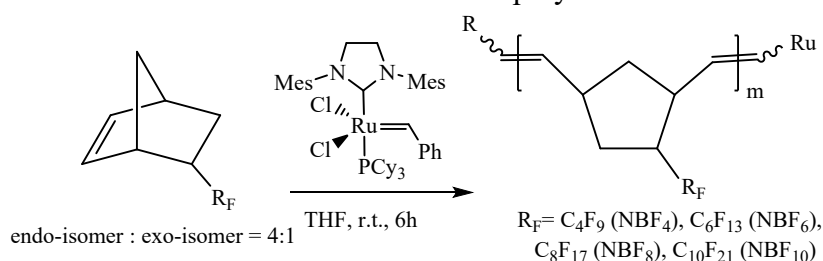
**pNBF<sub>4</sub>**: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.3-2.9 (7H, m), 5.2 (2H, m). <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ -81.6 (3F, s), -111.5 (2F, m), -122.4 to -122.2 (2F, m), -125.6 to -126.1 (2F, m).

**pNBF<sub>6</sub>**: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.2-2.8 (7H, m), 5.2 (2H, m). <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ -81.2 (3F, s), -111.5 (2F, m), -122.5 to -122.3 (2F, m), -125.1 to -124.3 (2F, m).

**pNBF<sub>8</sub>**: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.2-3.0 (7H, m), 5.2 (2H, m). <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ -81.8 (3F, s), -111.1 (2F, m), -122.6 to -122.3 (2F, m), -125.6 to -126.6 (2F, m).

**pNBF<sub>10</sub>**: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.2-2.8 (7H, m), 5.2 (2H, m). <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ -81.2 (3F, s), -111.8 (2F, m), -122.6 to -122.6 (2F, m), -125.8 to -126.3 (2F, m).

Table 1. ROMP of fluorinated norbornenes with Grubbs' 2nd catalyst and the characterization of the polymers



Monomer	[M]/[I] <sup>a)</sup>	Yield <sup>b)</sup> (%)	M <sub>caled</sub> <sup>c)</sup> kDa	M <sub>n</sub> <sup>d)</sup> (GPC) kDa	M <sub>w</sub> /M <sub>n</sub> <sup>d)</sup>
NBF <sub>4</sub>	50	79	0.76	4.77	1.26
NBF <sub>4</sub>	100	81	1.80	6.94	1.18
NBF <sub>4</sub>	150	76	2.43	6.28	1.25
NBF <sub>4</sub>	200	73	3.42	5.73	1.34
NBF <sub>6</sub>	100	85	2.96	7.93	1.12
NBF <sub>8</sub>	100	92	4.09	7.41	1.16
NBF <sub>12</sub>	100	89	4.65	6.89	1.21

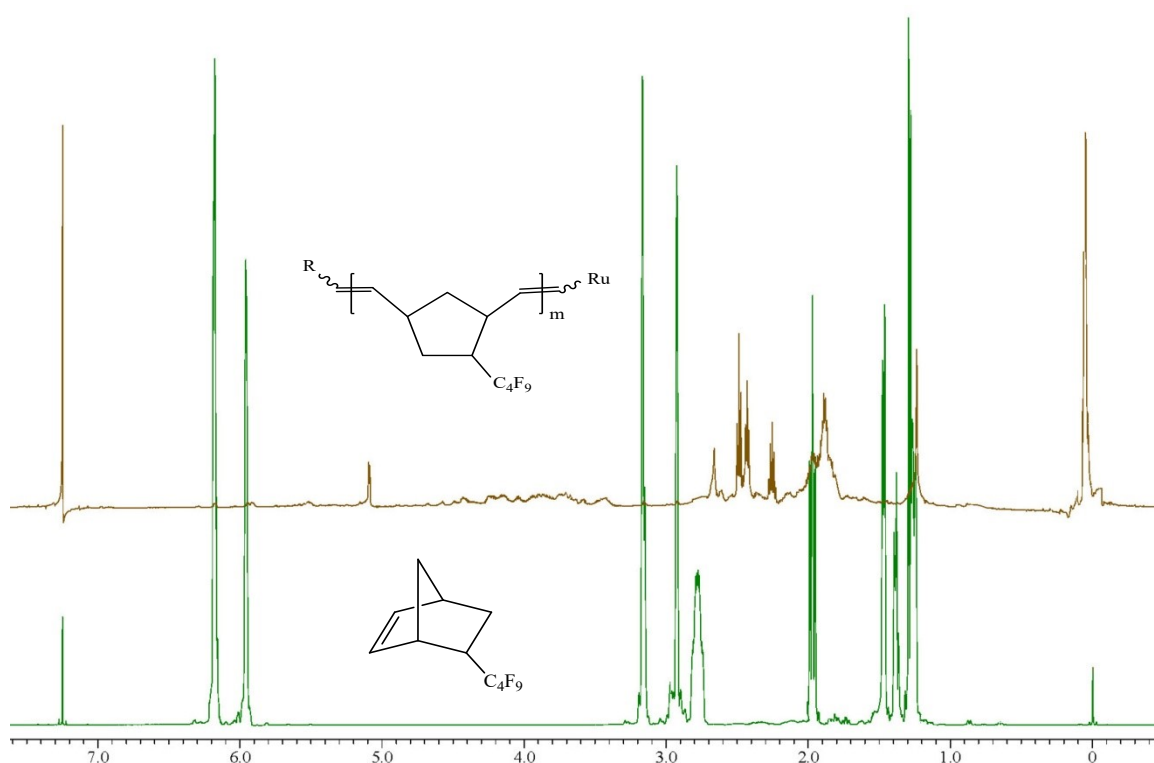


Figure 1.  $^1\text{H}$  NMR spectra for  $\text{NBF}_4$  monomer and  $\text{pNBF}_4$  polymer

### Typical procedures for ring opening metathesis polymerization of $\text{pNb-PEG}$ monomers

To a solution of Nb-PEG monomers (0.12 mmol) in anhydrous THF (1.0 mL) was added Grubbs catalyst 2<sup>nd</sup> generation in THF (1.0 mL) via syringe at room temperature under nitrogen atmosphere. The reaction mixture was stirred for 6 hours at room temperature, quenched with ethyl vinyl ether ( $1.4 \times 10^{-2}$  mL, 0.14 mmol), and stirred for overnight. The reaction mixture was slowly added to 100 mL of vigorously stirred cold hexane. The polymer thus obtained was separated by filtration, dried under reduced pressure.

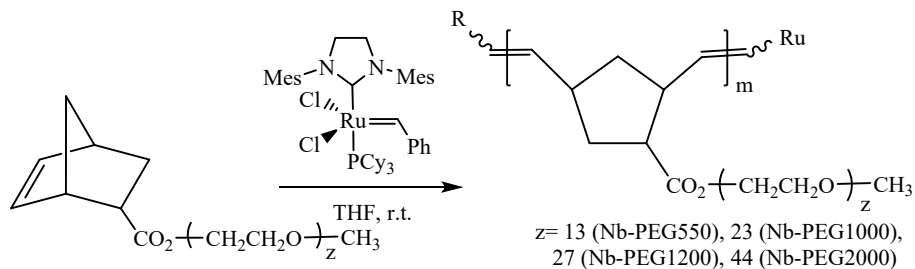
**pNb-PEG550:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.21 (1H, s), 1.80 (3H, m), 1.90 (2H, m), 2.45 (1H, s), 2.60 (1H, s), 3.54-3.60 (protons from PEG group), 3.67 (2H, m), 4.10 (2H, m), 5.47 (2H, m).

**pNb-PEG1000:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.22 (1H, s), 1.81 (3H, m), 1.92 (2H, m), 2.47 (1H, s), 2.64 (1H, s), 3.56-3.62 (protons from PEG group), 3.68 (2H, m), 4.12 (2H, m), 5.48 (2H, m).

**pNb-PEG1200:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.22 (1H, s), 1.82 (3H, m), 1.93 (2H, m), 2.48 (1H, s), 2.66 (1H, s), 3.57-3.63 (protons from PEG group), 3.68 (2H, m), 4.13 (2H, m), 5.49 (2H, m).

**pNb-PEG2000:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.23 (1H, s), 1.83 (3H, m), 1.94 (2H, m), 2.51 (1H, s), 2.68 (1H, s), 3.58-3.64 (protons from PEG group), 3.69 (2H, m), 4.14 (2H, m), 5.50 (2H, m).

Table 2. ROMP of macromonomer Nb-PEG norbornenes with Grubbs' 2nd catalyst and the characterization of the polymers



Monomer	[M]/[I] <sup>a)</sup>	Reaction time (h)	Yield <sup>b)</sup> (%)	M <sub>caled</sub> <sup>c)</sup> kDa	M <sub>n</sub> <sup>d)</sup> (GPC) kDa	M <sub>w</sub> /M <sub>n</sub> <sup>d)</sup>
Nb-PEG550	50	6.0	79	2.33	5.10	1.37
Nb-PEG550	100	6.0	82	4.86	7.32	1.11
Nb-PEG550	150	6.0	75	6.58	7.55	1.28
Nb-PEG550	200	6.0	63	7.16	7.89	1.29
Nb-PEG1000	100	6.5	74	7.20	6.67	1.24
Nb-PEG1200	100	6.5	63	7.02	6.54	1.19
Nb-PEG2000	100	7.5	56	9.780	5.77	1.38

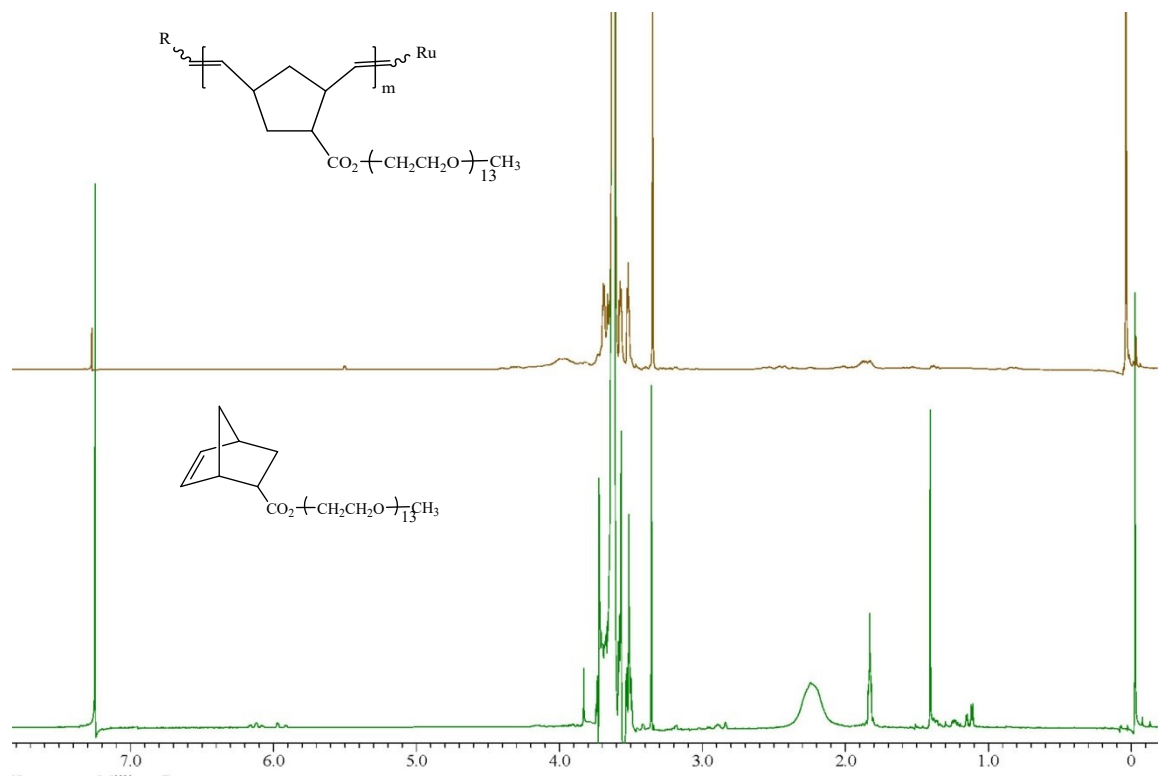


Figure 2. <sup>1</sup>H NMR spectra for Nb-PEG550 monomer and pNb-PEG550 polymer

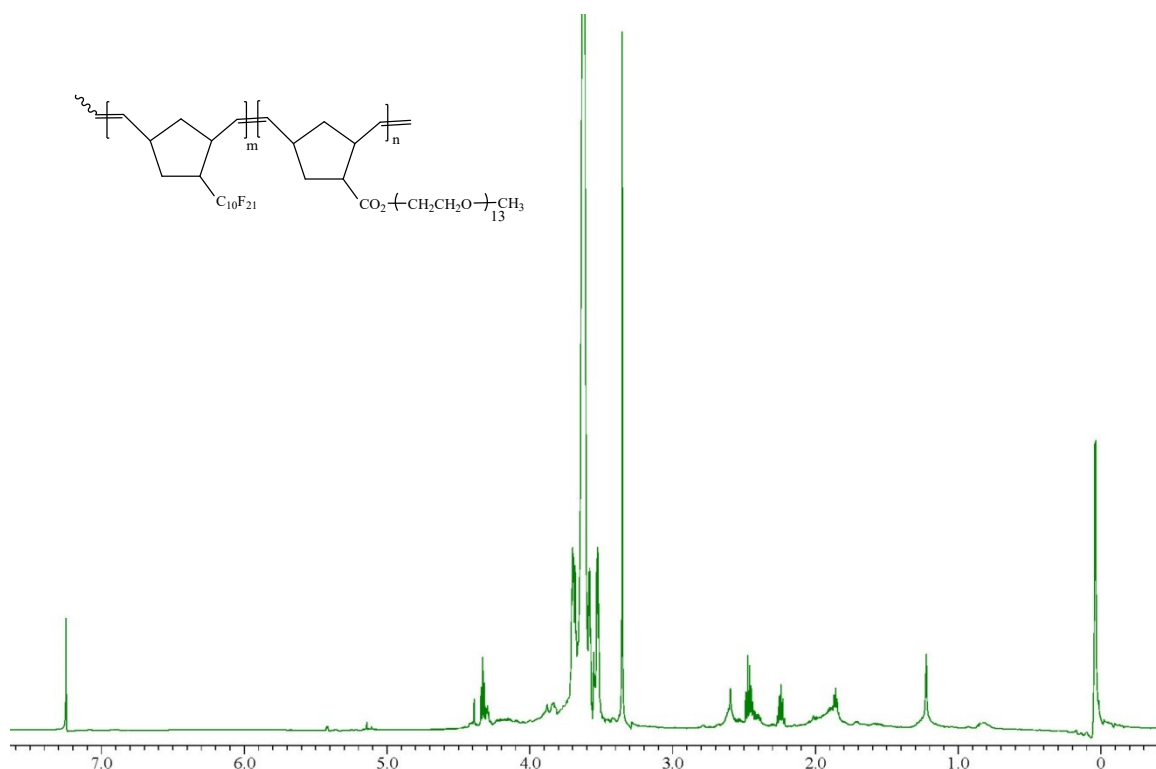


Figure 3.  $^1\text{H}$  NMR spectra for  $\text{pNBF}_{10}\text{-pNb-PEG550}$  copolymer

### Preparation of functionalized GO- $\text{pNBF}_n$ by SI-ROMP

SI-ROMP was employed for grafting functionalized polynorbornenes on GO surface. GO-NBE (25 mg) was dispersed in anhydrous THF (5 mL) by sonication under the protection of  $\text{N}_2$ . A solution of Grubbs 2<sup>nd</sup> catalyst (4 mg,  $4.8 \times 10^{-3}$  mmol) in anhydrous THF (2 mL) was then added to the reaction mixture and stirred at room temperature for 25 min. Subsequently, the GO-[Ru] was separated by repeated centrifugation of the reaction suspension with anhydrous THF. The obtained GO-[Ru] was used immediately. GO- $\text{pNBF}_n$  was synthesized by ROMP using  $\text{NBF}_n$  as monomers. The above-prepared GO-[Ru] was dispersed in anhydrous THF (5 mL) by treating with an ultrasonic bath for 15 min and bubbled with nitrogen for 3 min. Then the  $\text{NBF}_n$  monomer solution (dissolved in anhydrous THF) was injected into GO-[Ru]/THF. The polymerization was carried out at room temperature.

Table 3. Grafting ration of GO-pNBF<sub>n</sub> with a screening of monomers concentration, polymerization time

sample no.	monomers	concentration [g·mL <sup>-1</sup> ]	polymerization time (min)	grafting ratio <sup>a)</sup> (%)
1	NBF <sub>4</sub>	0.01	45	7.42
2	NBF <sub>4</sub>	0.025	45	12.51
3	NBF <sub>4</sub>	0.05	45	20.68
4	NBF <sub>4</sub>	0.10	45	32.44
5	NBF <sub>4</sub>	0.20	45	32.10
6	NBF <sub>4</sub>	0.1	10	12.43
7	NBF <sub>4</sub>	0.1	60	22.31
8	NBF <sub>4</sub>	0.1	90	29.85
10	NBF <sub>6</sub>	0.1	45	31.59
11	NBF <sub>8</sub>	0.1	45	30.32
12	NBF <sub>10</sub>	0.1	45	33.36

a) Grafting ratio =  $[m_{(\text{GO-pNBE})} - m_{(\text{GO-NBE})}] / m_{(\text{GO-NBE})} \times 100\%$ .

Reaction temperature: 25°C.

## Reference

- [1] E. Perez, J. P. Laval, M. Bon, et al. Synthesis of bicyclo [2·2·1] hept-2-enes with mono and disubstituted long perfluorinated chains C<sub>n</sub>F<sub>2n+1</sub> (n = 4,6,8,10) investigation of association in solution by <sup>19</sup>F NMR study of polymerization via a metathetic reaction [J]. Journal of Fluorine Chemistry, 1988, 39, 173-196.
- [2] Ahmad E. Madkour, Amelie H. R. Koch, Karen Lienkamp, et al. End-functionalized ROMP polymers for biomedical applications [J]. Macromolecules, 2010, 43, 4557-4561.