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Synthesis of Well-Defined ω-Oxanorbornenyl Poly(ethylene oxide) Macromonomers via Click Chemistry and Their Ring-Opening Metathesis Polymerization

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ABSTRACT: ω-Oxanorbornenyl poly(ethylene oxide) monomethyl ether macromonomers were synthesized with molecular weights ranging from 500 g/mol to 5000 g/mol through the Huisgen 1,3-dipolar cycloaddition between acetylene-functionalized oxanorbornene and ω−azido poly(ethylene oxide) monomethyl ether. Thermal analysis showed that the ω-*exo*-norbornenyl end-group of the macromonomers is converted into a maleimide group through a retro-Diels−Alder process at 130 °C. Ring-opening metathesis polymerization (ROMP) of these macromonomers was investigated using Grubbs' catalyst in dichloromethane at room temperature. Poly(oxanorbornene)-*g*-poly(ethylene oxide)s were obtained with polydispersities between 1.04 and 1.17 and molecular weights between 9900 and 57 800 g/mol leading to comb or brush copolymers according to the lengths of backbone and graft chains.

Introduction

Macromonomers are unique precursors for the preparation of well-defined graft copolymers using the so-called "grafting through" strategy which allows the control of grafts, backbone length, and grafting density.[1−3] The combination of ring-opening metathesis polymerization (ROMP) and various ionic and radical processes has been used for the preparation of graft copolymers starting from inimers (initiator-monomers) bearing "ROMP-able" entities such as norbornene,[4−26] oxanorbornene,[27−29] cyclobutene,[30−34] and cyclooctadiene moieties.[35]

Poly(ethylene oxide) (PEO), also referred as poly(ethylene glycol) for structures bearing hydroxyl end-groups, is one of the most important and most widely used polymer in pharmaceutical and biomedical applications. Despite considerable work devoted to PEO in the literature, very little has been reported on PEO macromonomers which undergo ROMP.[20−24,35−37] The synthesis of such "ROMP-able" PEO macromonomers was pioneered by Héroguez et al., who polymerized ethylene oxide anionically from a norbornene functionalized initiator.[36,37]

Huisgen 1,3-dipolar cycloaddition reaction between azides and terminal alkynes, one of the different "click" reactions described by Sharpless and co-workers,[38] has attracted widespread attention in polymer science.[25,26,39−50] "Click" chemistry provides an ideal platform for the synthesis of various well-defined macromonomers starting from commercially available polymers such as PEO. However, while 1,3-dipolar "click" reactions have been widely used for the functionalization of ROMP polymers, only a few examples of such a combination have been reported so far in the literature for the preparation of graft copolymers.[25,26]

Herein, we report the synthesis of new ω-oxanorbornenyl-PEO macromonomers using Huisgen 1,3-dipolar cycloaddition (click chemistry) and their ROMP using third generation Grubbs' catalyst ([1,3-bis(2,4,6-trimethylphenyl)-2-imidazolinylidene] dichloro(phenylmethylene)bis(3-bromopyridine) ruthenium).[51] The oxanorbornene-based group was chosen as the "ROMP-able" entity for two reasons. First, pure *exo*-oxanorbornene diastereoisomers are easily prepared starting from *exo*-7-oxabicyclo-[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride, available in high yield through Diels−Alder cycloaddition.[52] Indeed, it is well-known that *exo*-diastereoisomers are much more reactive in ROMP than their *endo*- counterparts.[53−59] Second, as pointed out by Czelusniak et al.,[28] it is expected that the oxygen in the oxanorbornene group makes the backbone more hydrophilic[60] and hence increases the probability of biocompatibility of the resulting graft copolymers. The simple and flexible method reported in this work, precluding the need for anionic polymerization of ethylene oxide, yields polymers of unique structures, which are potential candidates for biomedical applications.

Experimental Section

Materials. Dichloromethane (DCM, 99%+) and triethylamine (99%) were distilled over CaH_2 and were stored at −4 °C after purification. Prior to use, PEO monomethyl ether (PEO−OH) 500 ($\overline{M}_{n,NMR}$ = 530 g/mol), 2000 ($\overline{M}_{n,NMR}$ = 2010 g/mol) and 5000 ($\overline{M}_{n,NMR}$ = 4590 g/mol) were heated at 120 °C for 3 h under nitrogen atmosphere to remove excess water. Grubbs' catalyst [1,3-bis(2,4,6-trimethylphenyl)-2-imidazolinylidene] dichloro(phenylmethylene)bis(3-bromopyridine) ruthenium(II) $C_{38}H_{40}Br_2Cl_2N_4Ru$ (G3)[51] and *exo*-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride[22,52] (**1**) were prepared according to literature procedures. All other chemicals were purchased from commercial sources and used without further purification. Azido-terminated PEO monomethyl ethers (PEO−N_3) were synthesized according to literature procedures.[61,62]

General Characterization. NMR spectra were recorded on a Bruker Avance 400 spectrometer for ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz). Chemical shifts are reported in ppm relative to the deuterated solvent resonances. Molecular weights and molecular weight distributions were measured using size exclusion chromatography (SEC) on a system equipped with a

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SpectraSYSTEM AS 1000 autosampler, with a Guard column (Polymer Laboratories, PL gel 5 μm Guard column, 50 × 7.5 mm) followed by two columns (Polymer Laboratories, 2 PL gel 5 μm MIXED-D columns, 2 × 300 × 7.5) and with a SpectraSYSTEM RI-150 detector. The eluent used was tetrahydrofuran (THF) at a flow rate of 1 mL·min^{-1} at 35 °C. Polystyrene standards (580 to 4.83 × 10^5 g mol^{-1}) were used to calibrate the SEC. High resolution mass spectra were recorded on Waters-Micromass GCT Premier spectrometers. MALDI−TOF MS analyses were realized on a Bruker Biflex III using 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as the matrix. Thermogravimetric analyses (TGA) were performed on a TA Instruments Q500 apparatus measuring the total mass loss on approximately 10 mg samples from 30 °C up to 600 °C at a heating rate of 10 °C. min^{-1} in a nitrogen flow of 90 mL·min^{-1}.

***exo*-*N*-Prop-2-ynyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (2).** Anhydride **1** (2.00 g, 12.0 mmol) was suspended in MeOH (50 mL) and the mixture cooled to 0 °C. A solution of *N*-propargylamine (1.07 g; 18.0 mmol) in 20 mL of MeOH was added dropwise (10 min), and the resulting solution was stirred for 5 min at 0 °C and then 30 min at ambient temperature and finally refluxed for 72 h. After cooling the mixture to ambient temperature, the solvent was removed under reduced pressure, and the yellow residue was dissolved in 150 mL of DCM and washed with 3 × 100 mL of water. The organic layer was dried over $MgSO_4$ and filtered. Removal of the solvent under reduced pressure furnished **2** as a yellow solid. Yield: 1.97 g (9.72 mmol, 81%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.54 (s, 2H, =C*H*), 5.30 (s, 2H,−C*H*−O), 4.24 (d, 2H, CH_2−N), 2.90 (s, 2H, C*H*−CO), 2.20 (t, 1H, ≡C*H*). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 172.81 (*C*=O), 134.58 (=*C*H), 78.92 (*C*H−O), 74.48 (*C*≡CH), 69.52 (≡*C*H), 45.58 (*C*H−CO), 25.84 (N−*C*H_2). HRMS (CI−H$^+$): calcd for $C_{11}H_9NO_3$ + H$^+$, 204.2060; found, 204.0661.

General Procedure for Synthesis of Macromonomers via "Click" Coupling Reactions between Azido-Terminated PEO Monomethyl Ethers and 2. In a typical experiment, the azido-terminated PEO monomethyl ether (0.4 mmol) and *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA; 0.1 g, 0.6 mmol) were charged to a dry Schlenk tube along with degassed DMF (5 mL). The tube was sealed with a rubber septum and subjected to six freeze−pump−thaw cycles. This solution was then cannulated under nitrogen into another Schlenk tube, previously evacuated and filled with nitrogen, containing Cu^{I}Br (0.023 g, 0.16 mmol), **2** (0.1 g, 0.4 mmol), and a stir bar. The resulting solution was subsequently stirred at room temperature for 4 h. The reaction mixture was diluted with DCM and then washed with 3 × 100 mL of an aqueous ethylenediaminetetraacetate solution (0.03 mol/L) to remove the catalyst. The organic layer was dried over $MgSO_4$ and filtered. The resulting macromonomers were isolated by precipitation into diethyl ether for the *ω-exo*-oxanorbornenyl PEO monomethyl ethers **M 2000** and **M 5000** or by removal of the solvent under high vacuum for the *ω-exo*-oxanorbornenyl PEO monomethyl ether **M 500**.

***ω-exo*-Oxanorbornenyl PEO Monomethyl Ether M 500.** Yellow-brown oil. Yield: 80%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.68 (s, 1H, triazole), 6.50 (s, 2H, =C*H*), 5.29 (s, 2H, C*H*-O), 4.78 (s, 2H, N−CH_2), 4.49 (t, *J* = 5.1 Hz, 2H, $N_{triazole}$−CH_2−CH_2−O), 3.85 (t, *J* = 5.1 Hz, 2H, $N_{triazole}$−CH_2−CH_2−O), 3.60−3.70 (m, 40H, CH_2−CH_2−O), 3.38 (s, 3H, O−CH_3), 2.96 (s, 2H, C*H*-CO). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 175.53 (*C*O), 141.93 (*C*=C−$N_{triazole}$), 136.57 (=*C*H), 123.73 (*C*=*C*−$N_{triazole}$), 80.97 (*C*H−O), 71.91 (*C*H_2−O−CH_3), 70.48 (−*C*H_2−O), 69.38 ($N_{triazole}$−CH_2−*C*H_2−O), 59.02 (*C*H_3−O), 50.28 ($N_{triazole}$−*C*H_2−CH_2−O), 47.54 (*C*H−CO), 34.14 (N−*C*H_2).

***ω-exo*-Oxanorbornenyl PEO Monomethyl Ether M 2000.** White powder. Yield: 85%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.67 (s, 1H, triazole), 6.50 (s, 2H, =C*H*), 5.29 (s, 2H, C*H*-O), 4.78 (s, 2H, N−CH_2), 4.49 (t, *J* = 5.1 Hz, 2H, $N_{triazole}$−CH_2−CH_2−O), 3.85 (t, *J* = 5.1 Hz, 2H, $N_{triazole}$−CH_2−CH_2−O), 3.60−3.70 (m, 172H, CH_2−CH_2−O), 3.38 (s, 3H, O−CH_3), 2.89 (s, 2H, C*H*−CO). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 175.44 (*C*O), 141.98 (*C*=C−$N_{triazole}$), 136.59 (=*C*H), 123.69 (*C*=*C*−$N_{triazole}$), 80.98 (*C*H−O), 71.91 (*C*H_2−O−CH_3), 70.55 (−*C*H_2−O), 69.37 ($N_{triazole}$−CH_2−*C*H_2−O), 59.04 (*C*H_3−O), 50.26 ($N_{triazole}$−*C*H_2−CH_2−O), 47.55 (*C*H−CO), 34.15 (N−*C*H_2).

***ω-exo*-Oxanorbornenyl PEO Monomethyl Ether M 5000.** White powder. Yield: 78%. ^{1}H NMR (200 MHz, $CDCl_3$), δ = 7.68 (s, 1H, triazole), 6.52 (s, 2H, =C*H*), 5.29 (s, 2H, C*H*−O), 4.79 (s, 2H, N−CH_2), 4.50 (t, *J* = 5.1 Hz, 2H, $N_{triazole}$−CH_2−CH_2−O), 4.00 (t, *J* = 5.1 Hz, 2H, $N_{triazole}$−CH_2−*C*H_2−O), 3.50−3.90 (m, 412H, CH_2−CH_2−O), 3.38 (s, 3H, O−CH_3), 2.90 (s, 2H, C*H*−CO). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 175.47 (*C*O), 141.93 (*C*=C−$N_{triazole}$), 136.52 (=*C*H), 123.48 (*C*=*C*−$N_{triazole}$), 80.93 (*C*H−O), 71.97 (*C*H_2−O−CH_3), 70.48 (−*C*H_2−O), 69.38 ($N_{triazole}$−CH_2−*C*H_2−O), 59.08 (*C*H_3−O), 50.28 ($N_{triazole}$−*C*H_2−C$H_{>2}$−O), 47.4 (*C*H−CO), 34.09 (N−*C*H_2).

General Procedure for ROMP of Macromonomers. In a typical experiment, a dry Schlenk tube was charged with the macromonomer (100 mg) and a stir bar. The Schlenk tube was capped with a rubber septum, and cycled three times between vacuum and nitrogen to remove oxygen. The desired amount of degassed, anhydrous DCM ([M]$_0$ = 0.05−0.10 mol/L) was added via syringe under a nitrogen atmosphere to dissolve the macromonomer. A stock solution of catalyst G3 in degassed anhydrous DCM ([G3] = 24 μmol/L for **M 500** and **M 2000** in [**M 2000**]$_0$/[G3]$_0$ ratio = 10, [G3] = 7 μmol/L for the other experiments) was prepared in a separate vial. The desired amount of catalyst was injected into the macromonomer solution to initiate the polymerization. The Schlenk tube was stirred at room temperature under nitrogen. The polymerization was terminated by the addition of two drops of ethyl vinyl ether. The solvent was removed under reduced pressure for NMR and SEC measurements. The reaction mixture was then diluted in DCM and precipitated into 10 mL of stirring cold diethyl ether.

Polyoxanorbornene-*g*-PEO monomethyl ether 500 PONB-*g*-PEO 500. Brown plastic. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.72 (bs, 1H, triazole), 6.05 (bs, 2H, C*H*=C*H*, *trans*), 5.75 (bs, 2H, C*H*=C*H*, *cis*), 5.00 (bs, 2H, C*H*−O−C*H*, *cis*), 4.75 (bs, 4H, C*H*−O−C*H*, *trans;* N−CH_2), 4.49 (bs, 2H, $N_{triazole}$−CH_2−CH_2−O), 3.84 (bs, 2H, $N_{triazole}$−CH_2−CH_2−O), 3.80−3.50 (m, 40H, CH_2−CH_2−O), 3.38 (s, 3H, C*H*−C=O, O−CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 175.17 (*C*O), 141.43 (*C*=C−$N_{triazole}$), 130.92 (=*C*H), 123.86 (*C*=*C*−$N_{triazole}$), 80.73 (*C*H−O), 71.89 (*C*H_2−O−CH_3), 70.54 (−*C*H_2−O), 69.35 ($N_{triazole}$−CH_2−*C*H_2−O), 59.00 (*C*H_3−O), 53.36 ($N_{triazole}$−*C*H_2−CH_2−O), 50.51 (*C*H−CO), 34.07 (N−*C*H_2).

Polyoxanorbornene-*g*-PEO monomethyl ether 2000 PONB-*g*-PEO 2000. Brown powder. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.76 (bs, 1H, triazole), 6.02 (bs, 2H, C*H*=C*H*, *trans*), 5.70 (bs, 2H, C*H*=C*H*, *cis*), 5.02 (bs, 2H, C*H*−O−C*H*, *cis*), 4.76 (bs, 4H, C*H*−O−C*H*, *trans;* N−CH_2), 4.50 (bs, 2H, $N_{triazole}$−CH_2−CH_2−O), 3.82 (bs, 2H, $N_{triazole}$−CH_2−CH_2−O), 3.80−3.60 (m, 172H, CH_2−CH_2−O), 3.40 (s, 3H, C*H*−C=O, O−CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 174.99 (*C*O), 141.41 (*C*=C−$N_{triazole}$), 131.72 (=*C*H), 123.70 (*C* = *C*-$N_{triazole}$), 80.71 (*C*H−O), 71.89 (*C*H_2−O−CH_3), 70.52 (−*C*H_2−O), 69.31 ($N_{triazole}$−CH_2−*C*H_2−O), 58.99 (*C*H_3−O), 53.35 ($N_{triazole}$−*C*H_2−CH_2−O), 50.22 (*C*H−CO), 34.12 (N−*C*H_2).

Polyoxanorbornene-*g*-PEO monomethyl ether 5000 PONB-*g*-PEO 5000. Brown powder. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.73 (bs, 1H, triazole), 6.05 (bs, 2H, C*H*=C*H*, *trans*), 5.78 (bs, 2H, C*H*=C*H*, *cis*), 5.04 (bs, 2H, C*H*−O−C*H*, *cis*), 4.78 (bs, 4H, C*H*−O−C*H*, *trans;* N−CH_2), 4.51 (bs, 2H, $N_{triazole}$−CH_2−CH_2−O), 3.80 (bs, 2H, $N_{triazole}$−CH_2−CH_2−O), 3.80−3.60 (m, 412H, CH_2−CH_2−O), 3.38 (s, 3H, C*H*−C=O, O−CH_3).

Results and Discussion

Synthesis of Oxanorbornenyl PEO Macromonomers. The oxanorbornene-based monomer with an alkyne functionality was designed and prepared from *exo*-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (**1**) and *N*-propargylamine,

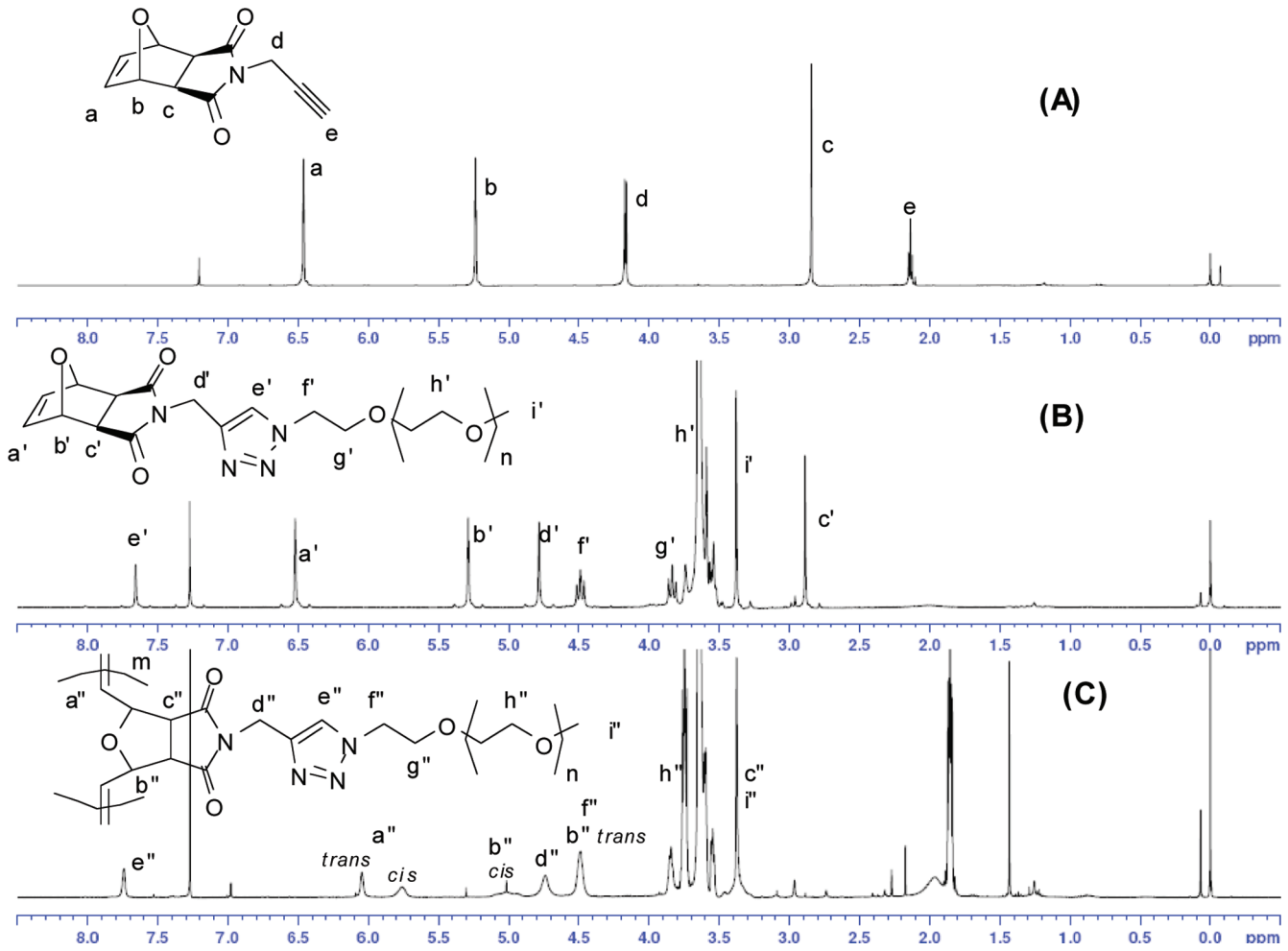
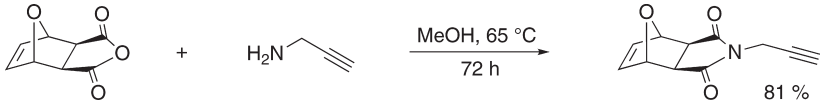


Figure 1. ^{1}H NMR spectra of (A) **2**, (B) *ω-exo*-oxanorbornenyl PEO monomethyl ether **M 500**, and (C) polyoxanorbornene-*g*-PEO 500 (Table 2, run 2); solvent: $CDCl_3$.

Scheme 1. Synthesis of Compound 2



and the synthetic route is illustrated in Scheme 1. An excess of *N*-propargylamine is necessary to increase the yield, and the suitable ratio of *N*-propargylamine to **1** was 1.5:1. Under these conditions, *exo*-*N*-prop-2-ynyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (**2**) was obtained with a 81% yield. The ^{1}H NMR spectrum (Figure 1A) shows the resonance signal of N−C*H*$_2$−C≡CH at 4.24 ppm, while the signal of C*H*═C*H* protons at 6.54 ppm are still observed, and importantly the integration area ratios of the characteristic resonances of 2:2 are in agreement with the ratios of corresponding protons, which demonstrates that full condensation occurred. Furthermore, the molecular weight ($M+H^+ = 204.0661$) of **2** from HRMS analysis was in good accordance with the calculated value ($M + H^+ = 204.2060$).

Azido-terminated linear PEO monomethyl ether chains (PEO−N_3; $\overline{M}_{n,NMR}$ = 530, 2010, and 4590 g/mol, see Table S1 in the Supporting Information) have been synthesized from hydroxyl-terminated PEO monomethyl ether chains (PEO−OH) with different molecular weights. PEO−OH were first converted to mesylate-terminated PEO monomethyl ether chains (PEO-OSO_2CH_3) by reaction with methanesulfonyl chloride, followed by transformation of mesylate chain-end groups into azido groups via reaction with NaN_3 in DCM for PEO−N_3 500[61] or in THF for PEO−N_3 2000 and PEO−N_3 5000.[62] The presence of an azido group at the chain-end was checked by ^{13}C NMR spectroscopy. The carbon bearing the azido group appears at 50.66 ppm, whereas the one carrying the terminal hydroxyl is located at 61.66 ppm. Moreover, the chain-end functionality was proved to be quantitative, as evidenced by the disappearance of the *C*H_2OH peak in the PEO-O−SO_2CH_3 spectra and the disappearance of the -O−SO_2*C*H_3 peak in the PEO−N_3 spectra (Figure S2 in the Supporting Information).

Next, macromonomers were synthesized by coupling azido-terminated PEO−N_3 and alkyne-containing **2**. The "click" reactions were carried out in DMF at room temperature using a stoichiometric molar ratio between PEO−N_3 and alkynyl groups in the presence of a catalytic amount of Cu(I)Br with PMDETA as the ligand (Scheme 2). After 4 h of reaction, click chemistry afforded the targeted *ω-exo*-oxanorbornenyl PEO monomethyl ether macromonomers with different molecular weights **M 500**, **M 2000** and **M 5000**, obtained from PEO−N_3 500, 2000, and 5000, respectively.

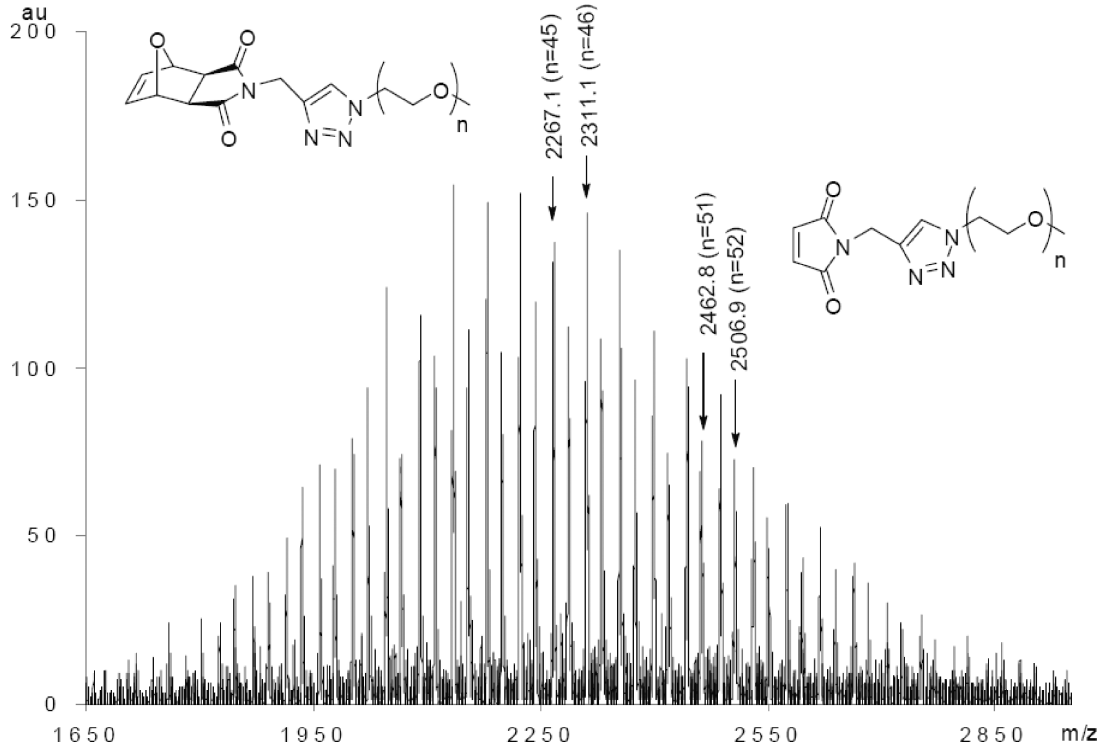


Figure 2. MALDI−TOF spectrum of *ω-exo*-oxanorbornenyl PEO monomethyl ether macromonomer **M 2000** (matrix: DCTB + sodium trifluoroacetate).

Scheme 2. Synthesis of Macromonomers

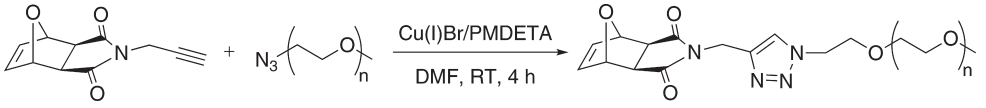


Table 1. Characteristics of *ω-exo*-Oxanorbornenyl Poly(ethylene oxide) Monomethyl Ether Macromonomers

sample name	convn[a] (%)	Yield[b] (%)	$\overline{M}_{n,NMR}$[c] (g/mol)	$\overline{M}_{n,SEC}$[d] (g/mol)	PDI[d]
M 500	100	80	757	890	1.05
M 2000	100	85	2240	3400	1.06
M 5000	100	78	4817	7800	1.05

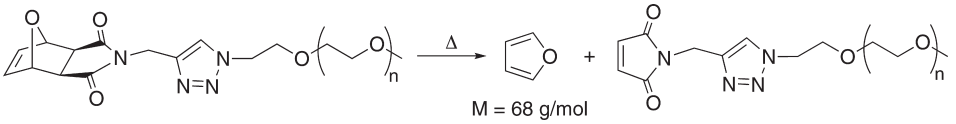
[a] Determined by ^{1}H NMR from the reaction mixture, $CDCl_3$ as solvent. [b] After purification. [c] Number-average molecular weight determined by ^{1}H NMR, $CDCl_3$ as solvent. [d] Number-average molecular weight and polydispersity measured by THF SEC with RI detector; calibration with linear polystyrene standards.

The results of the coupling reactions are reported in Table 1. The ^{1}H NMR spectrum of **M 500** (Figure 1B) clearly indicates the shift of the alkyne proton at 2.20 ppm (e, Figure 1A) to 7.68 ppm (e′, Figure 1B) as well as the shift of the methylene group next to the alkyne group at 4.24 ppm (d, Figure 1A) to 4.78 ppm (d′, Figure 1B), which corresponds to the proton linked to the formed triazole ring. The "click" reaction occurred in a quantitative way since integrations of norbornenyl olefin peak (a′, Figure 1B at 6.50 ppm) and the proton on the triazole ring (e′, Figure 1B at 7.68 ppm) gave a 2:1 ratio. The same conclusions could be drawn from the reactions between **2** and PEO−N_3 2000 or 5000 (Figure S4 in the Supporting Information). The SEC traces (Figure S5 in the Supporting Information) show that the coupling product **M 500** has a slightly higher apparent molecular weight than the PEO−N_3 500 precursor, determined by SEC in THF with linear PS standards, indicating the formation of the macromonomer.

The MALDI−TOF spectrum of **M 2000** is shown in Figure 2. It is interesting to note that besides the expected product, i.e., the macromonomer plus one sodium ion, an additional series was observed which differs by 68 mass units from the main series. The difference in mass of each signal of both series was roughly estimated as 44, indicating the signals were assignable to the PEO homologues. Since no side reactions were detectable by NMR (see Figure S4 in the Supporting Information), the fragment signals can be ascribed to the retro-Diels−Alder reaction[63] (Scheme 3) caused by ionization.

The conversion of the *ω-exo*-norbornenyl end-group of the macromonomer to a maleimide group could also be monitored by thermogravimetric analysis (TGA) (Figure S6 in the Supporting Information). **M 2000** TGA thermogram clearly exhibits a first loss of 3.07 wt % between 134 and 150 °C, which is attributed to the release of furan[64] (calculated % weight loss = 3.04 for **M 2000**, $\overline{M}_{n,NMR}$ = 2 240 g/mol). Additionally, the macromonomers exhibited a major thermal degradation at 405 °C (50% weight loss). The presence of the maleimide functionality was checked after a thermal treatment of **M 2000** at 250 °C. The resulting ^{1}H NMR spectrum (Figure S7 in the Supporting Information) clearly shows the disappearance of the oxatricyclo vinyl signals (C*H*=C*H* and C*H*−O protons at 6.50 and 5.29 ppm, respectively) and the appearance of the maleimide peak at 6.74 ppm. It should be noted that such maleimide end-functionalized poly(ethylene oxide) can undergo further Diels−Alder cycloaddition or thiol−ene reaction, giving access to modular block copolymers, stars, bioconjugates, and other functional telechelics.[50]

Scheme 3. Retro-Diels-Alder Reaction of Macromonomers



Scheme 4. Ring-Opening Metathesis Polymerization of Macromonomers

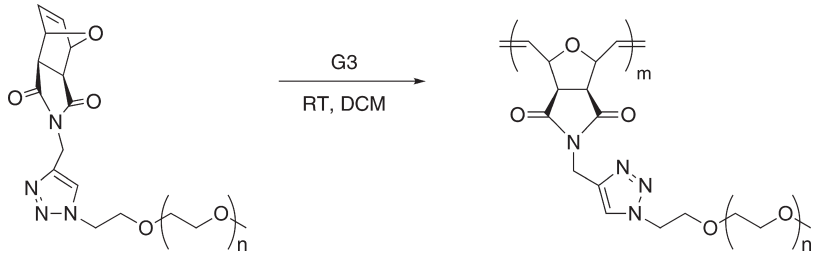


Table 2. ROMP of Macromonomers Using Catalyst G3[a]

run	macromonomer	$[M]_0/[G3]_0$[b]	$\overline{M}_{n,theo}$[c] (g/mol)	t (h)	convn[d] ^{1}H NMR (%)	convn[e] SEC (%)	$\overline{M}_{n,SEC}$[f] (g/mol)	yield (%)	PDI[f]	trans/cis[g]
1	**M 500**	10	7661	1	100	99	9900	97	1.06	50/50
2	**M 500**	50	37 941	1	100	99	22 800	97	1.17	50/50
3	**M 500**	100	75 791	1	90	90	20 000	95	1.09	50/50
4	**M 500**	100	75 791	4	100	100	23 500	100	1.15	50/50
5	**M 2000**	10	22 491	1	100	98	29 300	100	1.07	57/43
6	**M 2000**	50	112 091	1	25					
7	**M 2000**	50	112 091	4	61	58	37 700		1.10	57/43
8	**M 2000**	50	112 091	24	60	60	46 300		1.04	57/43
9	**M 2000**	100	224 091	24		5				
10	**M 5000**	10	48 261	4	90	90	57 800	98	1.06	75/25
11	**M 5000**	10	48 261	24		90	57 800	93	1.06	
12	**M 5000**	50	240 941	24		61	67 500		1.08	
13	**M 5000**	100	481 791	24		1				

[a] Results are representative of at least duplicated experiments. [b] Macromonomer to Grubbs' catalyst G3 ratio. [c] $\overline{M}_{n,theo} = \overline{M}_{n,NMR}[M]_0/[G3]_0 + M_{extr.}$. [d] Determined by comparing the peak areas of grafted copolymer and residual macromonomer from SEC measurement of the crude product. [e] Determined by comparing the peak areas of oxanorbornenyl ring of the grafted copolymer and residual macromonomer from ^{1}H NMR of the crude product. [f] Number-average molecular weight and polydispersity measured by THF SEC with RI detector, calibration with linear polystyrene standards. [g] Determined by comparing the peak areas of H_{cis} and H_{trans} of the CH= groups of the backbone from ^{1}H NMR of the grafted copolymer.

The MALDI−TOF spectrum of **M 500** also exhibits the second minority series. For **M 5000**, only the series resulting from the retro-Diels−Alder reaction was detected (Figure S8 in the Supporting Information).

ROMP of Macromonomers. Third generation Grubbs' catalyst (G3) was used to polymerize the macromonomers (Scheme 4). Reactions were carried out in DCM with various macromonomer-to-catalyst ratios at room temperature with a macromonomer concentration of 0.05 M (Table 2). DCM was preferred to THF since **M 2000** and **M 5000** show a poor solubility in THF at the used concentrations. **M 500** was easily polymerized to near quantitative yield in 1−4 h depending on the desired molecular weight (Table 2, runs 1−4). ^{1}H NMR spectroscopy indicated the disappearance of the vinyl proton signal at 6.50 ppm (H_a) as shown in Figure 1C and the emergence of the *trans* and *cis* vinyl proton resonances at 6.05 and 5.75 ppm, respectively (Figure 1C, Table 2, run 2). NMR spectroscopy also evidenced that the triazole moieties are preserved throughout the ROMP process (resonances in ^{1}H NMR: 7.72 ppm; triazole-H). GPC traces of the polymers are shown in Figure 3. As can be seen (Figure 3, parts B and C), the line profile is perfectly symmetrical with no observable high or low molecular weight shoulders, which occur frequently when macromonomers are polymerized. All polymers issued from **M 500** were obtained with low polydispersities (Table 2, runs 1, 2 and 4) ranging from 1.06 to 1.17. These results are in contrast to those already reported in literature,[21,22,65] where broad polydispersities were observed, typically around 1.6, when (co)polymerizing PEO functionalized imide monomer (however using other Ru-based catalysts), suggesting to be caused by the combination of PEO with the imide functionality.[22] The number-average molecular weights obtained from SEC in THF (calibrated with polystyrene) were as

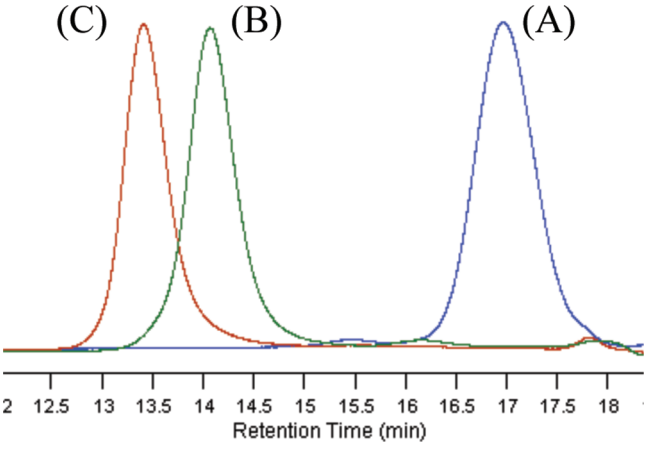


Figure 3. SEC traces of (A) *ω-exo*-oxanorbornenyl PEO monomethyl ether **M 500**, (B) polyoxanorbornene-*g*-PEO 500 (Table 2, run 1) and (C) polyoxanorbornene-*g*-PEO 500 (Table 2, run 2).

much more lower than the targeted ones as the macromonomer-to-catalyst ratio is high (Table 2, runs 1−4). This disparity can be attributed to different hydrodynamic volumes of these polymers compared to linear polystyrene standards.[66] It is also well-known in the literature that the measured values for the molecular weights underestimate the true molecular weights of comb polymers by up to a factor of 10.[20] Additionally, THF is a poor solvent for PEO in which the copolymer contracts substantially, leading to a dramatic decrease in hydrodynamic volume.[35]

However, **M 2000** and **M 5000** were only able to form polyoxanorbornene-*g*-PEO with relatively short backbone length (Table 2, runs 5 and 10). The resulting grafted copolymers have been characterized using both SEC and NMR techniques. The grafted copolymers had higher apparent molecular weights than the macromonomers precursors, and the molecular weight distribution of the grafted copolymers remained as narrow as PDI = 1.06−1.07 (Table 2, runs 5 and 10, Figures S10 and S11 in the Supporting Information). The ^{1}H NMR results (see Figure S12 in the Supporting Information) were similar to the one shown in Figure 1C. Increase of the reaction time for macromonomer to catalyst ratios of 50 and 100 did not allow reaching the complete conversion of the macromonomers (Table 2, runs 6−9 and 12). The macromonomer chain length seems to be a critical factor toward the conversion, probably due to the limiting effect of the macromonomer steric hindrance during the propagation step. Furthermore, the rich-oxygen macromonomers could give competitive coordination with the ruthenium with the result of lowering the rate of polymerization. Indeed, the trapping of catalyst has already been described for PEO macromonomers.[36]

Polyoxanorbornene-*g*-PEO 500 was shown by ^{1}H NMR to have a backbone tacticity that was equally *cis* and *trans* (Table 2, runs 1−4) whereas polyoxanorbornene-*g*-PEO 2000 and 5000 had tacticities that were 57% and 75% *trans*, respectively. Similar results have already be mentioned in the literature for polynorbornene-*g*-PEO 700, 1200, and 2300.[67]

The thermal behavior of PEO-grafted oxanorbornene copolymers (Table 2, runs 1, 5 and 10) was evaluated by TGA under N_2 conditions in order to determine the degradation temperature of each copolymer (Figure S13 in the Supporting Information). The PEO-grafted oxanorbornene copolymers exhibited a one-step degradation process, and the temperature range of the first 5% weight loss decomposition was determined to lie between 372 and 386 °C, indicating no influence of the PEO length.

Conclusion

Combination of ROMP and the highly efficient 1,3-dipolar cycloaddition process was successfully used to prepare well-defined poly(oxanorbornene)-*g*-PEO via the "grafting through" strategy. First, ω-oxanorbornenyl macromonomers of PEO monomethyl ether were generated by "click" coupling reaction between acetylene-functionalized oxanorbornene and ω-azido poly(ethylene oxide) monomethyl ether. The length of PEO chains was modulated ranging from 500 and 5000 g/mol. The end-functionalized ω-*exo*-norbornenyl macromonomers can be quantitatively converted to the corresponding ω-maleimide end-functionalized PEO monomethyl ether via thermal deprotection through retro-Diels−Alder reaction, that makes them ideal candidates for the synthesis of block copolymers, stars, bioconjugates, and other functional telechelics. The ROMP of macromonomers was carried out using the Grubbs' catalyst G3, leading to a variety of well-defined comb polymers, although the efficiency of the ROMP process was affected by the molecular weight of the macromonomers. A series of poly(oxanorbornene)-*g*-PEO 500 with various lengths of the overall backbone was prepared by controlling the macromonomer-to-catalyst ratio, giving access to narrowly dispersed brush copolymers. This synthetic approach is very general and is applicable to a wide range of macromonomers, derived from various azido end-functionalized polymers and bearing other "ROMP-able" entities such as norbornene or cyclobutene.

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Supporting Information Available: Figures showing additional ^{1}H and ^{13}C NMR spectra, SEC traces and MALDI−TOF spectra of PEO precursors, macromonomers, and copolymers, and TGA thermograms and a table of characteristics of azido-terminated poly(ethylene oxide) monomethyl ether chains. This material is available free of charge via the Internet at http://pubs.acs.org.

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