ARTICLE

Effect of Radical Copolymerization of the (Oxa)norbornene End-group of RAFT-prepared Macromonomers on Bottlebrush Copolymer Synthesis via ROMP†

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Bottlebrush polymers are attractive for use in a variety of different applications. Here we report synthesis of two novel trithiocarbonate RAFT agents bearing either a oxanorbornenyl or norbornenyl moiety for bottlebrush synthesis via ROMP grafting-through polymerization. RAFT polymerization kinetics were evaluated as a function of monomer type, degree of polymerization (DP) and RAFT agent structure. The correlation between oxa/norbornenyl moiety and the type of RAFT monomer (methyl acrylate, *n*-butyl acrylate, and styrene) has been investigated. The reactivity of the oxa/norbornenyl group of the RAFT agent towards the radical propagating species during RAFT polymerization influences the molar mass, molar mass distribution and the residual olefinic end-group functionality of the resulting polymeric macromonomers. The RAFT synthesized macromonomers (MMs) are subjected to "grafting-through" ROMP using Grubbs 3rd generation catalyst, resulting in bottlebrush polymers. The 'defects' in MMs structure have been found responsible for higher MMs residue after the ROMP process and hence affect the microstructure of synthesized bottlebrush polymers.

Introduction

Due to outstanding and tunable properties molecular bottlebrush polymers have attracted high interest in the last few years.[1-3] Molecular bottlebrushes consist of long linear polymeric backbone densely grafted with short side-chains. Based on their well-defined structure and fascinating properties they can be functionalized and utilized in many applications such as coatings, lubrication, nanomedicine, drug delivery, and photonics.[4-6]

There are three main approaches for the preparation of bottlebrush polymers: 1) 'grafting-to' – attachment of side chains to the polymeric backbone; 2) 'grafting-from' – polymerization of monomers from the backbone; and 3) 'grafting-through' – polymerization of macromonomers.[7] Each method has its own advantages and limitations. Generally, these well-defined bottlebrushes are synthesised via combination of two or more polymerization techniques.[8, 9]

The grafting-through strategy is the polymerization of macromonomers (MMs) that contain polymerizable end-groups. The grafting density and dispersity play a crucial role in the performance of these bottlebrush polymers. Unlike the two other strategies, the grafting-through technique ensures high grafting density as well as low brush dispersity and hence extraordinary properties and high efficacy toward application. Often, ring-opening metathesis polymerization (ROMP), using Grubbs-type Ru catalysts, has been utilized for the grafting-through technique due to its rapid polymerization rates. In addition, the molar mass of MMs and the reactivity of polymerizable moiety are key factors in the grafting-through strategy.[1, 10]

For the preparation of functional MMs with tailored molecular properties (i.e. targeted molar mass, low dispersity) reversible deactivation radical polymerization (RDRP) techniques are highly attractive. Reversible addition-fragmentation chain transfer (RAFT) polymerization is arguably the most versatile RDRP method as it has a superior tolerance for wide range of functional groups;[11] the RAFT technique is compatible with non-ionic, cationic, and anionic monomers. Through careful selection of the RAFT agent and reaction conditions, MMs amenable to polymerization by "grafting-through" ROMP polymerization can be prepared.[1, 10, 12]

In the broader scientific literature *exo*-norbornenes are the cyclic olefin (monomer) of choice for ROMP; their rapid ring opening metathesis kinetics and low incidence of chain transfer renders their polymerization 'living'.[13] An added advantage of norbornenes is their thermal stability. While less commonly used, *exo*-oxanorbornenes (i.e. oxygen-bridged analogues of norbornenes) are also widely reported in ROMP.[7]

In the context of functional RAFT agent synthesis, *exo*-oxanorbornene derivatives are quite attractive starting materials as they are relatively inexpensive. In contrast, *exo*-norbornenes tend to be quite expensive and are often prepared 'in-house' by laborious isomerization methods from the

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cheaper *endo*-isomers. Whilst this suggests oxanorbornenes as an attractive alternative to norbornenes, for the synthesis of 'ROMP-able' RAFT agents, their main drawback is their thermal lability; they can readily undergo retro-Diels-Alder reactions extruding furan.[14]

Herein, we directly compare the utility of oxanorbornene- and norbornene-based trithiocarbonate RAFT agents for the preparation of bottlebrush polymers via sequential RAFT/ROMP. The influence of the identities of the RAFT polymerizable monomer (i.e. methyl acrylate (MA), *n*-butyl acrylate (BA), and styrene (St)) and the strained olefin end-group (i.e. oxanorbornenyl, norbornenyl) on macromonomer (MM) synthesis is investigated in detail. While both norbornene[1, 12, 15-17] and oxanorbornene[5, 18] end-groups have been used for the synthesis of polymers via a sequential RAFT/ROMP strategy (or other RDRP/ROMP methods) in the past, the incidence and effect of radical propagation to the end-group has largely been ignored and a direct comparison is lacking; here we seek to remedy these points. Additionally, the effect of the resultant MM structure on the subsequent ROMP grafting-through polymerization is also investigated.

Experimental

Materials.

2-Bromopropionyl bromide, carbon disulfide (CS_2), chlorobenzene, dodecanethiol, ethanolamine, *n*-heptane, neutral alumina Brockmann activity I (70-230 mesh), *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride, potassium *tert*-butoxide, pyridine, triethylamine (TEA) and all solvents were purchased from Fisher Scientific. Solvents were of analytical reagent grade unless otherwise stated. *exo*-3,6-Epoxy-1,2,3,6-tetrahydrophthalic anhydride **1**, 3rd generation Grubbs' catalyst (**G3**) (dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](benzylidene)bis(3-bromopyridine) ruthenium(II)), and anhydrous sodium sulfate (Na_2SO_4) were obtained from Sigma-Aldrich. Methyl acrylate (MA), *n*-butyl acrylate (BA) and styrene (St) were purchased from Sigma-Aldrich and freed from inhibitor by passage through neutral alumina activity I (70-230 mesh). 2,2'-Azobis[2-methyl propionitrile] (AIBN) was purchased from Acros and purified by recrystallization twice from methanol prior to use. All NMR solvents were produced by Cambridge Isotope Laboratories and obtained through Goss Scientific. Silica gel (ZEO prep 60 HYD 40-63 µm) was obtained from Apollo Scientific. Hydrochloric acid was purchased from Better Equipped.

Characterization.

Nuclear magnetic resonance (NMR) spectra were recorded on a Joel 400 MHz spectrometer at room temperature. ^{1}H and ^{13}C NMR spectra were internally referenced to residual solvent.[19] Size exclusion chromatography (SEC) was conducted on an EcoSEC-HLC 8320GPC system with Dual Flow RI Detector and TSKgel super HZM-N 3µm (4.6 ×150mm) column. THF was used as the eluent at a flow rate of 0.35 mL/min at 40 °C and low dispersity polystyrene standards were used for the calibration.

Synthesis.

Preparation of alcohol-functional oxanorbornene imide (3)

To a mixture of *exo*-3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride **1** (15 g, 90 mmol) and methanol (375 mL) was added ethanolamine (6.6 mL, 6.53 g, 107 mmol, 1.2 equiv.) and trimethylamine (12.6 mL, 9.15 g, 90mmol, 1 equiv.). The reaction mixture was heated under reflux at 70°C for 24 h. The solution was concentrated to half the volume under reduced pressure at ambient temperature. Crystallisation in the freezer (-18°C) gave the oxanorbornene imide **3** as white crystals (13.0 g, 62.1 mmol, 69 %); ^{1}H NMR (400 MHz, *CDCl$_3$*) δ 2.92 (s, 2H, 2 × *endo*-C*H*), 3.89 (m, 4H, NC*H*$_2$ and OC*H*$_2$), 4.78 (br t, 1H, O*H*), 5.12 (s, 2H, 2 × bridgehead-C*H*), 6.55 (s, 2H, 2 × =C*H*). These data agree with Kötteritzsch et al.[20]

Preparation of oxanorbornene alkylating agent (5)

To a solution of *N*-(2-hydroxyethyl)-*cis*-5-oxanorbornene-*exo*-2,3-dicarboximide **3** (13.0 g, 62.1 mmol) in anhydrous tetrahydrofuran (THF) (125 mL) was added dry pyridine (5.65 g, 5.8 mL, 71.4 mmol, 1.15 equiv.). Subsequently, a solution of 2-bromopropionyl bromide (14.75 g, 7.16 mL, 68.3 mmol, 1.1 equiv.) in dry THF (25 mL) was added dropwise to the reaction mixture at 0 °C. The reaction mixture is allowed to stir for 24 h at RT under nitrogen. The resulting reaction mixture was poured into dilute aq. HCl solution (350 mL, 0.1 M) and was extracted with DCM (3 × 100 mL), the combined organics washed with dilute aq. HCl solution (100 mL, 0.1 M), water (100 mL), and dried over anhydrous sodium sulfate (Na_2SO_4). The solvent was removed under reduced pressure giving the oxanorbornene-functional alkylating agent **5** as an greyish-white solid (20.3 g, 59.0 mmol, 95 %); ^{1}H NMR (400 MHz, *CDCl$_3$*) δ 1.77 (d, *J* 7.0 Hz, 3H, C*H*CH$_3$), 2.85 (s, 2H, 2 × *endo*-C*H*), 3.77 (m, 2H, NC*H*$_2$), 4.31 (m, 3H, OC*H*$_2$ and BrC*H*), 5.24 (d, *J* 0.6 Hz, 2H, 2 × bridgehead-C*H*), 6.49 (d, *J* 0.6 Hz, 2H, 2 × =C*H*); ^{13}C NMR (50 MHz, *CDCl$_3$*) δ 21.5, 37.6, 39.9, 47.5, 62.0, 80.9, 136.6, 170.0, 176.0. These data agree with Runge and Bowden.[21]

Preparation of oxanorbornene RAFT agent (7-ONb)

Dodecane-1-thiol (6.36 g, 31.5 mmol, 1 equiv.) was added to dry THF (100 mL). After 10 min potassium *tert*-butoxide (KO^{t}Bu) (3.54 g, 31.5 mmol, 1 equiv.) was added to the solution and kept under stirring for 15 min at ambient temperature. Then, carbon disulfide (CS_2) (4.8 g, 63 mmol, 2 equiv.) was added and stirred for 30 min. Subsequently, the oxanorbornene-functional alkyl bromide **5** (10.89 g, 31.5 mmol, 1 equiv.) was added to the reaction mixture and allowed to stir for 20 hours at room temperature. Afterwards, the reaction mixture was diluted with water (200 mL), extracted with DCM (3 × 75 mL), washed with brine and dried over anhydrous sodium sulfate. The solvent was reduced *in vacuo* at ambient temperature and precipitated into 50 mL of *n*-heptane. The resulting yellow precipitate was isolated by filtration and dried under reduced pressure at ambient temperature to give the RAFT agent **7-ONb** (10.0 g, 18.5 mmol, 59%); ^{1}H NMR (400 MHz, *CDCl$_3$*) δ 0.87 (t, *J* 6.7 Hz, 3H, C*H*$_3$), 1.20-1.30 (m, 16H, alkyl C*H*$_2$), 1.37 (m, 2H, SCH$_2$CH$_2$C*H*$_2$), 1.56 (d, *J* 7.3, 3H, CHC*H*$_3$), 1.67 (p, *J* 7.4 Hz, 2H,

SCH_2CH_2), 2.85 (s, 2H, 2 × *endo*-C*H*), 3.33 (m, 2H, SCH_2), 3.76 (m, 2H, NCH_2), 4.28 (m, 2H, OCH_2), 4.79 (q, *J* 7.3, 1H, $CHCH_3$), 5.26 (d, *J* 0.6 Hz, 2H, 2 × bridgehead-C*H*), 6.50 (d, *J* 0.6 Hz, 2H, 2 × =C*H*); ^{13}C NMR (50 MHz, *CDCl*$_3$) δ 14.2, 16.8, 22.8, 27.9, 29.0, 29.2, 29.4, 29.5, 29.6, 29.7, 29.7, 32.0, 37.4, 37.7, 47.6, 47.6, 47.8, 62.0, 77.3, 136.6, 171.0, 176.0, 222.1.

Synthesis of exo-5-norbornene-2,3-dicarboxylic anhydride (2) via thermal isomerisation

The isomerization of *endo*-5-norbornene-2,3-dicarboxylic anhydride to *exo*-5-norbornene-2,3-dicarboxylic anhydride **2** was adapted from the procedure reported by Yu et al.[22] Briefly, *endo*-5-norbornene-2,3-dicarboxylic anhydride (20.0 g, 121.8 mmol) was heated under nitrogen atmosphere at 200 °C for 12 h. The resulting material was recrystallized three times from toluene to give *exo*-5-norbornene-2,3-dicarboxylic anhydride **2**; the residue can be recycled and treated in the same manner a several times to increase the yield (after three cycles; 10 g, 60.9 mmol, 50 %; isomeric ratio 95% *exo*/5 % *endo*). ^{1}H NMR (400 MHz, *CDCl*$_3$) δ 1.44 (d, *J* 10.3 Hz, 1H, C*H*H), 1.66 (dm, *J* 10.3 Hz, 1H, CH*H*), 2.99 (m, 2H, 2 × *endo*-C*H*), 3.45 (br s, 2H, 2 × bridgehead-C*H*), 6.32 (br s, 2H, 2 × =C*H*).These data agree with Matson and Grubbs.[23]

Preparation of N-(2-hydroxyethyl)-cis-5-norbornene-exo-2,3-dicarboximide (4)

To a mixture of *exo*-5-norbornene-2,3-dicarboxylic anhydride **2** (10.0 g, 61 mmol) and toluene (100 mL) was added ethanolamine (4.06 mL, 67 mmol, 1.1 equiv.) and triethylamine (0.92 mL, 6.8 mmol, 0.11 equiv.). A Dean-Stark trap was attached and the reaction mixture was refluxed at 125 °C for 20 h. The resulting mixture was concentrated and DCM (100 mL) was added. The combined organics were washed with aq. HCl (1 M, 30 mL) and brine (30 mL). The organic layer was dried over anhydrous sodium sulfate and the solvent removed under reduced pressure to give *N*-2-(hydroxyethyl)-*cis*-5-norbornene-*exo*-2,3-dicarboximide **4** as a white solid (11.4 g, 54.5 mmol, 90 %); ^{1}H NMR (400 MHz, C*DCl*$_3$) δ 1.32 (br d, *J* 9.9 Hz, 2H, C*H*H), 1.50 (dm, *J* 9.9 Hz,1H, CH*H*), 2.19 (s, 1H, O*H*), 2.69 (d, *J* 1.2 Hz, 2H, 2 × *endo*-C*H*), 3.26 (m, 2H, 2 × bridgehead-C*H*), 3.67 (m, 2H, NCH_2), 3.76 (m, 2H, OCH_2), 6.27 (t, *J*1.7 Hz, 2H, 2 × =C*H*);^{13}C NMR (50 MHz, *CDCl*$_3$) δ 41.4, 42.9, 45.3, 48.0, 60.3, 137.9, 178.9. These data agree with Matson and Grubbs.[23]

Preparation of norbornene alkylating agent (6)

N-(Hydroxyethyl)-*cis*-5-norbornene-*exo*-2,3-dicarboximide **4** (9 g, 43 mmol) was added to anhydrous THF (100 mL), followed by pyridine (4.2 mL, 4.1 g, 52 mmol, 1.2 equiv.). Then, 2-bromopropionyl bromide (5.4 mL, 11.1 g, 52 mmol, 1.2 equiv.) in THF (20 mL) was added dropwise to the reaction mixture at 0 °C. The reaction mixture was allowed to stir for 48 hrs at RT under nitrogen. Then, the solvent was reduced and DCM (100 mL) was added, washed with aq. HCl (0.1 M, 30 mL) and brine (30 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated to give the norbornene-functional alkylating agent **6** as a viscous oil (12.3 g, 35.9 mmol, 83%); ^{1}H NMR (400 MHz, *CDCl*$_3$) δ 1.28 (d, *J* 10.0 Hz, 1H, C*H*H), 1.50 (d, *J* 10.0 Hz, 1H, CH*H*), 1.77 (d, *J* 7.0 Hz, 3H, $CHCH_3$), 2.68 (s, 2H, 2 × *endo*-C*H*), 3.25 (s, 2H, 2 × bridgehead-C*H*), 3.76 (m, 2H, NCH_2), 4.31 (m, 3H, OCH_2 and BrC*H*), 6.26 (s, 2H, 2 × =C*H*); ^{13}C NMR (50 MHz, *CDCl*$_3$) δ 20.4, 36.2, 38.6, 41.8, 44.2, 46.8, 61.2, 136.7, 168.8, 176.7.

Synthesis of norbornene RAFT agent (8-Nb)

Dodecane-1-thiol (4.93ml, 20.5 mmol, 1 equiv.) was added to dry THF (80 mL). After 10 mins potassium *tert*-butoxide (KO^tBu) (2.3 g, 20.5 mmol, 1 equiv.) was added to the solution and kept under stirring for 15 min at ambient temperature. Then, CS_2 (2.5 g, 32.3mmol, 1.6 equiv.) was added and stirred for 30 min. Subsequently, the alkylating agent **6** (7.0 g, 20.5 mmol, 1 equiv.) in dry THF (10 mL) was added to the reaction mixture and allowed to stir for 20 hours at room temperature. Afterwards, the reaction mixture was diluted with water (200 mL), extracted with DCM (3× 50 mL), washed with brine and dried over anhydrous sodium sulfate. The solvent was reduced *in vacuo* at ambient temperature. The crude product was purified by column chromatography (silica gel; ethyl acetate/*n*-hexane (1:2)). Removal of solvent under reduced pressure, gave the norbornene-functional RAFT agent **8-Nb** as a yellow solid (6.1 g, 11.3 mmol, 55%); ^{1}H NMR (400 MHz, *CDCl*$_3$) δ 0.86 (t, *J* 6.8 Hz, 3H, CH_3), 1.20-1.30 (m, 16H, alkyl CH_2), 1.29 (d, *J* 9.7 Hz, 1H, C*H*H), 1.37 (m, 2H, $SCH_2CH_2CH_2$), 1.51 (m, 1H, C*H*H), 1.56 (d, *J* 7.3 Hz, 3H, $CHCH_3$), 1.66 (p, *J* 7.3 Hz, 2H, SCH_2CH_2), 2.69 (d, *J* 1.2 Hz, 2H, 2 × *endo*-C*H*), 3.28 (m, 2H, 2 × bridgehead-C*H*), 3.33 (t, *J* 7.3 Hz, 2H, SCH_2), 3.76 (m, 2H, NCH_2), 4.38 (m, 2H, OCH_2), 4.80 (q, *J* 7.3, 1H, $CHCH_3$), 6.28 (t, *J* 1.8 Hz, 2H, 2 × =C*H*); ^{13}C NMR (50 MHz, *CDCl*$_3$) δ 14.2, 16.8, 22.8, 28.0, 29.0, 29.2, 29.4, 29.6, 29.7, 32.0, 37.4, 37.5, 43.0, 45.4, 47.6, 48.0, 62.1, 137.9, 170.9, 177.8, 221.9.

RAFT polymerization

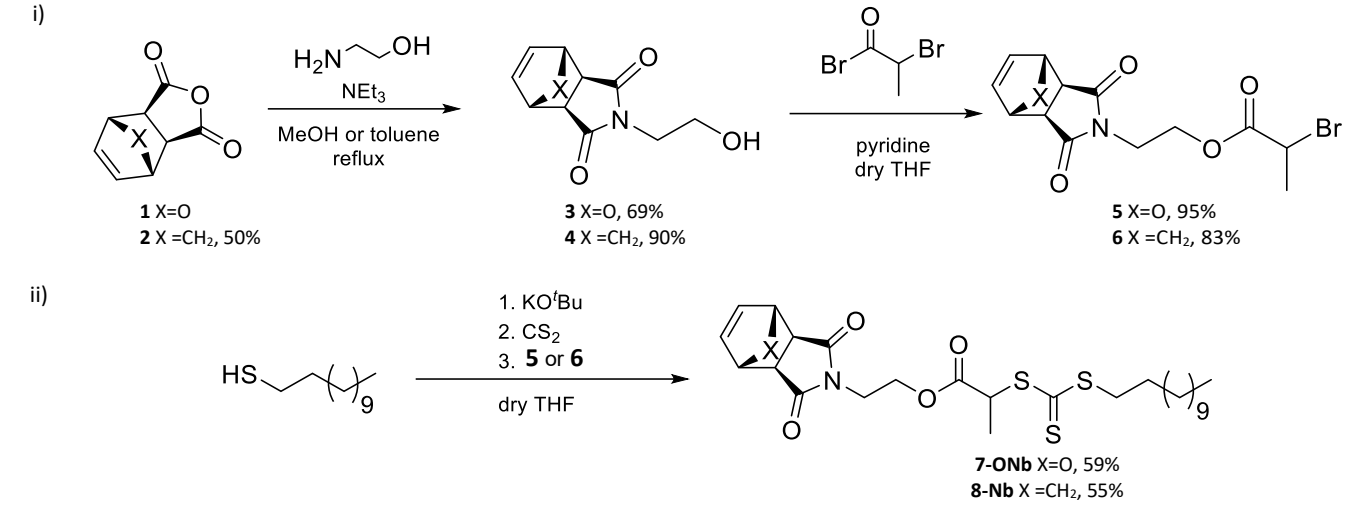
RAFT polymerization of methyl acrylate and butyl acrylate

Methyl acrylate (MA) or *n*-butyl acrylate (BA) (60 wt % in toluene), oxanorbornene RAFT agent **7-ONb** or norbornene RAFT agent **8-Nb**, and AIBN in ratio (200:1:0.1) or (50:1:0.1) were mixed in a 25 mL round bottomed flask (RBF), and the resulting solution was degassed by sparging with nitrogen for 30 min. The solution polymerization was initiated by raising the temperature to 60 °C. For kinetic studies, an aliquot of the reaction mixture (0.3 mL) was taken at predetermined times and quenched by rapid cooling in liquid nitrogen. The polymer was recovered by precipitation three times in methanol/water solution.

RAFT polymerization of Styrene

RAFT polymerization of styrene was performed in bulk. Styrene (St), oxanorbornene RAFT agent **7-ONb** or norbornene RAFT agent **8-Nb**, and AIBN in ratio (250:1:0.1) or (50:1:0.1) were mixed in a 25 mL RBF, and the resulting solution was degassed by sparging with nitrogen for 30 min. The polymerization was initiated by raising the temperature to 65 °C. For kinetic studies, an aliquot of the reaction mixture (0.3 mL) was taken at predetermined times and quenched by rapid cooling in liquid

nitrogen. The polymer was recovered by precipitation three times in methanol.



Scheme 1: Synthesis of (i) alkylating agents **5** and **6** and (ii) RAFT agents **7-ONb** and **8-Nb**

Grafting through polymerization via Ring Opening Metathesis Polymerization

Preparation of Macromonomers

Defined macromonomers with low molar mass (~2000-4000 g mol^{-1}) derived from both RAFT agents (**7-ONb** or **8-Nb**) are prepared as described above (M:RAFT:I = 50:1:0.1) and the polymerization was quenched after certain time to obtain the desirable molar mass.

ROMP of Macromonomers via 'Grafting through' ROMP

The defined macromonomer was added to a dry, 5 mL RBF charged with a stir bar. The flask was then degassed by applying vacuum for 30 min, and the desired amount of degassed, anhydrous THF was added (total macromonomer concentration was ~0.03 M). The required amount of degassed Grubbs catalyst **G3** solution was transferred to the reaction flask containing the macromonomer to initiate the polymerization and stirred at room temperature for at least 3 h. The reaction was quenched by addition of few drops of ethyl vinyl ether. The product was collected by precipitation in methanol and dried under vacuum.

Results and Discussion

RAFT Agent Design and Synthesis

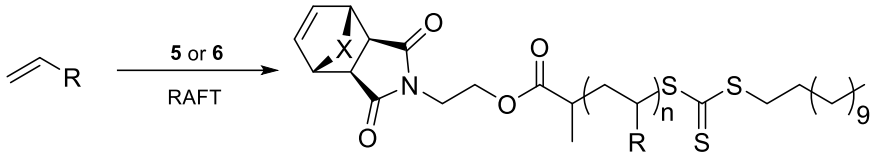
To probe the differences in performance between oxanorbornene and norbornene strained olefinic groups in both (a) RAFT-based macromonomer (MM) synthesis and (b) ROMP-based bottlebrush polymer synthesis via grafting-through polymerization, two RAFT agents were prepared; these were the oxanorbornenyl RAFT agent **7-ONb** and the norbornenyl RAFT agent **8-Nb** (see Scheme 1). Briefly, the alcohol functional imides **3** and **4** were obtained in moderate to high yield from the relevant *exo*-anhydrides **1** and **2** by treatment with ethanolamine as per published literature procedures.[20, 23] Subsequent reaction of the alcohols **3** and **4** with 2-bromopropionyl bromide adapted from the procedure of Keddie *et al*.[24] delivered the alkylating agents **5** and **6**. The RAFT agents **7-ONb** and **8-Nb** were isolated in moderate yield following standard RAFT agent syntheses;[25] i.e. alkylation of the carbodithioate salt derived from dodecanethiol and CS_2.[26]

Kinetic Analysis of RAFT Polymerization

Three monosubstituted monomers of interest were selected for preparation of macromonomers via RAFT polymerization; methyl acrylate (MA), *n*-butyl acrylate (BA), and styrene (St) (see Scheme 2). Importantly, these monomers allow us to probe the effect of electronics and/or sterics in the preparation of (oxa)norbornenyl-functional macromonomers.

MA was the first monomer investigated. Initially, we targeted a number average degree of polymerization (X_n) of 50 (i.e. [MA]:[RAFT] = 50:1), using the RAFT agents **7-ONb** (see Table 1, Entry 1, and Figure 1 (a, b)) or **8-Nb** (see Table 1, Entry 2, and Figure 1 (c, d)). From the SEC data, it can be clearly observed that the oxanorbornene RAFT agent **7-ONb** delivered polymers of higher molar mass and higher dispersity (see Table 1, Entry 1, and Figure 1 (b)) than that of the analogous norbornene RAFT agent **8-Nb** (see Table 1, Entry 2, and Figure 1 (d)). Note, the high percentage "livingness" (*L*%)[27, 28] calculated from kinetic factors indicates the high molar mass shoulder(s) observed in the SEC traces are due to 'branching', formed via reaction of the olefinic RAFT end-groups, rather than chain-coupling via termination by combination (see Table 1). The degree of branching (DB%), a quantification of the presence of branched polymers (i.e. polymer dimers, trimers etc.) calculated by either NMR analysis of olefinic RAFT end-group consumption# or SEC deconvolution, was significantly higher for **7-ONb** than for **8-Nb** (see Table 1 Entries 1 and 2). This is also clearly evidenced by kinetic analysis of the rate of olefinic end-group consumption during polymerization; the oxanorbornene end-group is consumed to a greater extent than that of the norbornene (see Table 1, Entries 1 and 2, and Figure 1 (a) and (c)). Clearly the propensity for cross-propagation of poly(methyl

acrylate) propagating radical (PMA•) to the olefinic polymer end-group is higher for the **7-ONb** based systems than those that use **8-Nb**. We postulate this is likely due to a retro Diels-Alder extrusion of furan from **7-ONb** derived chain-ends during the reaction to produce a more reactive maleimido end-group,‡



Monomers
MA: R = CO_2Me
BA: R = $CO_2{}^nBu$
St: R = Ph

RAFT Macromonomers
PMA-7-ONb: X= O, R = CO_2Me
PBA-7-ONb X= O, R = $CO_2{}^nBu$
PSt-7-ONb X= O, R = Ph
PMA-8-Nb: X= CH_2, R = CO_2Me
PBA-8-Nb X= CH_2, R = $CO_2{}^nBu$
PSt-8-Nb X= CH_2, R = Ph

Scheme 2: RAFT polymerization of MA, BA and St using RAFT agents RAFT agents **7-ONb** and **8-Nb**

Table 1: Details of polymers prepared via RAFT Polymerization

Entry[a]	monomer	[M] (mol L^{-1})	RAFT agent	*T* (°C)	time (h)	M conv. (%)[b]	M_n(calc)[c]	M_n[d]	$Đ$[d]	*L*% (ω-end)[e]	DB% (NMR)[b,f]	DB % (SEC)[f,g]
1	MA	6.79	**7-ONb**	60	0.5	32	1920	2200	1.19	99.9	7	7.3
					1.5	69	3510	4500	1.37	99.6	24	24.3
					2.5	80	3980	5900	1.49	99.4	37	26.5
					3.5	85	4200	7000	1.64	99.2	42	32.7
					5	92	4500	7900	1.80	98.9	47	35.4
2	MA	6.79	**8-Nb**	60	0.5	19	1360	1100	1.12	99.9	4	0
					1.5	57	2990	3200	1.13	99.6	10	4.1
					2.5	76	3810	4400	1.17	99.4	13	9.7
					3.5	85	4200	5000	1.22	99.2	15	14.2
					5	90	4410	5500	1.25	98.9	15	19.2
3	BA	4.68	**7-ONb**	60	0.5	34	2720	2900	1.19	99.9	17	3.4
					1.5	68	4900	6300	1.33	99.6	33	35.3
					2.5	78	5540	7800	1.43	99.4	40	41.6
					3.5	84	5920	8900	1.51	99.2	45	41.6
					4.5	87	6120	9400	1.60	99.0	47	39.2
					6	90	6310	10300	1.69	98.7	49	44.5
4	BA	4.68	**8-Nb**	60	0.5	23	2010	2100	1.14	99.9	5	0
					1.5	63	4580	5000	1.16	99.6	7	5.5
					2.5	77	5470	6200	1.19	99.4	10	9.9
					3.5	83	5860	6900	1.22	99.2	16	13.4
					4.5	87	6120	7400	1.24	99.0	18	15.5
					6	92	6440	7900	1.28	98.7	21	20.0
5	St	8.73	**7-ONb**	65	2	9	1010	–	–	99.1	7	–
					4	12	1160	1500	1.13	98.3	9	5.0
					7	31	2150	2200	1.18	97.4	15	9.4
					10	42	2730	2900	1.20	96.6	20	14.2
					22.5	68	4080	4800	1.33	94.7	34	27.9
6	St	8.73	**8-Nb**	65	2	11	1110	–	–	99.1	4	–
					4	21	1630	1400	1.09	98.3	5	0
					7	36	2410	2000	1.10	97.4	8	0
					10	47	2990	2500	1.09	96.6	11	0
					22.5	82	4810	4200	1.09	94.7	17	1.2

[a][M]$_0$:[RAFT]$_0$:[AIBN]$_0$ =50:1:0.1;[b]calculated from ^{1}H NMR; [c]M_n(calc) = ([M]$_0$ – [M]$_t$)/([RAFT]$_0$) × MW$_{monomer}$+ MW$_{RAFT}$; [d]SEC THF eluent, T = 40°C (data reported in polystyrene equivalents); [e]L%= ([CTA]$_0$/([CTA]$_0$+ df ×[I]$_0$ ×1-e^{kdt}) × 100%,[27, 28] where f is the initiator efficiency (= 0.7),[29]d is number of chains formed by radical-radical termination (= 1),[30]and k_d = 9.67 × 10^{-6} s^{-1}at 60°C[31]or k_d = 1.95 × 10^{-5} s^{-1}at 65°C (calculated from Arrhenius parameters)[31]; [f]DB% = percentage degree of branching; [g]calculated following deconvolution of SEC chromatograms.

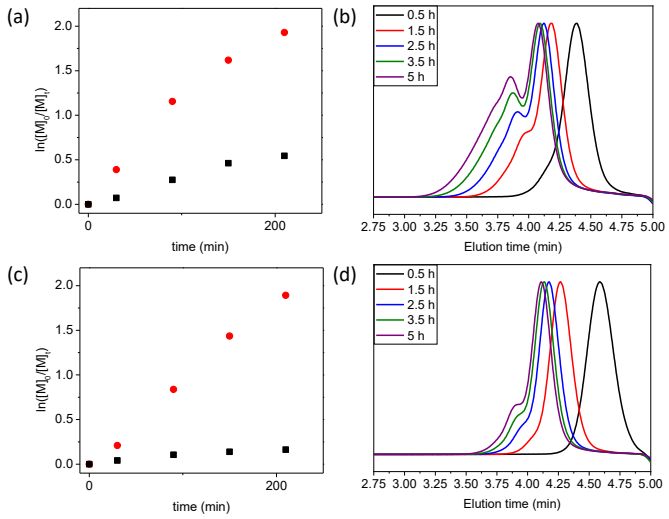
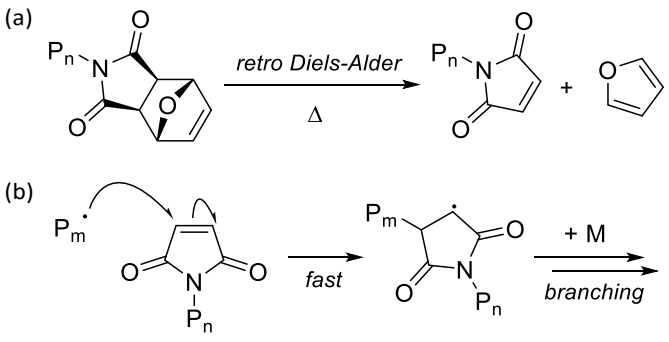


Figure 1: Pseudo-first order kinetics plots (a, c) for conversion of MA (red circles) and (oxa)norbornene end-group (black squares), and SEC chromatograms illustrating the evolution of the molar mass distribution with reaction time (b, d) for polymerizations of MA with the RAFT agents **7-ONb** (a, b) or **8-Nb** (c,d). All polymerizations performed with [MA]:[RAFT] = 50:1.

which can then undergo rapid copolymerization with PMA• (see Scheme 3 (a) and (b)). Indeed estimations of indicative copolymerization reactivity ratios, using the Alfrey-Price Q-e system,[32, 33] indicate a significantly larger preference for PMA• to cross-propagate to a maleimide than to a norbornene.§,¶ When targeting higher chain lengths of X_n = 200 (i.e. [MA]:[RAFT] = 200:1) much the same trends were observed as were for the X_n = 50 examples, with the oxanobornene-based materials displaying higher number-average molar mass (M_n), molar mass dispersity ($Đ$) and degree of branching (DB%) (see Table S1, Entries 1 and 2, and Figure S1 (a) and (b)).

To probe the effect of the acrylate ester chain length on the RAFT system, BA was the next monomer investigated, targeting X_n = 50. Unsurprisingly, the additional sterics from the *n*-butyl ester of the monomer made little difference to the reactivity of the poly(*n*-butyl acrylate) propagating species (PBA•) towards the different end-groups of **7-ONb** and **8-Nb** when compared to the PMA• systems. PBA prepared in the presence of the oxanorbornene **7-ONb** displayed significantly higher M_n, $Đ$ and



Scheme 3: (a) Proposed formation of a maleimide chain-end via retro Diels-Alder reaction, and (b) cross-propagation of propagating polymer species to the maleimide chain-end leading to branching, during RAFT polymerization reactions using the oxanorbornene RAFT agent **7-ONb**. P_n, P_m = polymer chains, M = monomer.

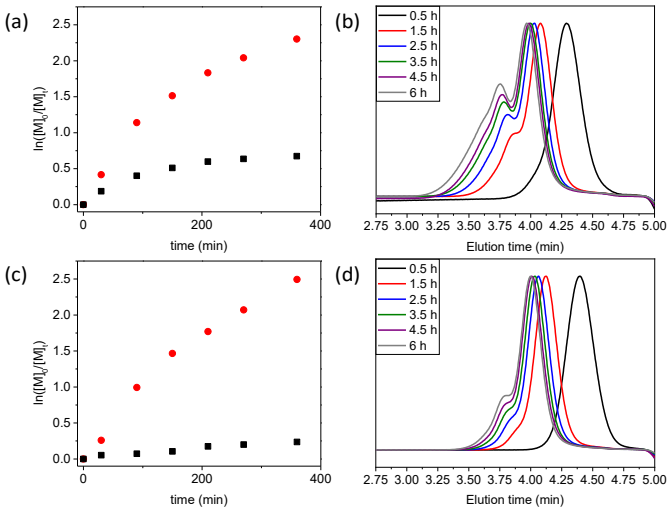


Figure 2: Pseudo-first order kinetics plots (a, c) for conversion of BA (red circles) and (oxa)norbornene end-group (black squares), and SEC chromatograms illustrating the evolution of the molar mass distribution with reaction time (b, d) for polymerizations of BA with the RAFT agents **7-ONb** (a, b) or **8-Nb** (c, d). All polymerizations performed with [BA]:[RAFT] = 50:1.

DB% than the norbornene **8-Nb** prepared PBA examples (see Table 1, Entries 3 and 4, and Figure 2). Again, analogous outcomes were observed when targeting PBA of X_n =200 (see Table S1, Entries 3 and 4, and Figure S1 (c) and (d)).

The final monomer investigated was St, again initially targeting X_n = 50 (i.e. [St]:[RAFT] = 50:1). As with the previous examples discussed above, for St polymerization the oxanorbornene RAFT **7-ONb** agent led to significantly higher M_n, $Đ$ and DB% than the norbornene RAFT agent **8-Nb** (see Table 1, Entries 5 and 6, and Figure 3). Interestingly, for polymerization of St controlled with the norbornene RAFT agent **8-Nb** minimal branching (DB% = 1.2%) was observed, particularly when compared to the acrylate systems (cf. DB% ~20% for MA and BA at ~90% monomer conversion). We attribute this to electronic differences between the electron-rich polystyryl radical (PSt•) and the electron-poor acrylate-based radicals (i.e. PMA• and PBA•). PSt• cross-propagates to the electron-rich norbornene end-group more slowly than do either of the acrylate-based radicals; this observation is in agreement with indicative copolymerization reactivity ratios.[32, 33]§ It appears electronics play a less significant role in the DB% for the oxanorbornene case, which provides further indirect evidence for the contribution of retro Diels-Alder to branching. Indicative copolymerization reactivity ratios, between St and maleimide, suggest a tendency towards alternation which would lead to consumption of a maleimide the chain end. On the other hand an unreacted, electron-rich oxanorbornene

would be expected to behave in much the same way as norbornene in St polymerization (i.e. display conversion via cross-propagation to the chain end). Similar polymerization outcomes were obtained when targeting PSt of X_n = 250 (i.e. [St]:[RAFT] = 250:1) with **7-ONb** delivering materials with higher M_n, $Đ$ and significantly higher DB% than **8-Nb** (see Table S1, Entries 5 and 6, and Figure S1 (e) and (f)).

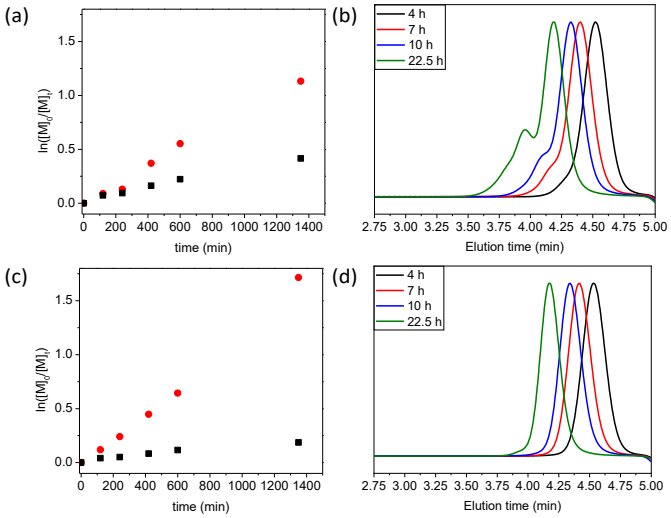


Figure 3: Pseudo-first order kinetics plots (a, c) for conversion of St (red circles) and (oxa)norbornene end-group (black squares), and SEC chromatograms illustrating the evolution of the molar mass distribution with reaction time (b, d) for polymerizations of St with the RAFT agents **7-ONb** (a, b) or **8-Nb** (c, d). All polymerizations performed with [St]:[RAFT] = 50:1.

In summary, cross propagation of the propagating species (PMA•, PBA• and PSt•) to the olefinic RAFT chain-end was found to occur in all cases discussed, albeit to varying degrees. This results in a proportion of branched structures, a generally undesired topological 'impurity' in the final polymer sample.

This is also is expected to adversely impact the preparation of the targeted bottlebrush copolymers due to the (partial) consumption of the ROMP polymerizable end-group. It is clear from the results discussed above that **8-Nb** is the preferred RAFT agent for preparing macromonomers from monosubstituted monomers via RAFT. Significantly more 'defects' in the macromonomer structure is the trade-off of using the more easily prepared **7-ONb** instead of **8-Nb**. It should be noted, even when using the norbornene-based RAFT agent **8-Nb** in the polymerization of the acrylates MA and BA significant end-group consumption was observed (up to 20%, see Table 1, Entries 2 and 4). To decrease the incidence of these 'defects' in the synthesis of MMs we recommend targeting higher molar masses and quenching the reaction at lower conversion; from a copolymerization standpoint this effectively decreases the monomer feed ratio of the norbornene chain-end reducing the rate of cross-propagation.

Macromonomer synthesis via RAFT Polymerization

Following on from the kinetic investigations described above, we successfully prepared three macromonomers based on MA, BA, and St with low molar masses (~2000-4000 g mol^{-1}) by RAFT polymerization using the RAFT agents (**7-ONb** or **8-Nb**). The reactions used to prepare the MMs were quenched after the desired time and purified by precipitation three times in methanol to completely remove any unreacted monomer present. ^{1}H-NMR spectroscopy and size exclusion chromatography (SEC) were used to characterize the resulting MMs. The properties of prepared MMs are summarized in Table 2 and SEC chromatograms are shown in Figure 4 (black traces). Akin to the data described above, the norbornenyl RAFT agent **8-Nb** delivered MMs with the lowest $Đ$ and DB% in the case of each monomer (see Table 2 entries 2, 4 and 6.). The oxanorbornenyl RAFT agent **7-ONb** resulted in higher dispersities (and biomodality in the molar mass distribution) (see Entries 1, 3 and 5, Table 2). Compared to styrene MMs, the acrylates MMs exhibit slightly higher dispersities and DB% (see Table 2 and Figure 4-black traces).

ROMP of Macromonomers

Grafting-through polymerization via ROMP of the (oxa)norbornene macromonomers (see Table 2) was carried out in THF using MM to catalyst ratio 25:1 with Grubbs' third generation catalyst **G3** (see Scheme 4 and Table 3). Exhibiting rapid initiation kinetics and high functional-group tolerance, **G3** is well known to successfully polymerize sterically hindered substrates, allowing for synthesis of polymers with narrow molar mass distributions.

Due to the difference in thermal stability between the RAFT agents **7-ONb** and **8-Nb** and their behaviour in RAFT polymerization (i.e. higher DB%) as described above, it was found that the bottlebrush polymers based on the **7-ONb** have higher levels of residual MM than those prepared using **8-Nb**; ROMP of MMs based on **8-Nb** gives bottlebrush polymer with low amount of MMs residue (≤5%).

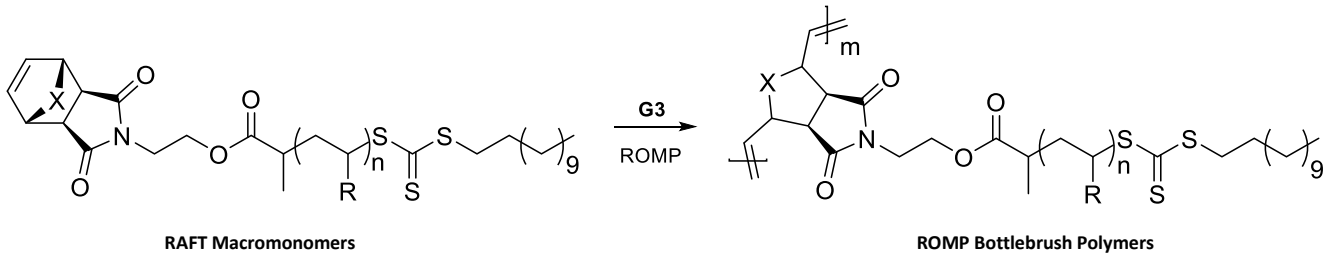
Bottlebrush polymers with [MM]/[I] ratio of 50:1 were prepared and full characterization attempted, however the polymers contained fractions that were larger than the exclusion limit of our SEC columns, limiting the ability to assess their molar masses and dispersity accurately (see Table S2 and Figure S2 in the supplementary information). With this drawback aside these materials displayed similar MM incorporation for the [MM]/[I] 25:1 samples.

From these experiments it is clear that using the less effective **7-ONb** in the RAFT synthesis of MMs also leads to a less desirable outcomes (e.g. higher residual MM%) in the sequential RAFT/ROMP process for preparation of bottlebrush polymers than the use of **8-Nb**. We postulate that the altered architecture of the MMs derived from **7-ONb** and the related decrease in the amount of "ROMP-able" end-groups per unit mass of MM (both due to the enhanced presence of branched MMs formed during the RAFT syntheses) contributes to the poorer performance of oxanorbornene-based MMs in the preparation of bottlebrush polymers.

Table 2: Details of macromonomers prepared via RAFT Polymerization

Entry	Macromonomer	time (h)	$M_{n(NMR)}$ (g mol^{-1})[a]	$M_{n(GPC)}$ (g mol^{-1})[b]	Đ[b]	L (ω-end)[c]	DB % (SEC)[d,e]
1	**PMA-7-ONb**	1	2700	3300	1.24	99.8	15
2	**PMA-8-Nb**	1.5	3100	3600	1.15	99.6	6
3	**PBA-7-ONb**	1	4300	5600	1.28	99.8	20
4	**PBA-8-Nb**	1	3400	3900	1.14	99.8	2
5	**PSt-7-ONb**	10	3100	2900	1.19	96.6	1
6	**PSt-8-Nb**	10	2800	2500	1.08	96.6	0

[a]Calculated from ^{1}H NMR; [b]SEC THF eluent, T = 40°C (data reported in polystyrene equivalents); [c]L%= ([CTA]$_0$/([CTA]$_0$+ df ×[I]$_0$ ×1-e^{kdt}) × 100%,[27, 28] where f is the initiator efficiency (= 0.7),[29]d is number of chains formed by radical-radical termination (= 1),[30] and k_d = 9.67 × 10^{-6} s^{-1} at 60°C[31] or k_d = 1.95 × 10^{-5} s^{-1} at 65°C (calculated from Arrhenius parameters)[31]; [d]DB % = percentage degree of branching; [e]calculated following deconvolution of SEC chromatograms.



Scheme 4: Grafting-through ROMP polymerization of RAFT Macromonomers (**PMA-7-ONb**, **PBA-7-ONb**, **PSt-7-ONb**, **PMA-8-Nb**, **PBA-8-Nb**, **PSt-8-Nb**).

Table 3: Details of bottlebrush polymer prepared via ROMP

Entry[a]	Macromonomer (MM)	MM M_n (g mol^{-1})[b]	Residual MM %	M_n(GPC) (g mol^{-1})[d]	Đ[c]
1	**PMA-7-ONb**	2700	11	117000	1.29
2	**PMA-8-Nb**	3100	3	125000	1.35
3	**PBA-7-ONb**	4300	37	162000	1.27
4	**PBA-8-Nb**	3200	5	117000	1.23
5	**PSt-7-ONb**	2900	20	53000	1.40
6	**PSt-8-Nb**	2800	4	90000	1.58

[a][MM] = 0.33M in THF, [MM]/[**G3**]=25, t = 3 h, [b]Calculated from ^{1}H NMR; [c]From SEC THF eluent, T = 40°C (data reported in polystyrene equivalents)

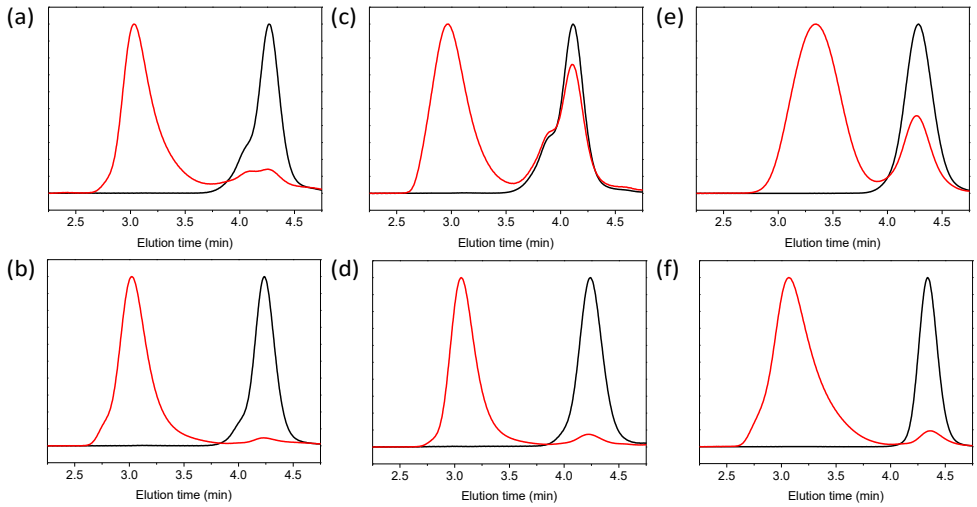


Figure 4: SEC chromatograms of macromonomers (black) and bottlebrush copolymers (red) for polymerizations of (a) **PMA-7-ONb**, (b) **PMA-8-Nb**, (c) **PBA-7-ONb**, (d) **PBA-8-Nb**, (e) **PSt-7-ONb** and (f) **PSt-8-Nb**. Polymerizations were performed [MM]:[**G3**] = 25:1.

Conclusions

Two new RAFT agents with either an oxanorbornenyl or norbornenyl moiety were successfully prepared. The design of RAFT agent has been found to affect the RAFT polymerization and hence the sequential ROMP process. Three different monomers (MA, BA, and St) were selected for RAFT polymerizations. The thermal stability of RAFT agents, as well as the monomer electronics and sterics, were found to affect the resultant MMs structure and molar mass distribution.

In the case of oxanorbornenyl RAFT agent **7-ONb**, the polymerization analysis revealed the increasing of branching as function of conversion, due to copolymerization to a maleimide end-group following thermal extrusion of furan. On the other hand, the RAFT agent with norbornenyl moiety **8-Nb** is more thermally stable and yields MMs with low branching, due to the limited copolymerization reactivity of norbornenyl alkene towards acrylate or styrene propagating species. The more significant "imperfections" in the **7-ONb** derived MMs (in comparison to those prepared using **8-Nb**) were found to affect the molecular properties of the bottlebrush polymers prepared via ROMP; NMR and SEC analysis revealed significant differences residual MM concentration following polymerization.

Author Contributions

MN: investigation, data analysis, drafted sections of original manuscript, review and editing of manuscript; KN: data analysis, peak fitting and deconvolution of SEC data, review and editing of the manuscript; DJK: conceptualization, investigation, data analysis, drafted sections of original manuscript, supervision, review and editing of manuscript.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

[#]The conversion of the (oxa)norbornene end-group is calculated in the same standard manner that conversion of the vinyl monomer is achieved; the resonances from vinylic end-groups are well resolved in all cases. A representative example can be found in the supplementary information (Figure S1).

‡No categorical evidence of *in situ* maleimide end-group formation could be observed in NMR analysis of the kinetic samples or of the final product polymers. We believe this is due to its rapid consumption upon its formation and coupled the low feed ratio rendering analysis of the molecular microstructure difficult. Additionally, the furan by-product was also not observed, presumably due to its volatility; all kinetic samples were taken directly from the polymerization reaction mixtures which were higher in temperature than the boiling point of furan (31 °C).

§Indicative copolymerization reactivity ratios, calculated from Q-e values, for norbornene systems: methyl acrylate (MA)/norbornene (Nor): - r_{MA} = 3.90, r_{Nor} = 0.181; *n*-butyl acrylate (BA)/norbornene (Nor) -r_{BA} = 5.83, r_{Nor} = 0.146; styrene (St)/norbornene (Nor) -r_{St} = 7.25 r_{Nor} = 0.045.

¶Indicative copolymerization reactivity ratios, calculated from Q-e values, for maleimide systems: methyl acrylate (MA)/maleimide (MI) - r_{MA} = 0.36, r_{MI} = 2.62; *n*-butyl acrylate (BA)/maleimide (MI) - r_{BA} = 0.47, r_{MI} = 1.81; styrene (St)/maleimide (MI) - r_{St} = 0.178, r_{MI} = 0.170.

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