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ROMP from ROMP: A New Approach to Graft Copolymer Synthesis

Matthew J. Allen,[†,§] Kittikhun Wangkanont,[†] Ronald T. Raines,[†,‡] and Laura L. Kiessling*[,†,‡]

[†]*Department of Chemistry and* [‡]*Department of Biochemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706.* [§]*Present address: Department of Chemistry, Wayne State University, Detroit, MI 48202*

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ABSTRACT: A new strategy is presented for the synthesis of graft copolymers using only the ring-opening metathesis polymerization (ROMP). From a ROMP-derived main chain, pendant maleimide functional groups are converted into norbornene moieties via a Diels−Alder reaction with cyclopentadiene. The norbornene groups serve as sites of initiation, and subsequent ROMP from the main chain yields graft copolymers with both main and side chains derived from ROMP. This strategy offers ready access to defined graft copolymers.

Introduction

Graft copolymers are essential components of many materials, including chemically and thermally resistant plastics, thermoplastic elastomers, compatibilizers, and polymeric emulsifiers.[1] Graft copolymers must be produced in large quantities for products that range from food packaging materials to automobile parts and biomaterials.[2] Methods are needed to generate new graft copolymers of varying architectures and chemical compositions because these features directly influence bulk physical, mechanical, and electronic properties.[3]

Discrete branched polymers are generated by using one of three complementary methods: grafting *onto* a main chain, grafting *through* macromonomers, or grafting *from* a main chain.[4] Typically, two orthogonal polymerization techniques are used to avoid cross-linking during the synthesis of the main chain and side chains.[5] An exception to the use of orthogonal polymerization techniques involves ROMP *through* ROMP-derived macromonomers to form all ROMP-derived graft copolymers.[6] In this synthetic strategy, both the main chain and side chains benefit from the attributes of ROMP, which include the high functional group tolerance of the ruthenium-based initiators, the ability to conduct a living polymerization, and the availability of bulk quantities of monomers.[7] Still, synthetic methods that complement this approach would be valuable. Specifically, a method that provides access to lower density graft copolymers would facilitate the preparation of new kinds of materials.

We postulate that the unique structures of branched polymers could render them powerful probes for chemical biology.[8] Following on the first disclosure that bioactive polymers can be generated by ROMP,[9] a number of researchers have used ROMP to produce polymers for biological applications.[10,11] Because of their architectures, ROMP-derived graft copolymers could function as scaffolds for the display of biologically active ligands in orientations inaccessible to linear polymers. Accordingly, methods to vary graft density would be valuable as the resulting materials could be used to probe biological recognition modes and to optimize potency. To date, all the ROMP-derived graft copolymers synthesized by grafting *through* ROMP-derived macromonomers yield grafts at every main-chain position. In contrast, the grafting *from* approach offers control of side-chain density.

ROMP has been used to generate polymers from solid supports,[12] yet there have been no reports of grafting *from* discrete, soluble polymers using ROMP.[13] Here, we describe the formation of soluble graft copolymers with main chains and side chains that both are derived from ROMP. In our approach, ROMP is used to assemble a main chain containing a high density of maleimide functional groups. Using the Diels−Alder reaction, these groups are converted into norbornene moieties from which ROMP can be initiated to form graft arms. The graft arms are designed to contain functional groups that allow for postpolymerization modification.[10,14] In this way, our strategy provides access to a new class of graft copolymers, whose attributes can be controlled.

Experimental Section

Materials. Commercial chemicals were of reagent-grade purity or better and were used without further purification unless noted otherwise. When employed as a solvent in reaction mixtures, tetrahydrofuran (THF) was distilled from sodium with benzophenone and methylene chloride from calcium hydride. THF used in size-exclusion chromatography (SEC) was inhibitor-free, high-performance liquid chromatography (HPLC) grade. Ethyl vinyl ether was distilled prior to use. Norbornene maleimide (**1**),[15] the ruthenium carbene (H_2IMes)(3-Br-py)$_2$Cl$_2$Ru=CHPh (**2**),[16] and norbornene α-chloroamide (**5**)[17] were synthesized following procedures described previously. Analytical thin-layer chromatography (TLC) was carried out on EM Science TLC plates precoated with silica gel 60 F_{254} (250 μm layer thickness). TLC visualization was accomplished by using a UV lamp and charring with potassium permanganate stain (3 g of $KMnO_4$, 20 g of K_2CO_3, 5 mL of 5% w/v aqueous NaOH, 300 mL of H_2O). Microwave reactions were performed in a CEM Discover microwave reactor that was monomode, equipped with an autosampler (CEM Explorer), and interfaced with a computer running CEM ChemDriver software (Version 3.5.4). Microwave reactions were carried out with stirring, a 275 W maximum power setting, and a 350 psi maximum pressure setting.

Characterization. ^{1}H NMR spectra were obtained with a Varian INOVA 600 (600 MHz) spectrometer. Chemical shifts were referenced relative to residual solvent signal (DMSO-d_6: ^{1}H: δ 2.50). Multiplets are reported as "m", and resonances that

*Corresponding author. E-mail: kiessling@chem.wisc.edu.

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Table 1. Molecular Weights of Polymers 6a−i

polymer	initiator (equiv)[a]	$M_{n,theory}$ (g mol^{-1})	$M_{n,SEC}$ (g mol^{-1})	$M_{w,SEC}$ (g mol^{-1})	M_w/M_n
6a	55	17 000	26 000	84 000	3.18
6b	50	16 000	23 000	72 000	3.09
6c	45	14 000	22 000	69 000	3.15
6d	40	12 000	22 000	64 000	2.98
6e	35	9 800	19 000	67 000	3.48
6f	26	16 000	24 000	43 000	1.84
6g	20	14 000	21 000	40 000	1.90
6h	15	12 000	15 000	41 000	2.64
6i	8	9 500	16 000	44 000	2.66

[a] Equivalents of initiator per 100 potentially reactive main-chain sites.

appear as broad singlets are designated as "br s". Room temperature SEC was performed using THF as an eluant (1.0 mL/min) to determine M_w, M_n, and polydispersity index (M_w/M_n) values using a Beckman Coulter HPLC system equipped with two Polymer Laboratories PLgel 5 μm MIXED-D columns (300 × 7.5 mm) in series. Columns were calibrated with 10 narrow polystyrene standards (Polymer Laboratories EasiCal Polystyrene Standards (PS-1)), and data reduction was performed with Cirrus GPC offline GPC/SEC software Version 1.2.

Polynorbornene Maleimide, 3. A solution of norbornene maleimide, **1** (100 mg, 0.49 mmol, 15 or 30 equiv), in CH_2Cl_2 (2 mL) under Ar was protected from light and cooled to −78 °C. To this mixture, a solution of catalyst precursor **2** (1 equiv) in CH_2Cl_2 (0.5 mL) at −78 °C was added. The mixture was stirred vigorously and then allowed to warm to ambient temperature. After 1 h, monomer consumption was complete as judged by TLC. Ethyl vinyl ether (0.5 mL) was added to terminate the polymerization, and the mixture was stirred for 15 h. The polymer product was triturated into diethyl ether (45 mL). The resulting heterogeneous mixture was subjected to centrifugation, and the solvent was removed by decanting. The resulting solid was washed with diethyl ether (2 × 45 mL), and the product was dried under vacuum to yield **3** as a brown solid.

3 (n = 16). Yield = 90 mg (84%). ^{1}H NMR (600 MHz, DMSO-d_6): δ = 0.99 (br s), 1.36 (br s), 1.49 (br s), 1.78 (br s), 1.97 (br s), 2.46 (br s), 2.84 (br s), 4.98−5.52 (m, 28H, main-chain olefin protons), 6.31 (br s, 1H, end-cap olefin proton), 6.95 (br s, 27H, maleimide protons), 7.18−7.35 (m, 5H, phenyl end-cap protons); degree of polymerization (DP) (^{1}H NMR end-cap analysis) = 13; $M_{n,theory}$ = 3200 g mol^{-1}; $M_{n,NMR}$ = 2700 g mol^{-1}; $M_{n,SEC}$ = 5400 g mol^{-1}; $M_{w,SEC}$ = 8000 g mol^{-1}; M_w/M_n (SEC) = 1.48.

3 (n = 28). Yield = 76 mg (71%). ^{1}H NMR (600 MHz, DMSO-d_6): δ = 0.99 (br s), 1.36 (br s), 1.49 (br s), 1.78 (br s), 1.97 (br s), 2.46 (br s), 2.84 (br s), 4.98−5.52 (m, 52H, main-chain olefin protons), 6.31 (br s, 1H, end-cap olefin proton), 6.95 (br s, 51H, maleimide protons), 7.18−7.35 (m, 5H, phenyl end-cap protons); degree of polymerization (DP) (^{1}H NMR end-cap analysis) = 25; $M_{n,theory}$ = 6200 g mol^{-1}; $M_{n,NMR}$ = 5200 g mol^{-1}; $M_{n,SEC}$ = 8700 g mol^{-1}; $M_{w,SEC}$ = 17 000 g mol^{-1}; M_w/M_n (SEC) = 1.97.

Polynorbornene Norbornene, 4. Polymer **3** was dissolved in CH_2Cl_2 to a concentration of 20 mg/mL. The resulting solution (1 mL) was mixed with freshly cracked cyclopentadiene (2 mL). The reaction mixture was heated to 50 °C in a microwave for 5 min with a 30 s ramp time to reach the desired temperature. The resulting polymer product was triturated with diethyl ether (45 mL) and then subjected to centrifugation. The solvent was then removed by decanting. The resulting solid was washed with diethyl ether (2 × 45 mL), and the product was dried under vacuum to yield **4** as a tan solid.

4 (n = 16). Yield = 23 mg (84%). ^{1}H NMR (600 MHz, DMSO-d_6): δ = 1.01 (br s), 1.27 (br s), 1.44 (br s), 1.53 (br s), 1.80 (br s), 2.01 (br s), 2.41 (br s), 2.83 (br s), 5.05−5.52 (m, 32H, main-chain olefin protons), 6.01 (br s, 32H, side-chain norbornene olefin protons), 6.30 (br s, 1H, end-cap olefin proton), 7.18−7.51 (m, 5H, phenyl end-cap protons); DP (^{1}H NMR end-cap analysis) = 16; $M_{n,theory}$ = 3600 g mol^{-1}; $M_{n,NMR}$ = 4400 g mol^{-1}; $M_{n,SEC}$ = 6200 g mol^{-1}; $M_{w,SEC}$ = 9400 g mol^{-1}; M_w/M_n (SEC) = 1.50.

4 (n = 28). Yield = 20 mg (75%). ^{1}H NMR (600 MHz, DMSO-d_6): δ = 1.01 (br s), 1.27 (br s), 1.44 (br s), 1.53 (br s), 1.80 (br s), 2.01 (br s), 2.41 (br s), 2.83 (br s), 5.05−5.52 (m, 56H, main-chain olefin protons), 6.01 (br s, 56H, side-chain norbornene olefin protons), 6.30 (br s, 1H, end-cap olefin proton), 7.18−7.51 (m, 5H, phenyl end-cap protons); DP (^{1}H NMR end-cap analysis) = 28; $M_{n,theory}$ = 6800 g mol^{-1}; $M_{n,NMR}$ = 7600 g mol^{-1}; $M_{n,SEC}$ = 11 000 g mol^{-1}; $M_{w,SEC}$ = 39 000 g mol^{-1}; M_w/M_n (SEC) = 3.43.

Graft Copolymers, 6a−i. Diels−Alder product **4** was dissolved in CH_2Cl_2 and cooled to −78 °C. A cooled solution of initiator **2** (8−55 equiv) was added. The reaction mixture was stirred and warmed to ambient temperature for 10 min (color change from green to yellow was an indication of initiation). The solution was cooled to −78 °C, and a cooled solution of norbornene α-chloroamide monomer **5** was added. The mixture was stirred vigorously and then allowed to warm to ambient temperature. After 1 h, monomer consumption was complete, as indicated by TLC. Excess ethyl vinyl ether was added to terminate the polymerization, and the reaction mixture was stirred for 15 h. The polymer product was triturated into diethyl ether (45 mL) and collected by centrifugation. After decanting of the solvent, the resulting solid was precipitated from CH_2Cl_2 into diethyl ether twice, and the product, **6a−i**, was dried under vacuum. ^{1}H NMR (600 MHz, DMSO-d_6): δ = 1.07 (br s), 1.44 (br s), 1.57 (br s), 1.79 (br s), 2.08 (br s), 2.94 (br s), 3.13 (br s), 4.00 (br s, NC*H*$_2$), 4.86−5.56 (m, main-chain olefin protons), 6.00 (br s, norbornene olefin protons, **6g−i** only), 6.36 (m, end-cap olefin proton), 7.17−7.38 (m, phenyl end-cap protons), 8.11 (br s, N*H*). See Table 1 for $M_{n,theory}$, $M_{n,SEC}$, $M_{w,SEC}$, and M_w/M_n (SEC).

Results and Discussion

We envisioned using ROMP to synthesize a new class of graft copolymers. Our plan was to generate a linear polymer from which side chains could be introduced using ROMP. To avoid a complex mixture of elongated and cross-linked products, we designed a strategy that employs "latent norbornene" side chains. We had shown previously that maleimide groups are compatible with ROMP and that they can be converted to norbornene moieties via a postpolymerization Diels−Alder reaction.[15] Because of these favorable traits, we used maleimide side chains as latent norbornene groups that could serve as sites for subsequent side-chain elongation.

Norbornene-functionalized main-chain polymer **4** can be generated from a solution of homopolymer **3** using an approach we developed previously for preparing resin-bound block copolymers (Scheme 1).[15] A maleimide-containing monomer **1** was polymerized to yield "latent norbornene"-functionalized polymer **3** using Grubbs catalyst precursor **2**. Ruthenium carbene **2** was chosen for its excellent functional group tolerance and fast

initiation rate.[16,18] The resulting maleimide side chains were converted efficiently to the norbornene units of polymer **4** via a Diels−Alder reaction with cyclopentadiene (Figure 1).

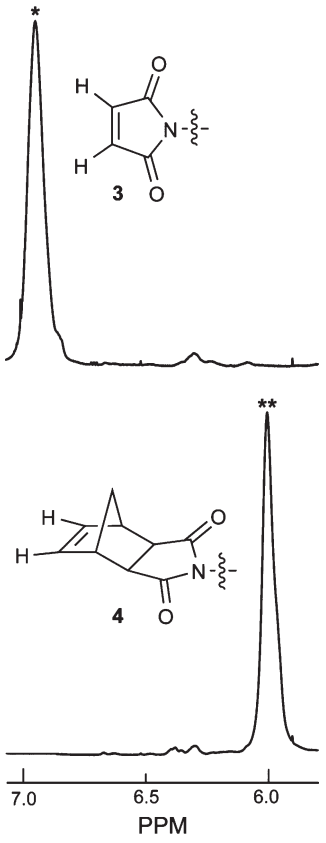


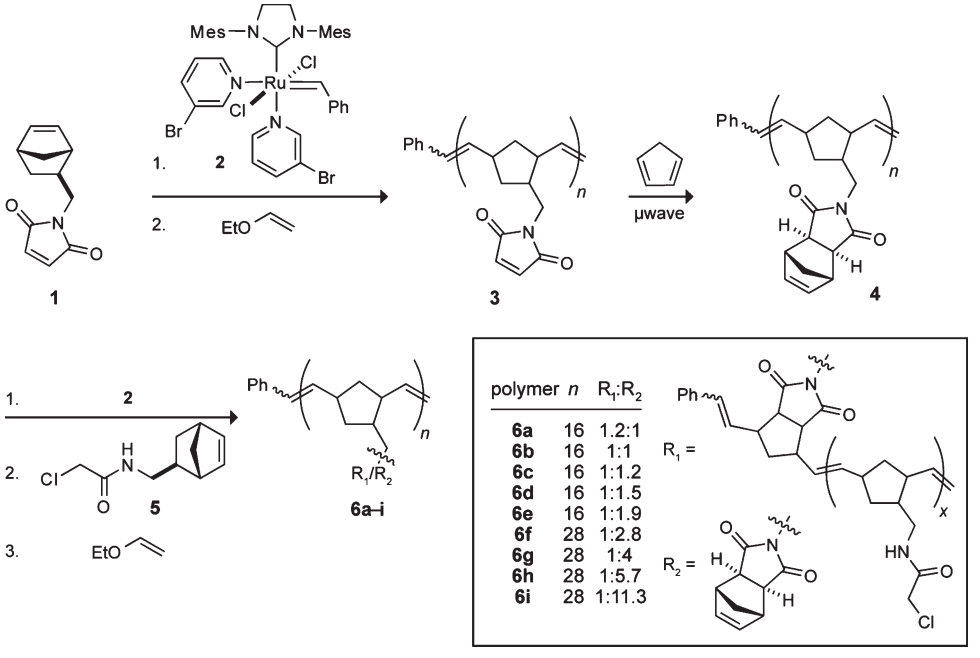
Figure 1. ^{1}H NMR spectra of maleimide-containing polymer **3** and norbornene containing polymer **4**. A region diagnostic of polymer modification is shown before (**3**) and after (**4**) the Diels−Alder reaction with cyclopentadiene. The spectra show that the olefinic protons of the maleimide groups (*) disappear and olefinic protons of norbornene moieties (**) appear, indicating that the conversion of **3** to **4** proceeds in high yield.

To assess the heterogeneity of main-chain polymers **3** and **4**, we used end-cap analysis and polydispersity index (M_w/M_n) determination. The number-average molecular weight determined using NMR spectroscopy ($M_{n,NMR}$) and that calculated based on theoretical yield ($M_{n,theory}$) were similar; these values were within 16% and 22% of each other for polymers **3** and **4**, respectively, and the difference in $M_{n,NMR}$ between **3** and **4** was close to that expected (values included in the Experimental Section). Polydispersity index (M_w/M_n) values were moderate but did not increase upon conversion of **3** to **4**. These properties demonstrate that our system offers control over the length and polydispersity of main-chain polymers **3** and **4** and that the conversion of maleimide to norbornene moieties is efficient.

We anticipated that the norbornene residues in **4** could function as sites of initiation of ROMP to generate graft copolymers (Scheme 1). Accordingly, we first exposed main-chain polymer **4** (n = 16) to various ratios of catalyst precursor **2**, such that the polymerization would yield side-chain graft densities of 35−55% (Table 1). In each case, a color change from green to yellow was observed, which is indicative of initiation; monomer **5** was added subsequently. This monomer was chosen because it contains an α-chloroacetamide group, which can be used to append biologically active ligands[17] and because it offers unique ^{1}H NMR chemical shifts to aid in product analysis. The polymerization of **5** was terminated by the addition of ethyl vinyl ether to yield graft copolymers **6a**−**e**, in which the graft density was between 35 and 55% of the maximum possible. We tested densities below 100% because our synthetic route was devised to provide access to low-density graft copolymers.

To explore the scope and utility of our system, we analyzed the polymer products by several methods, including size-exclusion chromatography (SEC) and ^{1}H NMR spectroscopy. We also determined M_w/M_n values of the synthetic copolymers (Table 1 and Figure 2). The results of these studies were consistent with the formation of graft copolymers; however, we observed another signal in the SEC traces that suggested a smaller polymer was formed (Figure 2A). This polymer appears to arise from the homopolymerization of monomer **5**. The ratio of the area of the homopolymer peak and the total polymer peak area was used to

Scheme 1. Synthetic Route to Graft Copolymers 6a−i[a]



[a] The n values refer to the degree of polymerization determined for polymer **4** by ^{1}H NMR analysis.

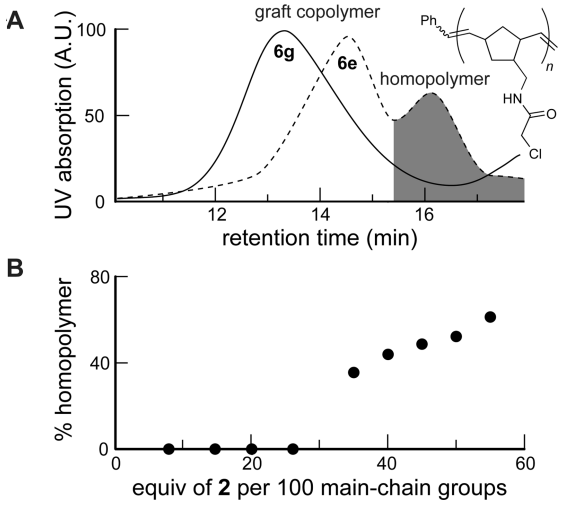


Figure 2. Control of side-chain density in graft copolymers. (A) SEC−UV (λ = 254 nm) traces of **6e** and **6g** showing presence or absence of a shoulder (gray area) with a retention time greater than that of the graft copolymer. The shoulder is likely due to the depicted homopolymer. (B) Graph of the ratio of homopolymer to total polymer as a function of catalyst equivalents, determined by measuring the area of the SEC traces of **6a**−**i**.

estimate the relative abundance of the products (Figure 2B). Because there was not baseline separation between the peaks, Cirrus software was used to determine the area of each peak, using a straight line from the trough between the peaks to the baseline (Figure 2A). This straight-line splitting of the peaks was used to determine the M_w/M_n values of graft copolymers **6a**−**e** that are listed in Table 1.

The amount of homopolymer increased as the graft density was raised from 35% to 55%. Because initiator **2** and graft copolymer precursor **4** were combined prior to the addition of monomer **5**, this monomer should undergo polymerization only if reactive sites on the backbone of **4** fail to participate in elongation. The generation of more homopolymer at higher initiator loadings would therefore arise if not all of the potentially reactive sites on polymer **4** are sterically accessible. Alternatively, homopolymer might arise because intrachain cross-linking (from one norbornene to another) terminates side-chain polymerization. If the latter process dominates, even low initiator loading levels should give rise to homopolymer.

To distinguish between these mechanisms, we synthesized a second series of polymers **6f**−**i**, using initiator loadings that should decrease the graft density to even lower levels (8−26%). This series was generated from a polymer of longer length (n = 28) because we reasoned that if intrachain cross-linking is the major unwanted side reaction, longer polymers would be more challenging substrates. Gratifyingly, with graft densities of 26% or lower, no homopolymer was produced. Thus, by decreasing the level of initiator, the formation of graft copolymers is preferred.

The aforementioned conclusions resulting from the SEC data rest upon three assumptions. First, monomer **5** is consumed completely, an assumption that is supported by thin-layer chromatography analysis of the reactions. Second, if a polymer does not begin as a graft *from* the main chain, then it is never incorporated into a graft copolymer. In principle, other grafting processes could occur; however, we minimized their contribution by exposing polymer **4** to the ruthenium carbene initiator prior to monomer addition. Third, we assumed that the extinction coefficients of the homopolymer and copolymers are similar. This assumption is reasonable given that the electronic environments of the alkene groups in the homopolymers and copolymers should not differ dramatically. Data analysis using these assumptions indicates that our synthetic approach is complementary to the grafting *through* strategy. The latter necessarily yields polymers of 100% graft density, and our approach provides access to materials with lower graft densities with excellent control.

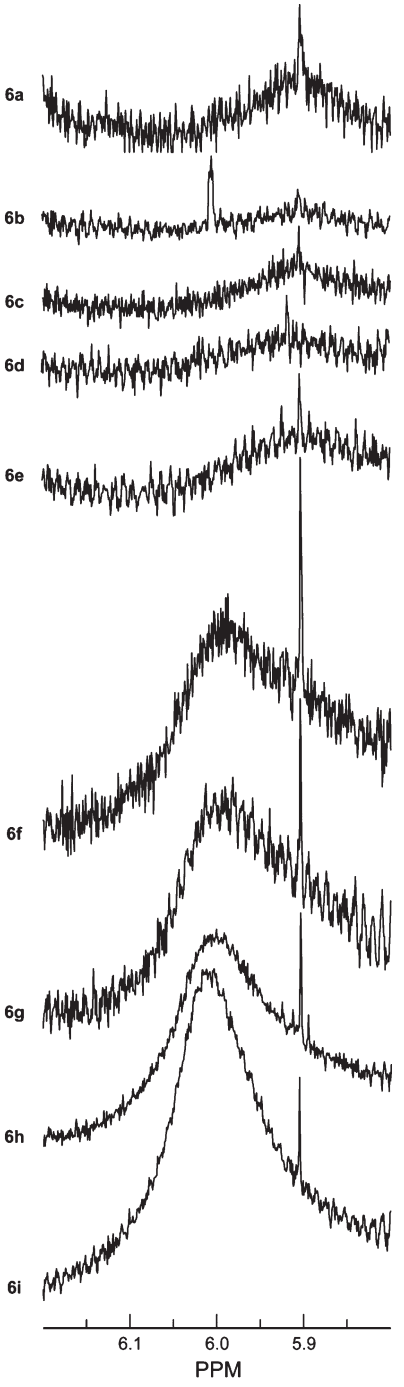


Figure 3. ^{1}H NMR spectra of graft copolymers **6a**−**i** indicates that only polymers **6f**−**i** give rise to the expected signal (~6 ppm) for the olefinic norbornene protons.

While the SEC analysis of polymers **6a**−**i** provides the means to evaluate the ratio of graft copolymer and homopolymer, it does not provide insight into the structure of the resulting materials. We therefore applied ^{1}H NMR spectroscopy to characterize graft copolymers **6a**−**e**. These substances, which were prepared using high initiator ratios, failed to give rise to a signal for the olefinic norbornene protons (Figure 3). This absence is likely is due to the formation of hyperbranched polymers. Although hyperbranching could occur through

interchain cross-linking (norbornene groups on different main chains undergo metathesis) or incorporation of main chains into side chains (norbornene groups on polymer **4** are incorporated into side chains during ROMP of monomer **5**), kinetic barriers should limit these processes. Consequently, the data are most consistent with intrachain cross-linking. Specifically, at high initiator loadings the density of side chains will increase, and the resulting unfavorable steric effects should slow the rate of side-chain elongation. In this situation, intrachain cross-linking should compete favorably with elongation. We would therefore expect that in the preparation of polymers **6f−i**, which possess low graft densities, side-chain elongation would be favored over hyperbranching. The presence of signals consistent with the unreacted norbornene alkene in polymers **6f−i** is consistent with these expectations. We conclude that steric effects have a major influence on the structure of the resulting graft copolymers.

Conclusions

We have described the first all-ROMP-derived graft copolymers generated in a grafting *from* strategy. Our grafting *from* a main-chain approach is useful for generating graft copolymers with a low density of side chains and hence is complementary to the grafting *through* macromonomers synthetic strategy. A key feature of our synthetic strategy is the use of a dienophilic precursor, which serves as a "latent norbornene". The Diels−Alder reaction, which provides an efficient means to install norbornene groups, is a mild and chemoselective process. Thus, the general strategy that we have outlined should be generally applicable to the synthesis of functionalized polymers. Moreover, the specific route we developed provides access to unique macromolecular scaffolds to which a wide variety of groups can be appended. In this way, the graft copolymers can be converted to a wide variety of new materials, including bioactive polymers. ROMP offers the ability to synthesize these new polymers on large scale, which facilitates the analysis of their material and biological properties.

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Supporting Information Available: SEC traces and ^{1}H NMR spectra of all polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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