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Synthesis of Star Block Copolymers by Controlled Ring-Opening Metathesis Polymerization

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ABSTRACT: The norbornadiene dimer, *exo-trans-exo*-pentacyclo[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradeca-5,11-diene (1), can be used in living ring-opening metathesis polymerization as a cross-linking reagent for the controlled synthesis of star-shaped polymers. Star polymers are formed when a few equivalents of 1 is added to living polynorbornene initiated with $W(CHR)(NAr)(O\text{-}t\text{-}Bu)_2$ or $Mo(CHR)(NAr)(O\text{-}t\text{-}Bu)_2$. Addition of 1 to the initiators first followed by addition of norbornene results in formation of a gel. The reactivity of the living alkylidene plays an important role in determining star formation, and certain functionalized polymers such as 2,3-dicarbomethoxynorbornadiene can form star copolymers quantitatively only when several equivalents of norbornene is added to the living polymer before 1 is added. Reactive alkylidenes such as living poly(5-cyanonorbornene) can be quantitatively converted into living star polymers, which upon treatment with relatively unreactive monomers such as 2,3-bis(trifluoromethyl)norbornadiene give "heterostar" polymers, since all the sites in the star core can serve as initiators.

Introduction

The development of particular macromolecular structures and architectures has been heavily influenced by the development of living polymerization systems.[1,2] So far these have been transition-metal-free polymerizations, i.e., anionic, cationic, and group-transfer systems.[3] The relatively recent discovery of well-defined transition-metal catalysts for the controlled ring-opening metathesis polymerization (ROMP) of mono- and polycyclic olefins[4] has permitted the synthesis of interesting materials such as functionalized block copolymers,[5] polyacetylene,[6] polyenes,[7] and stereoregular fluorinated polymers.[8] Therefore we set out to determine whether living ROMP technology could be employed to prepare star polymers in a way that imitates some of the previous living systems, but one that offers advantages characteristic of living ROMP with well-characterized complexes.

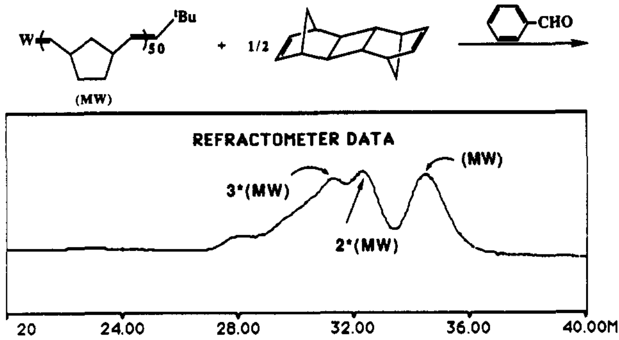
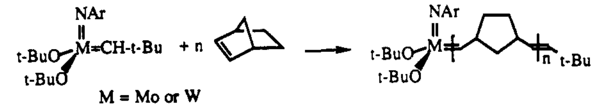


Figure 1. GPC trace of the mixture of polymers resulting from the addition of 0.5 equiv of 1 to a 50-mer of living polynorbornene followed by a benzaldehyde quench.



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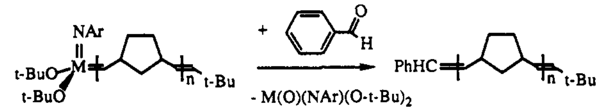
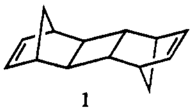


(2)

The catalysts chosen for this study are of the type $M(CHR)(NAr)(O\text{-}t\text{-}Bu)_2$ (M = W or Mo; NAr = N-2,6-$C_6H_3\text{-}i\text{-}Pr_2$).[9,10] They are relatively inactive for metathesis of ordinary (acyclic) olefins but will effect living ROMP of especially reactive cyclic olefins such as norbornene (eq 1). The organic polymer can be cleaved from the metal in a Wittig-like reaction with benzaldehyde that is rapid and quantitative at a concentration of 0.01 M in metal at room temperature (eq 2). Both molybdenum and tungsten *tert*-butoxide initiators (and related more active species containing more electron-withdrawing alkoxide ligands) are now available via relatively direct high-yield syntheses of versatile precursors of the type $M(CHR)(NAr)(triflate)_2(dme)$ (R = CMe_3 or CMe_2Ph; M = W[9] or Mo[10]). *tert*-Butoxide initiators that contain molybdenum are potentially the most interesting since molybdenum tolerates functionalities more than tungsten.[4c,8a] The mechanism of olefin metathesis using these catalysts is now reasonably well understood,[5,8b,11] although many potentially important details remain to be elucidated.

In this work we employ *exo-trans-exo*-pentacyclo$[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]$tetradeca-5,11-diene (**1**) as a cross-linking agent for ROMP by M(CHR)(NAr)(O-*t*-Bu)$_2$ complexes. We chose **1** since it contains two norbornene-like double bonds, its rigid backbone prevents metathesis of both olefins by the same metal center, and it is readily available by the catalytic dimerization of norbornadiene.[12] **1** also has been used to prepare a titanium-based bifunctional ROMP initiator.[13] Tricyclooctadiene also has been reported as a cross-linking reagent in ROMP using classical catalysts,[14] but the synthesis of tricyclooctadiene is relatively difficult and of low yield compared to **1**. **1** could be viewed as the ROMP analogue of divinylbenzene in living anionic polymerizations.[15]



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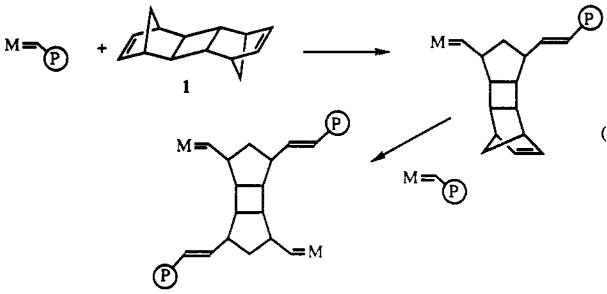
Results and Discussion

Reaction of 1 with Living Polynorbornene. Norbornene (NBE; 50 equiv) is consumed by W(CHR)(NAr)(O-*t*-Bu)$_2$ (**2**) in toluene in ~5 min. Addition of benzaldehyde yields polynorbornene with a polydispersity index (PDI) of 1.05. If 0.5 equiv of **1** is added before benzaldehyde, then a mixture is obtained, the GPC trace of which is shown in Figure 1. Because the polydispersity of the initial living 50-mer is so low, it is possible to observe GPC peaks for the star formed from two 50-mers and the star formed from three 50-mers in the final mixture, in addition to the 50-mer and higher oligomers. The star containing two 50-mers is formed when two living chains are joined by a single molecule of **1** (eq 3). Formation of the star containing three 50-mers can be rationalized by steps similar to those shown in Scheme I. Permutations of such cross-linking reactions would account for the higher molecular weight species. The fact that a distribution of cross-linked polymer chains is observed suggests that the cross-linking process is statistical, i..e., that unreacted **1** and a pendant norbornene have similar reactivities and that alkylidenes A, living polyl, and B have similar reactivities. If the GPC eluent is monitored by UV at 254 nm (where only the phenyl end cap absorbs), the result is identical with that obtained with the refractometer, a result that suggests that all chains contain a phenyl cap and therefore were living at the time of termination. Identical results were obtained with Mo(CHR)(NAr)(O-*t*-Bu)$_2$ (**3**) as the initiator.



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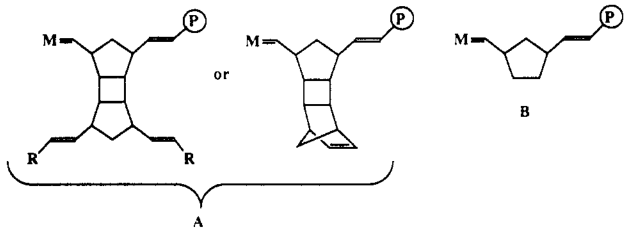
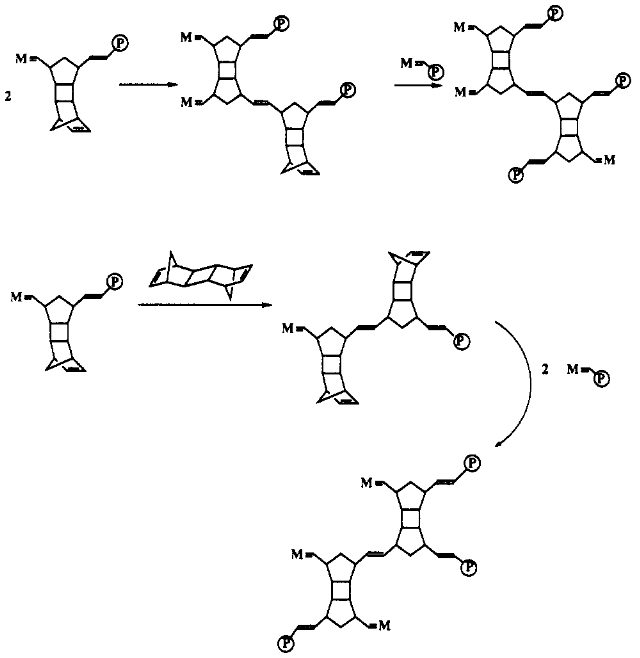


Scheme I



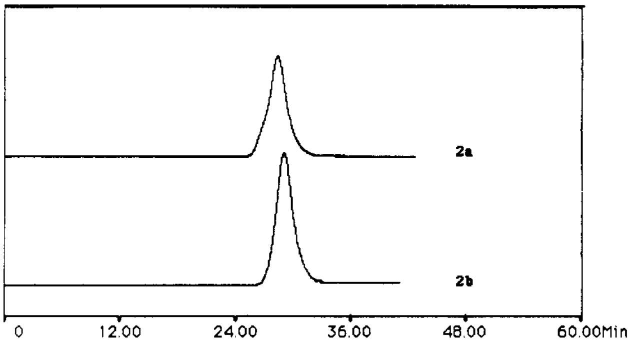


Figure 2. GPC traces (refractometer data) of the polymers obtained (a) after treatment of the 50-mer of living polynorbornene with 4 equiv of **1** and (b) after treatment of a 25-mer of living polynorbornene with 3 equiv of **1**. Both reactions were quenched with benzaldehyde. A slight "raggedness" in the traces is due to the output device; more data points were taken as a function of time and used in the calculation of molecular weights and polydispersities.

Addition of 4 equiv of **1** to the living 50-mer followed by benzaldehyde yields a soluble polymer with an apparent polydispersity of 1.24 (Figure 2a) and a molecular weight that is ca. 10 times that of the 50-mer (by GPC relative to polystyrene). Similarly, addition of 3 equiv of **1** to a living 25-mer yields a polymer with a polydispersity of 1.11 (Figure 2b). GPC results employing the UV detector again are identical with those obtained with the refractometer.

The relatively high molecular weight polymers observed upon addition of 3–4 equiv of **1** to living polynorbornene fall into the class of "star" polymers,[16] species that are characterized by a relatively localized core from which a number of polymer chains or "arms" emanate. In this case the number of arms and their lengths are not fixed but are relatively narrow distributions about the number average. Two methods that have been used extensively for synthesizing star polymers are the reaction of a poly-

Table I
GPC Characterization of the Polynorbornene Star Polymers

cat.	NBE, equiv	PDI(arm)	1, equiv	M_w	PDI(star)
2	100	1.04	5	173 251	1.25
2	50	1.05	4	77 213	1.24
2	25	1.07	3	60 240	1.18
3	100	1.04	4	151 134	1.10[a]

[a] Small amount of linear precursor was observed. All living polymers were quenched with benzaldehyde. GPC values are versus polystyrene standards.

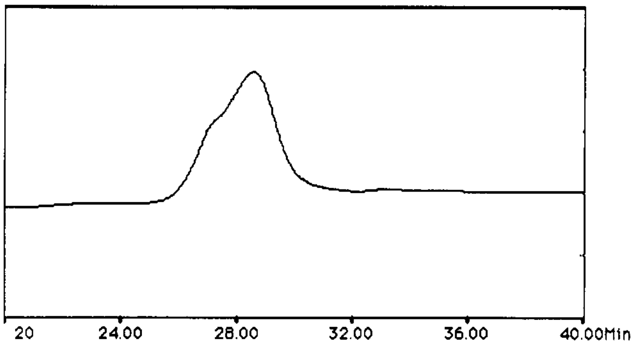


Figure 3. GPC trace (refractometer data) of the isolated polymers obtained from the reaction of 25 equiv of norbornene with living polymer prepared from 25 equiv of norbornene and 3 equiv of **1** (Figure 2b) followed by a benzaldehyde quench.

functional electrophile (i.e., SiCl$_4$) with monocarbanionic chains[17,18] and polymerization of styrene followed by the addition of divinylbenzene (DVB).[15] In the latter approach the coupling process is self-limiting, since once several chains have been coupled, the reactive sites become buried in the central nodule. Reactions within the same structure then become more favorable than reactions between active sites in separate structures.

Star polymers synthesized from living polynorbornene and **1** can be found in Table I. Note that the larger the initial living oligomer of norbornene, the more **1** is required for complete conversion to star polymer. (Similar results were found in anionic polymerization systems.[15]) Care must be exercised in interpreting GPC results, since the hydrodynamic volume of molecules, not their molecular weight or extended length, determines GPC retention times. With star polymers polydispersity can originate solely as a result of a fluctuation of the number of arms (assuming monodisperse initiator arms). Therefore, GPC cannot accurately determine polydispersities. However, GPC can be used to determine if unreacted linear polymer remains.[19] Low polydispersities were found for star-shaped polystyrenes prepared by the block copolymerization of styrene and DVB in benzene using *sec*-butyllithium as initiator, consistent with a random combination of chain ends.[19]

Since there is no mechanism for deactivation on the time scale of forming the star, it is possible to use living stars (the result of adding **1** to living norbornene) to initiate further polymerization of norbornene. Addition of 25 equiv of NBE to the star polymer shown in Figure 2b results in a new soluble polymer, the GPC of which (Figure 3) shows that, although the molecular weight is higher than that of the original star polymer, the distribution is bimodal. Different reaction conditions result in similar distributions. We attribute this result to a slower initiation at the core of the star and faster propagation as the reacting alkylidene centers move away from the sterically crowded core. Under these conditions one might expect some of the original star to remain, depending upon the rate of propagation versus initiation. The UV trace is identical with the refractomer trace shown in Figure 3.

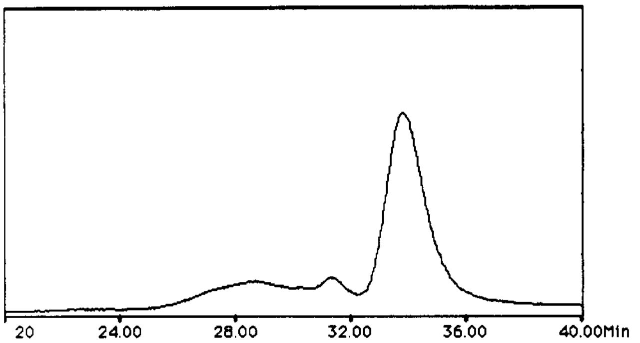


Figure 4. GPC trace (UV-vis detector data) of the mixture of polymers obtained by treatment of **2** with 0.5 equiv of **1** followed by 50 equiv of norbornene and a benzaldehyde quench.

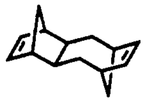
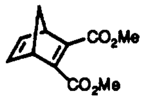
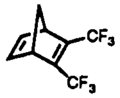
Reaction of 1 with 2 or 3. In a variation of the method employing DVB as the coupling agent, DVB can be polymerized first by butyllithium in dilute benzene solution to give soluble microgels that bear a large number of anionic end groups. These in turn can initiate polymerization of monomers suitable for anionic polymerization.[20,21]

In order to test this approach in ROMP 0.5 equiv of **1** was added to **2** in C$_6$D$_6$ and the reaction was followed by ^{1}H NMR. The neopentylidene resonance at 8.03 ppm decreased little relative to an internal standard, but careful integration showed that new alkylidene resonances were buried in the baseline in the region between 8.35 and 8.50 ppm and equally broad olefinic resonances were found between 5.3 and 5.6 ppm, all assigned to poly**1**. The spectrum did not change upon cooling or heating the sample. The breadth of the signals can be attributed to a crowded steric environment where many different conformations are present. To this mixture of alkylidenes 50 equiv of NBE was added followed by excess benzaldehyde. GPC analysis (Figure 4) shows that the molecular weight distribution is polymodal. The low molecular weight polymer must result from reaction of NBE with leftover initiator, while the broad, high molecular weight fraction probably results from reaction of NBE with new alkylidenes formed upon reaction of **2** with **1**. A peak corresponding to approximately a 100-mer, which appears at 31:54 min, also can be observed. The "double" molecular weight peak probably arises from a small amount of a bifunctional initiator formed upon addition of **1**.

A yellow gel precipitates quickly when 3 or 4 equiv of **1** is added to **2** in toluene at −30 or −25 °C. Addition of more (25 equiv) norbornene does not take the polymer into solution, but all the norbornene is consumed. Termination with benzaldehyde followed by stirring the gel in pentane gives a white solid. Addition of 2 equiv of **1** to **2** at −30 °C followed by 25 equiv of NBE gave a soluble polymer, which was shown by GPC to be approximately a 1:1 mixture of a high molecular weight polymer and linear oligomers that result from reaction of NBE with **2**. Evidently for complete consumption of **2** to give poly**1**, the amount of **1** required is such that the polymer becomes insoluble.

The above results are consistent with **1** reacting with A at a rate that is much larger than the rate of reaction of **1** with **2**. The ratio of k_p to k_i (where k_i is the rate constant for reaction of **1** with **2**) can be determined by measuring how much initiator remains after addition of x equiv of **1** to **2** (x is small; see Experimental Section). The value of k_p/k_i was found to be 9 (±1) (Table II); i.e., the propagating alkylidene is more reactive by approximately an order of magnitude. Consequently, it appears that addition of **1** to **2** or **3** first is not a good method for preparing star polymers. Note that these gels are living

Table II
Ratio of Rate of Propagation to Rate of Initiation for Selected Monomers in C_6D_6

monomer	k_p/k_i
	12.1 (5)[a]
 1	9 (1)
 5	7.0 (5)[b]
 4	3.0 (3)
 6	0.72 (5)

[a] Number in parentheses is the estimated error in the last significant digit. [b] Reaction carried out in THF-d_8. All polymerizations used 3 at a concentration of 0.02 M at 22 °C.

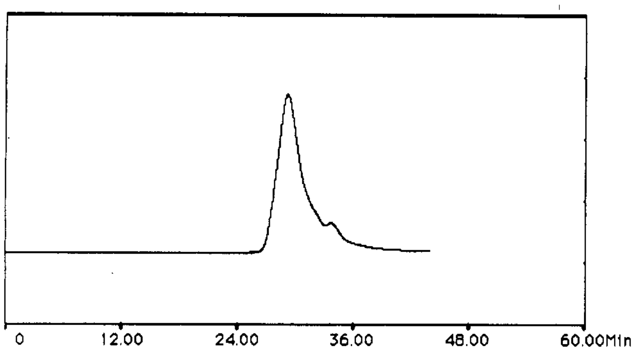
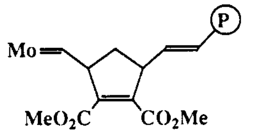


Figure 5. GPC trace (refractometer data) of the polymer mixture resulting from addition of 6 equiv of 1 to a living 25-mer of poly4 followed by a benzaldehyde quench.

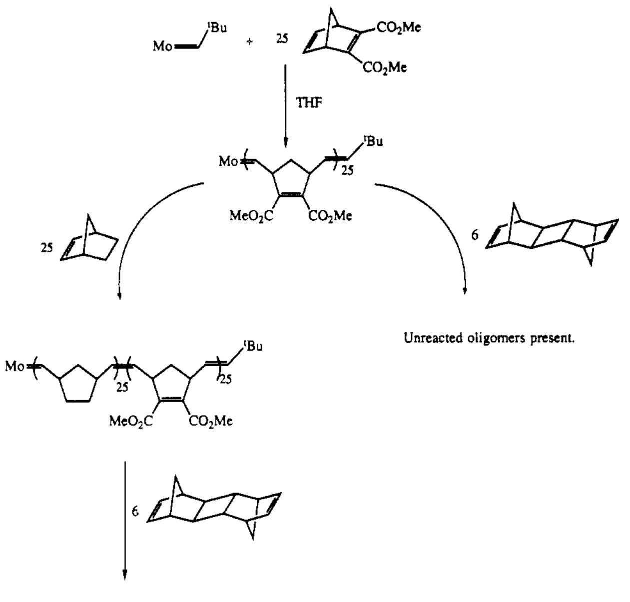
and therefore potentially could serve as a means of preparing partially soluble or relatively insoluble supported (immobilized) functionalities or catalysts.

Formation of Functionalized Star Polymers. Addition of 25 equiv of 2,3-dicarbomethoxynorbornadiene (4) to 3 completely consumes 3 and produces oligomers with a narrow molecular weight distribution (PDI = 1.08). Reaction of 6 equiv of 1 with these living 25-mers results in the formation of star polymers, but 25-mers of 4 remain (10–20%; Figure 5). This result contrasts with living polynorbornene, where only 3 equiv of 1 is needed for complete consumption of the linear precursor. This result can be attributed to a lower reactivity of C relative to A, which causes 1 to react preferentially with more reactive A formed in the initial stages of the reaction. In order to circumvent this problem 25 equiv of NBE was added to C followed by 6 equiv of 1. This strategy, which is summarized in Scheme II, allows soluble star polymers to be prepared. The final structure of this star is interesting since it contains a more polar "shell" around a less polar interior. This experiment illustrates the importance of the reactivity of the living alkylidene in determining conversion. If the propagating alkylidene is not reactive enough, then initiator remains and homopolymer remains in the final mixture. A cross-linking agent that has a low rate of propagation would seem to be ideal, but that would mean that it also would not efficiently cross-link living oligomers. A compromise is inevitable.



C

Scheme II



Unreacted oligomers present.

Only star polymer detected.

Values of k_p/k_i for different monomers roughly measure the reactivity of propagating alkylidenes. (See Experimental Section for a discussion of the assumptions.) A quantitative measure of the reactivity of different monomers would require that the rates of initiation also be determined. Unfortunately, these rates are too fast to measure by routine techniques. Values for k_p/k_i are listed in Table II. The rather low value of k_p/k_i for 4 is consistent with the poor conversion observed (see above). Conversely, k_p/k_i for 5-cyanonorbornene (5; 60:40 mixture of endo and exo isomers; k_p/k_i = 7.0 (±0.5)) compares favorably with that for 1 (k_p/k_i = 9 (±1)) and would be a better choice for a monomer that would form a functionalized star. 2,3-Bis(trifluoromethyl)norbornadiene (6; k_pk_i = 0.72 (±0.05)) is the poorest choice, since k_p (0.057 (7) M^{-1} s^{-1} at 22 °C)[8b] is small. However, 6 would be an ideal candidate for quantitative propagation from a living star center.

Polymerization of 50 equiv of 5 in THF followed by quenching with excess *p*-(trimethylsilyl)benzaldehyde[22] yields a polymer with a polydispersity of 1.05. (The properties of this and related functionalized homopolymers will be reported elsewhere.[23]) Reaction of this living 50-mer with 5 equiv of 1 followed by termination with *p*-(trimethylsilyl)benzaldehyde results in quantitative formation of a star polymer (Figure 6). The two end groups of these polymers have resonances in the ^{1}H NMR spectrum that are well separated from the rest of the polymer resonances and can be used to probe the environment surrounding them. In linear poly5 capped with *p*-(trimethylsilyl)benzaldehyde two sharp trimethylsilyl resonances are observed at 0.232 and 0.217 ppm (major) that can be assigned to trimethylsilyl groups in cis and trans double bonds,[24] while the *tert*-butyl group resonance

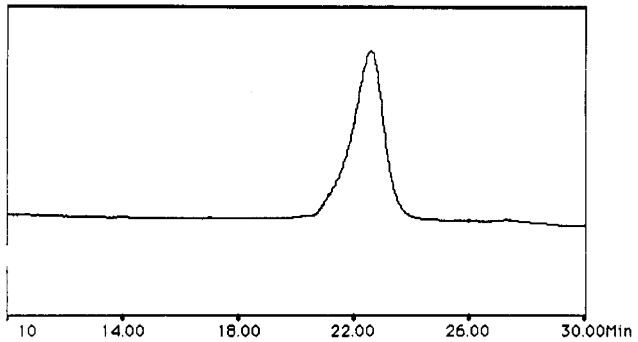


Figure 6. GPC trace (refractometer data) of a poly5 star prepared from a living 50-mer of 5.

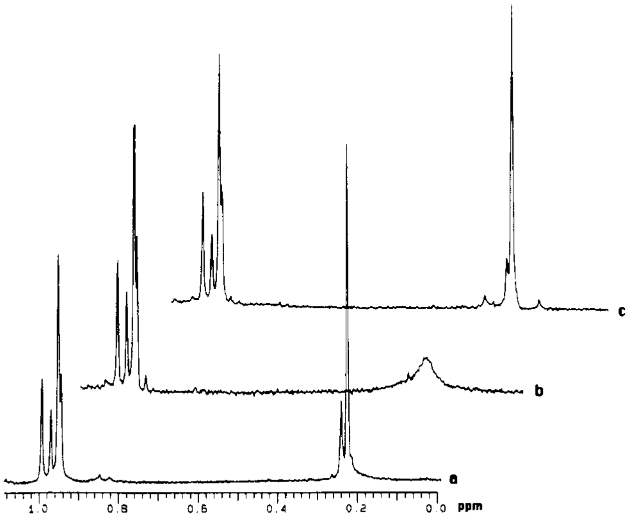


Figure 7. Proton NMR (trimethylsilyl and *tert*-butyl end group region) of (a) poly5, (b) poly5 star, and (c) poly5 star–poly6.

is split into four singlets at 1.004, 0.981, 0.963, and 0.956 ppm as a result of sensitivity to exo/endo and head/tail isomerism in an all-trans terminal double bond. (Initiation with 3 appears to always yield a trans olefin.[7b]) The ratio of initiator (*tert*-butyl) to terminator (trimethylsilyl) in poly5 is 1:1 according to integration of the respective resonances in the proton NMR spectrum. For a star polymer prepared from living poly5 the *tert*-butyl resonances are unchanged but the trimethylsilyl resonances are unusually broad, consistent with the broad alkylidene resonances previously observed for poly1. The trimethylsilyl resonances integrate at 70% of the *tert*-butyl resonance, a result that indicates that sites inside the core of the star were not all terminated by the aldehyde, probably for steric reasons. (We assume that the unreacted living sites are deactivated by dioxygen when the samples are exposed to air.)

Fifty equivalents of 6 is completely consumed by the living poly5 star. Quenching with (trimethylsilyl)benzaldehyde yields a white fluffy polymer. GPC analysis showed that the molecular weight has increased from that of the original poly5 star, and the molecular weight distribution was monomodal. Integration of the allylic proton resonances in the polymer backbone versus the total olefin resonance area indicates that the stoichiometry is that expected. The resonance for the trimethylsilyl cap is now sharp and integrates to 90% of the *tert*-butyl resonance (Figure 7), a result that suggests that the propagating alkylidenes most of the time were in a less crowded and accessible environment, i.e., outside the inner core of the star. This result also implies that the number of arms in poly5 is approximately the same as the number of poly6 within the same star. The ^{13}C NMR spectrum consists of a superposition of the spectra of poly5 and poly6. A single olefinic resonance for poly6 is observed at 132.30 ppm; it is characteristic of the stereoselective polymerization of 6 by Mo-based living poly6.[8]

Conclusion

Analogous behavior is observed employing 1 in living controlled ROMP as has been observed for DVB in living anionic systems, especially with regard to formation of star-shaped polymers. This paper has focused on the synthesis of these materials and not on their potentially interesting properties. The drybox or Schlenk line experimental procedures required for ROMP are not as severe as the high-vacuum, low-temperature procedures that have been used for anionic polymerization.[25] The reactivity of the living alkylidene ideally should be greater than that of alkylidenes formed upon addition of 1. If 1 is added to the initiator, then gels form rapidly as a result of relatively rapid cross-linking.

The ability of 3 to tolerate a wide range of functionalities[5] allows the preparation of star polymers with pendant functionalities. Star polymers in which the arms are block copolymers of different polarities can be prepared as well as star polymers in which the composition of the arms is different and again of very different solubility characteristics and stereochemical regularity. Such "heterostars",[26] in which the number of the different arms should be approximately equal, may exhibit interesting intramolecular phase separation. Synthesis of "heterostars" has not been reported using anionic polymerization systems,[27] in part because of gelation of the reaction medium and perhaps also in part because of the relatively low tolerance of the catalyst for many common unsaturated polar functionalities.

Experimental Section

General Details. All polymerizations were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by using standard Schlenk techniques. Tetrahydrofuran was dried over calcium chloride and distilled from sodium benzophenone ketyl under nitrogen immediately prior to usage. Toluene was distilled from molten sodium and stored over sodium–potassium alloy. All deuterated NMR solvents were passed through a column of activated alumina. Norbornene was doubly distilled from molten sodium. Commercially available 5-cyanonorbornene (60:40 mixture of exo and endo isomers) was distilled under nitrogen, passed through a column of activated alumina, and stored under nitrogen. 2,3-Dicarbomethoxynorbornadiene,[28] 2,3-bis(trifluoromethyl)norbornadiene,[29] *p*-(trimethylsilyl)benzaldehyde,[22] W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$,[9] and Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$[10] were prepared as described in the literature.

Proton and carbon NMR data are listed in parts per million downfield from TMS. Coupling constants are quoted in hertz. Obvious multiplicities and routine coupling constants usually are not listed. Gel permeation chromatographic (GPC) analyses were carried out with Shodex KF-802.5, -803, -804, -805, and -800P columns, a Knauer differential refractometer, and a Spectroflow 757 absorbance detector on samples 0.1–0.3% w/v in dichloromethane which were filtered through a Millex-SR 0.5-μm filter in order to remove particulates. GPC columns were calibrated versus commercially available polystyrene standards (Polymer Laboratories Ltd.) which ranged from 1206 to 1.03 × 10^6 MW.

Determination of the Ratio of k_p to k_i. For a given reaction in which M is the concentration of monomer, M_0 the initial concentration of monomer, I the concentration of initiator (in this case either 2 or 3), and I_0 the initial concentration of initiator, $M - M_0 = (1 - r)(I - I_0) + rI_0 \ln (I/I_0)$ as long as $I \neq 0$ and $r = k_p/k_i$.[30] If a given quantity of monomer is added to and polymerized by the initiator, then M approaches 0 and $M_0/I_0 + r \ln (I/I_0) + (1 - r)(I/I_0 - 1) = 0$. M_0/I_0 is the amount of monomer added to the initiator. By measuring the amount of remaining initiator (I), one can determine r. Since this technique is very sensitive to the rate of stirring, stirring should be rapid. For x equiv of 1 the number of equivalents of monomer is considered to be $2x$, and no correction is made for the fact that the second strained olefin is not available to the alkylidene formed from the first double bond in 1.

It is assumed that k_p is the same for all propagation steps. For example, we assume that the first double bond in 1 reacts at the same rate as the remaining double bond after one has been attacked. Another possibility is that k_p changes because some of the sites are buried etc. Since k_p/k_i is measured in the regime where small oligomers are formed, buried sites would not seem to be a significant problem.

Preparation of 1. The procedure is identical with that described in the literature,[12] except that it was purified differently. After distillation, the product was found to be 89% exo–trans–exo with the remainder begin exo–trans–endo and endo–trans–endo isomers. Double recrystallization from toluene gave the exo–trans–exo isomer in good yield. Its proton NMR suggested it to be free of other isomers and was found to be the same as that reported.[12]

Typical Preparation of a Polynorbornene Star Polymer. A solution of norbornene (41 mg, 0.43 mmol, 25 equiv) in toluene (5.0 mL) was added dropwise over a period of 1–2 min to a solution of W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (10 mg, 0.017 mmol) in toluene (10.0 mL). After the solution was stirred for 5 min, a solution of 1 (10 mg, 0.05 mmol, 3.1 equiv) in toluene (1.0 mL) was added quickly dropwise. After 10 min the reaction solution was divided into two 8.0-mL portions, one of which was immediately quenched with excess benzaldehyde (10 μL, 0.094 mmol; 30-min reaction time). The polymer was isolated by precipitation into 100 mL of methanol and centrifugation and dried under vacuum for several hours (yield 22 mg, 84%, GPC shown in Figure 2b). Norbornene (20 mg, 0.21 mmol, 25 equiv) in toluene (2.0 mL) was added dropwise to the second half of the reaction solution, and after 10 min the reaction was quenched and worked up as described above (yield 36 mg, 78%, GPC shown in Figure 3). Proton and carbon NMR spectra for both polymers were identical with those of homopolynorbornene prepared employing W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$;[4b] no resonances derived from ring-opened 1 could be observed.

Typical Reaction of 1 with Initiator. A solution of 1 (1.6 mg, 8.7×10^{-6} mol from a stock solution) in C_6D_6 (350 μL) was added to a vigorously stirred solution of W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ in C_6D_6. The proton NMR spectrum shows extremely broad resonances for living poly1: δ 8.4–8.5 (H_α), 5.3–5.6 (olefinic), 2.1–2.6 (aliphatic), 1.0–1.1 (*tert*-butyl cap). The NMR sample was brought back into the drybox, and the contents were diluted with an additional 5 mL of toluene. Norbornene (82 mg) in toluene (5 mL) was then added quickly dropwise to the vigorously stirred solution. After 10 min the reaction was terminated by adding benzaldehyde (15 μL, 0.14 mmol) and stirring for 30 min. The solvent was removed in vacuo to leave a gummy yellow solid, which was dissolved in a minimum amount of dichloromethane. The polymer was precipitated by pouring the dichloromethane solution into methanol (150 mL). The polymer was filtered off and placed under vacuum for several hours. Only resonances for polynorbornene were observed in the proton NMR spectrum. The GPC is shown in Figure 4.

Preparation of Poly4–Polynorbornene Star Block Copolymer. A solution of 2,3-dicarbomethoxynorbornadiene (4, 106 mg, 0.509 mmol, 24.8 equiv) in THF (2.00 mL) was added to a rapidly stirred solution of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (10 mg, 0.0205 mmol) in THF (2.00 mL). The color of the solution changed from yellow-orange to dark orange and back to yellow-orange over a period of 20 min. Norbornene (48 mg, 0.051 mmol, 24.9 eqiv) in THF was then added dropwise, and the solution was stirred for 5 min. The solution was divided into two 3-mL fractions, one of which was quenched with excess benzaldehyde (10 μL, 0.094 mmol, 30-min-reaction time) and saved for comparison with the star block copolymer (GPC data; M_n = 11 870, PDI = 1.09). A solution of 1 (13 mg, 6 equiv) in THF (2 mL) was added and the reaction after 5 min was quenched with benzaldehyde (10 μL, reaction time 30 min, final yield 82 mg, 91%) (GPC data: M_n = 98 542, PDI = 1.16). Both fractions were purified by precipitation in 500 mL of hexane, centrifugation, and drying under vacuum for several hours.

Preparation of Poly5. A solution of 5 (122 mg, 1.02 mmol) in THF (1.0 mL) was added quickly to a solution of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (10 mg, 2.05×10^{-5} mol) in THF (1.0 mL), and the solution was stirred for 15 min. The reaction was quenched by adding 15 μL of *p*-(trimethylsilyl)benzaldehyde (8.4×10^{-5} mol). The polymer was purified by precipitation in 250 mL of hexane. The final product was obtained as a cream-colored powder: yield 103 mg, 85%; ^{1}H NMR ($CDCl_3$) δ 5.70, 5.55, 5.37, 5.32, 5.20, 3.0, 2.73, 2.55, 2.30, 2.18, 2.03, 1.75, 1.43, (1.004, 0.981, 0.963, 0.956) ($C(CH_3)_3$), (0.232, 0.217) ($Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$) 135.3, 134.6, 132.3, 131.7, 129.7, 129.2 (*C*N), 120.9 (*C*N), 58.5, 44.8, 41.8, 41.2, 39.8, 39.2, 37.0, 36.9, 36.2, 33.8, 29.6 ($C(CH_3)_3$), 1.3 ($Si(CH_3)_3$); GPC: M_n = 24869, PDI = 1.05.

Preparation of Poly5 Star and Poly5–Poly6 Star Block Copolymer. A solution of 5 (122 mg, 1.02 mmol) in THF (1.0 mL) was added quickly to a solution of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (10 mg, 2.05×10^{-5} mol) in THF (1.0 mL), and the solution was stirred for 15 min. 1 (20 mg, 1.08×10^{-4} mol, ~5 equiv) in THF (2.0 mL) was added quickly dropwise to the rapidly stirred solution. The resulting solution was then divided into two 2.0-mL portions. One portion was quenched with *p*-(trimethylsilyl)benzaldehyde (15 μL, 8.4×10^{-5} mol, 2-h reaction time), and the polymer was worked up by precipitation in 150 mL of hexane (final yield of isolated polymer 65 mg, 85%): M_w = 259 875, PDI = 1.27; NMR identical with that of poly5). 6 (117 mg, 5.08×10^{-4} mol, 49.6 equiv) was added to the second half of the reaction solution. The reaction was stirred for 90 min and then quenched with *p*-(trimethylsilyl)benzaldehyde (2-h reaction time), and the polymer was isolated as described above; yield 150 mg, 79%; M_w = 536 994, PDI = 1.32. NMR spectra were identical were the superposition of spectra for poly5 and poly6.[8b]

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Registry No. 1, 1624-12-0; **2**, 107440-84-6; **3**, 108969-04-6; **4**, 947-57-9; **5**, 95-11-4; **6**, 58623-62-4; norbornene, 498-66-8; polynorbornene (homopolymer), 25038-76-0; poly4–polynorbornene (block copolymer), 131236-14-1; poly**5** (homopolymer), 30811-49-5; poly**5**–poly**6** (block copolymer), 131236-15-2.