Preparation of "Sugar-Coated" Homopolymers and Multiblock ROMP Copolymers

Kotohiro Nomura and Richard R. Schrock*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received August 25, 1995; Revised Manuscript Received October 26, 1995[⊗]

ABSTRACT: Ring-opened homopolymers of 5-norbornene-2-carboxylates or 5-norbornene-2,3-dicarboxylates that contain acetal-protected sugars (**1**: 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-*O*-yl 5-norbornene-2-carboxylate; **2**: bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-*O*-yl) 5-norbornene-*trans*-2,3-dicarboxylate; **3**: 5-norbornene-2-carboxylic acid ester containing 2,3-*O*-isopropylidene-D-ribonic γ-lactone; **4**: 3,4:5,6-di-*O*-isopropylidene-α-D-mannofuranos-1-*O*-yl 5-norbornene-2-carboxylate) were prepared in toluene using $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(O\text{-}t\text{-}Bu)_2$ as the initiator. These homopolymers showed narrow molecular weight distributions (PDI = 1.02−1.25) and a molecular weight dependent on the number of monomers added. Di-, tri-, and tetrablock copolymers containing **1**−**4**, methyltetracyclododecene (MTD, **5**), or *trans*-2,3-bis(((trimethylsilyl)oxy)methyl)-norborn-5-ene (**6**) were also prepared and found to have low polydispersities (M_w/M_n = 1.03−1.25). The cyclic acetal in polymers containing **1** or **2** could be removed using CF_3CO_2H/H_2O (9/1 v/v, 15 min, 22 °C) to afford the corresponding water-soluble polymers containing the parent sugar.

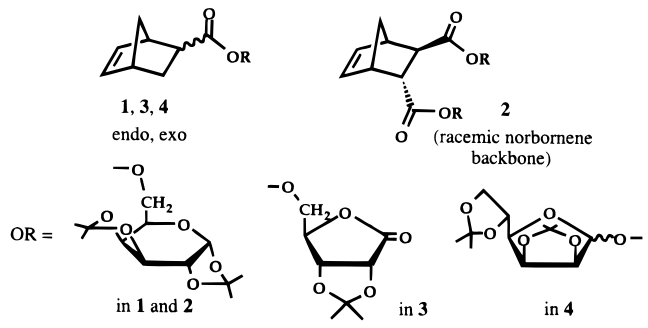
Introduction

Molybdenum alkylidene complexes of the type $Mo(CHR')(NAr)(OR)_2$ (Ar = 2,6-i-$Pr_2C_6H_3$ or other aryls, R = t-Bu, $CMe(CF_3)_2$, etc.; R′ = CMe_3 or CMe_2Ph)[1] are useful initiators for the living ring-opening metathesis polymerization (ROMP) of cyclic olefins, especially norbornenes and disubstituted norbornadienes.[2,3] The living nature of such polymerizations allows low-polydispersity (1.05−1.10) homopolymers and block copolymers to be prepared and the initiating and terminating groups to be specified. The fact that a wide variety of nonprotic functionalities also are tolerated by this catalyst (among them esters, amines, ethers, thioethers, and redox active groups) allows architectural and functional possibilities for ROMP polymers that are not possible for polymers prepared by other existing methods. Finally, the ability to control the cis/trans structure and tacticity of a ROMP polymer[4,5] and thereby create a regular supramolecular architecture adds yet another dimension to the method.

One of the potential applications of ROMP by well-defined initiators such as $Mo(CHR')(NAr)(OR)_2$ compounds is the synthesis of hydrophilic or water-soluble polymers by using a monomer that contains a protected functionality. For example, we have reported the synthesis of amphiphilic star block copolymers that consist of a hydrophobic "core" and hydrophilic "shell" employing bis(trimethylsilyl) norborn-5-ene)-2,3-dicarboxylate as one of the monomers.[6] Carbohydrate-based polymers, especially well-controlled low-polydispersity homopolymers and block copolymers that contain identified end groups, could be particularly interesting, not only from the viewpoint of solubility in water. For example, polymers that have an "unnatural" or abiological backbone but natural sugars as side groups could have applications in biology (e.g, cell surface recognition[7] or protein stabilization[8]). In fact, cell agglutination inhibitors recently were prepared by aqueous Ru-catalyzed ROMP of glucose-derivatized 7-oxynorbornene.[7] Such polymers were found to prevent erythrocyte agglutination at a glucose residue concentration at least 2000-fold lower than that required of methyl α-D-glucopyranoside. Ru-catalyzed ROMP was chosen in this case because of the compatibility of Ru catalysts with the free hydroxyl group, but such traditional catalysts do not produce low-PDI polymers or block copolymers. Related "sugar-coated" polymers have been synthesized before by more traditional free radical polymerizations of acrylamide derivatives.[9−13] We report here the results of our efforts to synthesize sugar-coated polymers by Mo-catalyzed living ROMP techniques using the *tert*-butoxide initiator $Mo(CHCMe_2Ph)(NAr)(O\text{-}t\text{-}Bu)_2$. These results should be compared to recently reported approaches involving tungsten[14] or ruthenium[15] catalysts.

Results and Discussion

Monomers **1**−**4** could be prepared in moderate yields from the corresponding norbornenecarbonyl chlorides (racemic in the case of the 5-norbornene-*trans*-2,3-dicarbonyl chloride) and the commercially available acetal-protected sugars in the presence of triethylamine at −30 to −50 °C.



(The cyclic acetal was chosen as the protecting group because it has been used extensively and its hydrolysis under a variety of reaction conditions has been explored thoroughly.[16]) This method is related to that reported for synthesizing monomers that contain liquid crystalline side chains.[17,18] Monomers **1**−**4** can be purified by recrystallization in a drybox from mixtures of ether or

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1995.

0024-9297/96/2229-0540$12.00/0

Table 1. Cleavage of Poly(1) from the Metal under Various Conditions

aldehyde	polym time (h)[a]	$10^{-4}M_n$[b]	$10^{-4}M_n$[c]	PDI	yield[d]
PhCHO	1	1.14	1.67	1.06	92
PhCHO	6	1.14	3.40	1.28	91
PhCHO[e]	1	1.14	3.20	1.32	>99
4′-formylbenzo-15-crown-4	1	1.14	1.75	1.13	>99
ferrocenecarboxaldehyde	1	1.14	1.80	1.06	96
p-FC_6H_4CHO	1	1.14	1.88	1.19	>99
none[f]	1	1.14	7.4 ± 3.2	1.24 ± 0.06	90

[a] Reaction conditions: 4 mg of catalyst, 4.8 g of toluene, 104 mg of **1**, 1 h at 22 °C, unless otherwise noted. [b] Calculated from monomer/catalyst ratio. [c] By light scattering at 690 nm in CH_2Cl_2 using the total elution method for estimating d*n*/d*c*. [d] Isolated yield (%). [e] Total amount of toluene is 0.67 g instead of 4.8 g. [f] The solvent was removed from the reaction mixture in vacuo, the residue was taken up in minimal THF, and the THF solution was poured into cold water. The results shown were an average of three independent runs.

THF and pentane chilled to −30 °C. Monomer purity is an important requirement in living polymerization systems, as impurities that react with the initiator or an intermediate alkylidene complex usually lead to polymers having higher molecular weights and polydispersities than expected for a living polymerization.

$Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(O\text{-}t\text{-}Bu)_2$[19] was chosen as the initiator, since it appears to be the mildest (least electrophilic) of the "well-defined" Mo catalysts prepared so far and therefore the least likely to react with the diol protecting group. In some cases, this initiator leads to all-trans polymers[20] that are likely to be syndiotactic on the basis of comparison with related polymers that contain chiral groups.[4] It has been proposed that unobservable *anti*-alkylidene rotamers (in rapid equilibrium with the observable *syn* rotamers) are actually the chain propagating species in the *tert*-butoxide system if the monomer is not reactive enough to react with *syn* rotamers.[21] Homopolymers were usually prepared in toluene by adding *n* equivalents of monomer to the initiator. Poly(**3**) was also prepared in tetrahydrofuran because of its low solubility in toluene. The polymers were cleaved from the metal in a Wittig-like reaction with benzaldehyde, a method that is widely employed for cleaving ROMP polymers from metal centers in systems of this general type, although we did not devise a test in the experiments reported here that would confirm quantitative cleavage. The polymer yields were 90% or greater in all cases, often essentially quantitative. The polydispersities were determined by gel permeation chromatography (GPC) and molecular weights by light scattering, as summarized in Table 2. The variation in polymer molecular weight and polydispersity as a function of the conditions employed for the cleavage reaction are shown in Table 1.

The data in Table 1 show that the molecular weight (as determined by light scattering; see Experimental Section) and the polydispersity depend upon the cleavage conditions. Molecular weight and polydispersity both increase if the polymerization time is lengthened (entry 2) or if the reaction mixture is more concentrated (entry 3). Other aldehydes can also be employed (entries 4−6). However, the observed molecular weights and polydispersities of poly(**1**) isolated by simply pouring a concentrated reaction mixture in THF into water were relatively high (last entry). Progressively longer reaction times before quenching produced poly(**1**) that had progressively higher than expected molecular weights and polydispersities (not shown in Table 1). These data suggest that increasing the concentration of catalyst and lengthening the polymerization reaction time lead to higher molecular weights and polydispersities. One possible explanation is that some cross-linking takes place over a period of several hours, a reaction that possibly involves destruction of the alkylidene functionality. Homopolymers made from other monomers showed similar characteristics.

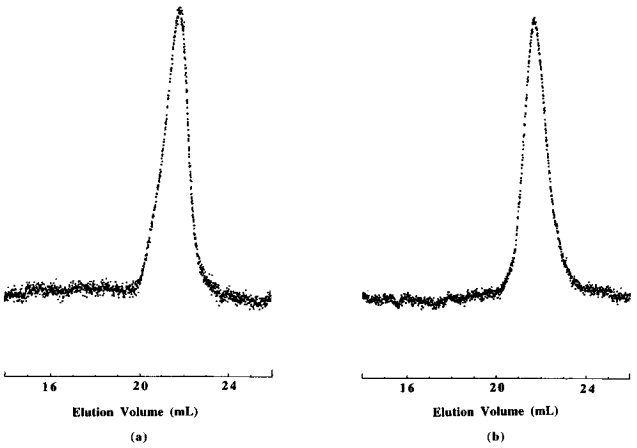


Figure 1. GPC traces of (a) poly(**1**)$_{30}$ (30 mer) and (b) poly(**3**)$_{30}$ (30 mer).

Homopolymers showed low polydispersities and unimodal GPC traces (Figure 1), and the relationship between the M_n(found) and the number of equivalents of **1** added to the initiator under a given set of conditions is approximately linear. The ratio of the M_n found by light scattering to the M_n predicted on the basis of initiator employed is smaller for poly(**1**) than for poly(**2**). The molecular weight distributions of poly(**2**) are relatively broad (PDI = 1.21−1.25) compared with those of poly(**1**) (PDI = 1.06−1.10). As we might expect on the basis of steric factors, **2** was polymerized more slowly than **1**. For example, a reaction involving 100 equiv of **1** was complete after 1 h, whereas 22% of **2** remained (by ^{1}H NMR) in a reaction involving 50 equiv under otherwise identical conditions.

Proton NMR spectra of poly(**1**) and poly(**4**) showed broad resonances at 5.1−5.4 ppm for the olefinic protons and broad resonances between 1.6 and 2.0 ppm and between 2.4 and 3.1 ppm characteristic of ring-opened polymers of this general type. Spectra of poly(**2**) were similar except that the broad olefinic resonances were observed at 5.3−5.5 ppm. In contrast, the resonances ascribable to the sugar group were relatively sharp, consistent with a relatively homogeneous environment of the side chains. ^{13}C NMR spectra of these polymers also showed relatively sharp resonances for the protected sugar, including those characteristic of the isopropylidene protecting group at ∼109 ppm (quaternary C) and 26 ppm (methyl C). We could not determine with certainty by NMR whether poly(**1**) or poly(**2**) was all trans or not. Almost certainly they do not have regular structures, but are probably a mixture of cis and trans double bonds and head-to-head, head-to-tail, and head-to-head arrangement of the repeat unit. The norbornene skeleton of **2** is racemic and therefore the structure of poly(**2**) is also likely to be complex. Therefore the structures drawn below for the homopolymers should not be taken literally. (See supporting information for examples of NMR and IR spectra.)

Table 2. Synthesis of Homopolymers

monomer	solvent	equiv	time (h)	$10^{-4}M_n$[a]	$10^{-4}M_n$[b]	PDI	yield[c]
1	toluene	20	1	0.76	1.47	1.06	>99
1	toluene	30	1	1.14	1.67	1.06	92
1	toluene	50	1	1.90	2.77	1.06	>99
1	toluene	100	1	3.80	6.31	1.10	94
2[d]	toluene	20	1	1.33	3.27	1.25	99
2[d]	toluene	30	1.5	2.00	5.33	1.21	99
3	THF	30	1	0.92	2.14	1.08	>99
3	THF	30	0.5	0.92	1.37	1.02	>99
3	toluene	30	1	0.92	1.81	1.14	>99
3	THF	50	1	1.54	2.59	1.04	98
3	THF	50	0.75	1.54	1.73	1.03	>99
3	toluene	50	1	1.54	2.53	1.23	>99
3	THF	100	1	3.08	3.89	1.09	>99
4	toluene	30	1	1.14	2.09	1.06	>99
4	toluene	50	1	1.90	3.25	1.16	>99
6	toluene	50	1	1.49	1.96	1.10	98

[a] Calculated based on the monomer/catalyst ratio. [b] Measured by light scattering at 690 nm in dichloromethane using the total elution method for estimating d*n*/d*c*. [c] Isolated yield (%). [d] A small high-MW shoulder was observed in the GPC trace.

Table 3. Synthesis of Diblock Copolymers

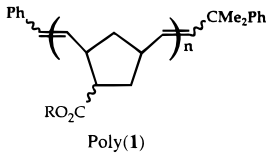
monomer[a]	equiv[a]	time (h)[a]	$10^{-4}M_n$[b]	$10^{-4}M_n$[c]	PDI	yield[d]
5/1	25/25	1/1	1.39	1.68	1.03	94
5/1	50/50	1/1	2.77	4.89	1.18	>99
5/2	25/25	1/1	2.10	2.64	1.17	96
5/4	25/25	1/1	1.39	2.18	1.07	>99
6/1	25/25	1/1	1.70	3.75	1.08	98
1/3	25/25	1/1	1.72	3.69	1.10	>99
1/4	25/25	1/1	1.90	2.99	1.13	>99

[a] The order in which monomers were added, the equivalents of each, and the time elapsed at each stage match the orders shown in columns 1−3. [b] Calculated from monomer/catalyst ratio. [c] Measured by light scattering at 690 nm in dichloromethane using the total elution method for estimating d*n*/d*c*. [d] Isolated yield (%).

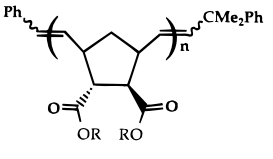
Table 4. Syntheses of Tri- and Tetrablock Copolymers

monomer[a]	equiv[a]	time (h)[a]	$10^{-4}M_n$[b]	$10^{-4}M_n$[c]	PDI	yield[d]
5/1/2	25/25/25	1/1/2	3.05	6.40	1.25	90
5/1/4	25/25/25	1/1/1	2.33	4.06	1.04	>99
5/6/1	50/25/25	1/1/1	2.57	4.30	1.09	97
5/6/1	50/25/50	1/1/1	3.52	5.51	1.17	98
5/6/2[e]	50/25/25	1/1/1.5	3.28	7.66	1.16	97
2/6/5[e]	25/25/50	1/1/1	3.28	7.31	1.13	96
5/6/1/2	50/25/25/25	1/1/1/1.5	4.24	10.75	1.05	98
5/6/1/2	50/25/25/25	1/1/1/1.5	4.24	10.39	1.08	96
1/2/1/2	25/25/25/25	1/1.5/1/1.5	5.24	11.26	1.03	96

[a] The order in which monomers were added, the equivalents of each, and the time elapsed at each stage match the orders shown in columns 1−3. [b] Calculated from monomer/catalyst ratio. [c] Measured by light scattering at 690 nm in dichloromethane using the total elution method for estimating d*n*/d*c*. [d] Isolated yield (%). [e] A small high-MW shoulder was observed in the GPC trace.



Poly(**1**)



Poly(**2**)

Syntheses of Multiblock Copolymers Containing Sugars. Methyltetracyclododecene (MTD, **5**) and (racemic) *trans*-2,3-bis(((trimethylsilyl)oxy)methyl)norborn-5-ene (**6**) were selected as comonomers in attempted syntheses of block copolymers. MTD has been used often before to synthesize block copolymers because of its relatively high T_g.[22−24] Since **6** hydrolyzes readily to the alcohol, block copolymer sequences containing **6** could serve as transition sequences between hydrophobic poly(**5**) and hydrophilic sugar-containing polymer chains. Poly(**6**)$_{50}$ prepared using Mo(CHCMe$_2$Ph)(NAr)(O-*t*-Bu)$_2$ as the initiator was shown to have a low polydispersity (1.10; Table 2) and a low value for M_n(found)/M_n(calcd) (1.32; Table 2).

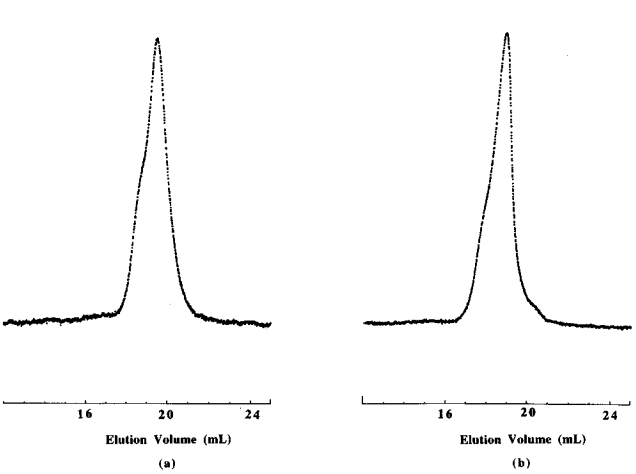
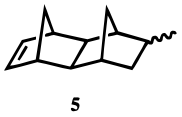


Figure 2. GPC traces of (a) the triblock copolymer **5**/**6**/**1** (50/25/25) and (b) the tetrablock copolymer **1**/**2**/**1**/**2**.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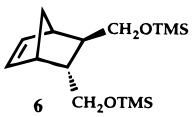

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Several diblock copolymers containing **1**−**6** were prepared by adding 25 or 50 equiv of the monomers sequentially to Mo(CHCMe$_2$Ph)(NAr)(O-*t*-Bu)$_2$, waiting 1 h at each stage (Table 3). The yields are 95% or greater in all cases. Tri- and tetrablock copolymers also could be prepared with PDI's as low as 1.03, as shown in Table 4. In one case, the order of addition was varied, but the resulting polymers had virtually identical molecular weights and PDI's. GPC traces for one of the triblock and one of the tetrablock copolymers are shown in parts a and b of Figure 2, respectively. The high molecular weight shoulder is variable, and typical for ROMP polymerizations of this general type; they have yet to be explained satisfactorily.

Polymer Hydrolysis. Hydrolysis of cyclic acetals of ketoses by acetic acid, oxalic acid, ion exchange resin, or mixtures of trifluoroacetic acid and water are well-known.[16,25] We chose a mixture of trifluoroacetic acid and water because deprotection at room temperature requires only 5−10 min and because many functional groups are not attacked. Trifluoroacetic acid/water was found to be effective for deprotecting polymers containing **1** or **2** at room temperature over a period of 15 min. Deprotected polymers were isolated by pouring the hydrolysis reaction mixture into cold THF. Both ^{1}H and ^{13}C NMR spectra of the deprotected polymers (in D$_2$O) showed no resonances for the cyclic acetals, and all other characteristic resonances of the intact deprotected sugar bound through an ester linkage to the backbone were present. IR spectra showed a broad absorption band at ~3415 cm^{-1} characteristic of hydroxyl groups but no absorption ascribable to a carboxylic acid. The deprotected polymers were soluble to varying degrees in dimethyl sulfoxide, dimethylformamide, and water, slightly soluble in THF, and insoluble in hexane and pentane.

Conditions for isolating polymers containing **3** or **4** that had been subjected to similar hydrolysis conditions

could not be devised. Therefore we cannot state that intact sugar residues survive the conditions employed to hydrolyze polymers containing **1** or **2**.

Conclusions

We have shown that various kind of norbornene-based homopolymers and multiblock copolymers that contain protected sugars can be prepared by ring-opening metathesis polymerization using $Mo(CHCMe_2Ph)(NAr)(O\text{-}t\text{-}Bu)_2$ (NAr = N-2,6-*i*-$Pr_2C_6H_3$) catalysts. The resultant polymers have relatively narrow molecular weight distributions and molecular weights that depend on the number of monomers added. The acetal groups in polymers containing 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-*O*-yl in the ester could be hydrolyzed rapidly under mild conditions using mixtures of trifluoroacetic acid and water to afford water-soluble "sugar-coated" polymers. Eventually it would be useful to know what other initiators and monomers can be employed and whether water-soluble all-cis,isotactic polymers can be prepared that have regular secondary structures.

Experimental Section

General Procedures. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques, unless otherwise specified. Diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl under nitrogen. Pentane for monomer synthesis was washed with sulfuric acid/nitric acid (95/5 v/v), sodium bicarbonate, and water, stored over calcium chloride, and distilled from sodium benzophenone ketyl under nitrogen. Polymerization grade toluene was distilled from Na, stored over sodium/potassium alloy, and passed through alumina prior to use. All chemicals were reagent grade (Aldrich) and purified by standard procedures. Benzaldehyde was freshly distilled and stored at −30 °C. 2-Norbornene-5-carboxylic acid chloride[18] and $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(O\text{-}t\text{-}Bu)_2$[19] were prepared as described in the literature. Polymerization grade methyltetracyclododecene was distilled in the presence of sodium.

HPLC grade solvents were used for gel permeation chromatography (GPC) and were degassed prior to use. GPC was performed on a Spectroflow 400 using a Mini Dawn light scattering detector (Wyatt Technologies) or a Viscotek differential refractometer on samples 0.1−0.3% w/v in CH_2Cl_2 that had been filtered through a Millex-SR 0.5 μm filter in order to remove particulates. GPC columns (Jordi Gel DVB Mixed Bed 250 × 10 mm ranging from 1206 to 1.03×10^6 MW) were calibrated versus polystyrene standards (Polymer Laboratories Ltd.). In the light scattering experiments, d*n*/d*c* was estimated by assuming that all of a carefully weighed sample eluted from the column and that the refractive index was the same for all chain lengths in that sample. In practice, we have found that although the molecular weights of polystyrene standards could be measured accurately, functionalized ROMP polymers so far have typically yielded molecular weights higher than expected and that the results are not highly reproducible. The reasons for higher than expected molecular weights are still being investigated.

NMR spectra (300 MHz (^{1}H) and 75.4 MHz (^{13}C)) were recorded on a Varian XL-300 spectrometer. All chemical shifts are given in ppm and are referenced to tetramethylsilane. Obvious multiplicities and routine coupling constants are usually not listed. All spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. All IR spectra were recorded on a Perkin-Elmer FT-IR as Nujol mulls between KBr plates. Microanalyses were performed on a Perkin-Elmer 2400 microanalyzer.

Synthesis of 1,2:3,4-Di-*O*-isopropylidene-α-D-galactopyranos-6-*O*-yl 5-Norbornene-2-carboxylate (1). A solution of 2-norbornene-5-carboxylic acid chloride (1.79 g, 11.4 mmol) in ether (20 mL) was added dropwise over a period of 1 h to a −50 °C solution of 1,2:3,4-di-*O*-isopropylidene-D-galactopyranose (3.0 g, 11.5 mmol) dissolved in ether (50 mL) and triethylamine (1.28 g, 12.68 mmol) under a nitrogen atmosphere. The reaction mixture was allowed to warm slowly to room temperature and was stirred for 10 h. The white precipitate was filtered off and dissolved in ether (50 mL). The ether solution was washed twice with 10% K_2CO_3 aqueous solution and dried over $MgSO_4$. The ether was removed in vacuo and the pale yellow residue was then dissolved in a minimum amount of THF (3−5 mL). Dropwise addition of the THF solution to vigorously stirred ice water (∼700 mL) yielded white granular chunks, which were filtered off and dried in vacuo overnight. The solid was redissolved in ether in a drybox, and the solution was passed through a Celite pad. The ether was evaporated in vacuo to give a granular product. The monomer was recrystallized in a drybox from a mixture of ether and pentane by chilling to −30 °C. Crystallization was induced by scratching the flask; yield 2.4 g (55%) in two crops. ^{1}H NMR ($CDCl_3$) 1.23−1.53 (m), 1.90 (m), 2.26 (m), 2.88 (br s), 2.97 (m), 3.19 (br s), 3.23 (br s) (nonolefinic norbornene protons of endo and exo isomers); 5.97 (dd) and 6.16 (dd) (endo olefinic protons); 6.14 (m) (exo olefinic protons); 5.54 (d) and 5.51 (d) [1H], 4.59 (dd) and 4.60 (dd) [1H], 4.30 (m) [1H], 4.20 (dd) [1H], and 3.92−4.38 (m) [3H] (sugar group protons); 1.48 (s, 3H), 1.43 (s, 3H), 1.31 (s, 6H) (cyclic acetal protons). ^{13}C NMR ($CDCl_3$) 174.7 (carbonyl), 137.7, 137.6, 133.0, 132.8 (olefinic carbon), 109.8, 108.9 (isopropylidene), 96.5, 71.3, 70.9, 70.6, 70.5, 66.4, 66.2, 63.5, 63.4, 63.3 (sugar group), 49.7, 46.6, 45.8, 43.4, 43.3, 42.7, 29.5, 29.2 (norbornene), 26.2, 25.1, 24.6 (isopropylidene methyl groups). Anal. Calcd for $C_{20}H_{28}O_7$: C, 63.14; H, 7.42. Found: C, 63.35; H, 7.38.

^{13}C NMR resonances for 1,2:3,4-di-*O*-isopropylidene-D-galactopyranose (in $CDCl_3$) are found at δ 109.1, 108.5 (isopropylidene C), 96.1, 71.1, 70.5, 70.4, 68.3, 61.5 (galactopyranose) and 25.8, 24.8, 24.2 (isopropylidene methyl).

Synthesis of Bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-*O*-yl) 5-Norbornene-*trans*-2,3-dicarboxylate (2). The procedure was similar to that for **1** except that *trans*-5-norbornene-2,3-dicarbonyl chloride was employed instead of 5-norbornene-2-carboxylic acid chloride; yield 80% before recrystallization. The monomer was further purified by recrystallization in a drybox from a mixture of ether and pentane until no improvement was seen in the polydispersity of polymers. ^{1}H NMR ($CDCl_3$) 1.40−1.61 [2H], 2.73 (t, 1H), 3.14 (br s) and 3.15 (br s) [1H], 3.25 (br s) and 3.29 (br s) [1H], 3.43 (q, 1H) (nonolefinic norbornene protons); 6.11 (dd) and 6.24 (m) [2H] (olefinic protons); 5.51 (t, 2H), 4.59 (d, 2H), 4.22 (m, 2H), 3.90−4.45 (m, 6H) (sugar group protons); 1.47 (d, 6), 1.43 (s, 6), 1.30 (s, 12) (cyclic acetal protons). ^{13}C NMR ($CDCl_3$) δ 174.5, 174.4, 173.3, 173.2 (carbonyl), 137.6, 135.8, 135.7 (olefinic carbon), 109.9, 109.8, 108.9 (isopropylidene), 96.5, 96.4, 71.2, 70.9, 70.7, 70.6, 66.4, 66.2, 66.1, 63.9, 63.8, 63.6 (sugar group), 47.9−48.2, 47.2−47.5, 46.0 (norbornene group), 26.2, 25.2, 24.6 (isopropylidene Me).

Synthesis of 3. A solution of 2-norbornene-5-carboxylic acid chloride (1.75 g, 11.2 mmol) in tetrahydrofuran (20 mL) was added dropwise over a period of 0.5 h to a solution of 2,3-*O*-isopropylidene-D-ribonic γ-lactone (2.12 g, 11.2 mmol) dissolved in a mixture of THF (50 mL) and triethylamine (1.48 g, 14.6 mmol) at −35 °C under a nitrogen atmosphere. The reaction mixture was allowed to warm slowly to room temperature and was stirred for 20 h. The white precipitate was filtered off and washed with ether (50 mL). The solvents were evaporated, and the residue was extracted with ether (>150 mL). The ether solution was washed twice with aqueous K_2CO_3 (2 × 100 mL) and then dried over $MgSO_4$. Removal of the solvent from the filtrate left white chunks. These were dissolved in a minimum amount of THF, and the solution was added dropwise to vigorously stirred ice water (∼700 mL) to yield massive white granular chunks. The white chunks were filtered off and dried in vacuo overnight; yield 2.88 g. The monomer for polymerization was purified by recrystallization in a drybox from chilled (−30 °C) tetrahydrofuran and pentane. ^{1}H NMR ($CDCl_3$) 1.24−1.45 (m), 1.90 (m), 2.16 (m), 2.89−2.97 (br and m), 3.11 (br s) (nonolefinic norbornene protons of both endo and exo isomers); 5.87 (dd) and 6.17 (dd) (endo olefinic protons); 6.04−6.22 (m) (exo olefinic protons); 4.80 (d, 1H), 4.74

(t, 1H), 4.69−4.65 (m) [1H], 4.10−4.43 (m) [2H] (protons of ribonic γ-lactone group); 1.47 (s), 1.39 (s), 1.38 (s, 3H) (cyclic acetal protons).

Synthesis of 2,3:5,6-Di-*O*-isopropylidene-α-D-mannofuranos-1-*O*-yl 5-Norbornene-2-carboxylate (4). A solution of 2-norbornene-5-carboxylic acid chloride (1.64 g, 10.5 mmol) in tetrahydrofuran (20 mL) was added dropwise over a period of 1 h into a solution of 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (2.73 g, 10.5 mmol) dissolved in THF (50 mL) and triethylamine (1.17 g, 11.5 mmol) at −35 °C under a nitrogen atmosphere. The reaction mixture was allowed to warm slowly to room temperature and to stir for 20 h. **4** was isolated as described for **3**. ^{1}H NMR ($CDCl_3$) 1.22−1.53 (m), 1.85 (m), 2.15 (m), 2.88 (br s), 2.97 (br s), 3.13 (br s), 3.22 (br s), 2.87−2.93 (m) (nonolefinic norbornene protons of both endo and exo isomers); 5.86 (m) and 6.16 (m) (endo olefinic protons); 6.06 (m) (exo olefinic protons); 6.10 (d) and 6.03 (d) [1H], 4.82 (m, 1H), 4.63 (m) and 4.67 (m) [1H], 4.35 (m, 1H), 4.00−4.09 (m) and 3.93−3.99 (m) [3H] (sugar group protons); 1.44 (s), 1.43 (s), 1.42 (s), 1.38 (s), 1.33 (s, 3H), 1.30 (s, 3H) (cyclic acetal protons). ^{13}C NMR ($CDCl_3$) δ 173.1 (carbonyl), 138.3, 138.2, 135.8, 135.7, 132.1 (olefinic carbon), 113.4, 109.5 (isopropylidene), 100.9, 100.8, 100.7, 100.5, 85.2 (d), 82.3, 79.5, 73.0, 67.1 (sugar group), 49.9, 46.5, 46.0, 43.6, 43.3, 42.7, 41.8, 29.2, 27.2 (nonolefinic carbon of norbornene), 26.1, 25.3, 24.9 (isopropylidene).

Synthesis of *trans*-2,3-Bis((trimethylsiloxy)methyl)-norborn-5-ene (6). Trimethylsilyl chloride (2.33 g, 21.4 mmol) dissolved in tetrahydrofuran (20 mL) was added dropwise to a THF (50 mL) solution containing *trans*-2,3-bis-(hydroxymethyl)norborn-5-ene (1.5 g, 9.73 mmol) and triethylamine (2.16 g, 21.4 mmol) at −30 °C under a nitrogen atmosphere. The reaction mixture was then allowed to warm slowly to room temperature and to stir for 3 h. The triethylamine hydrochloride was filtered off and washed with toluene (20 mL). Removal of the solvents in vacuo left the colorless liquid product in high yield (>80%). The product was purified for polymerization by passing through an activated alumina short column prior to use until no improvement was seen in polydispersity of the polymers. *trans*-2,3-Bis(hydroxymethyl)-norborn-5-ene was synthesized from *trans*-2,3-bis(carboxymethyl)norborn-5-ene by reduction with $LiAlH_4$ in THF (yield >95%). ^{1}H NMR δ 0.10 (d, 18H, TMS), 1.02 (m, 1H), 1.39 (s, 2H), 1.68 (m, 1H), 2.67 (br s, 1H), 2.83 (br s, 1H), 3.15 (t, 1H), 3.30−3.45 (m, 2H), 3.69 (dd, 1H), 5.98 (dd, 1H), 6.18 (dd, 1H).

Synthesis of Homopolymers of 1, 2, 3, and 4. A toluene solution of $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(O\text{-}t\text{-}Bu)_2$ (2−7 mg/0.3−1.0 mL of toluene) was added in one portion to a rapidly stirred solution of monomer in toluene (2−5 mL) at room temperature, and the solution was stirred for the prescribed time (1 h). The polymerization was quenched by adding benzaldehyde (∼10 mg). The solvents were removed in vacuo after 1 h, and the resultant solid was dissolved in the minimum amount of THF (∼2 mL). This solution was poured dropwise into vigorously stirred cold water (∼80 mL) to afford white to pale yellow precipitates. The polymer was collected by filtration and dried in vacuo.

Syntheses of poly(**1**) in Table 1 were carried out in the same manner. The catalyst solution (4 mg) was added in one portion to the toluene (4.8 g) solution containing **1** (104 mg), and the reaction mixture was allowed to sitr at room temperature for the prescribed time.

Poly(1): ^{1}H NMR ($CDCl_3$) 1.60 (br), 1.92 (br), and 2.3−3.2 (br) (protons of the five-membered ring); 5.1 (br, olefinic H), 5.1−5.5 (br, olefinic H); δ 1.31 (s, 6, Me), 1.43 (s, 3, Me), 1.48 (s, 3, Me) (cyclic acetal group); 3.95 (br s), 4.18 (br d), 4.27 (br s), 4.58 (br), 5.48 (br s), 3.9-4.1 (br) (sugar group protons). ^{13}C NMR ($CDCl_3$) δ 174.8 (carbonyl), 135.0, 129.9, 129.2, 128.2, 126.3 (olefinic carbon), 109.7, 108.9 (isopropylidene), 96.5, 71.2, 70.9, 70.6, 66.0, 63.4, 63.1 (sugar group), 43.0−43.1, 40.8−41.2, 39.9, 36.0−36.8, 29.1 (five-membered ring), 26.2, 25.2, 24.7 (isopropylidene); IR (Nujol) 1731 cm^{-1} (carbonyl).

Poly(2): ^{1}H NMR ($CDCl_3$) 1.58 (br), 1.82 (br), 2.70 (br), 2.90 (br), 3.20 (br) (protons of five-membered ring); 5.51 (br s), 5.3−5.6 (br) (olefinic protons); 1.30 (s, Me), 1.41 (s, Me), 1.47 (s, Me) (protons of cyclic acetal group); 3.95 (br s), 4.20 (br s), 4.25 (br s), 4.59 (br s) (protons of sugar group). ^{13}C NMR ($CDCl_3$) 174.1, 173.8, 173.0−173.3 (carbonyl), 134.6, 130.7, 129.9, 129.2, 128.4, 125.5 (olefinic carbon), 109.6, 108.9 (isopropylidene), 96.4, 71.1, 70.9, 70.7, 65.8, 63.6 (sugar group), 52.8−53.2, 51.7−52.3, 46.5−47.2, 45.3−45.6, 38.7−39.0 (carbons of five-membered ring), 26.2, 25.2, 24.7 (isopropylidene); IR (Nujol) 1731 cm^{-1} (carbonyl).

Poly(3): ^{1}H NMR ($CDCl_3$) 1.30 (s, Me), 1.35 (s, Me), 1.39 (s, Me), 1.43 (s, Me) (isopropylidene); 1.70 (br), 1.95 (br), and 2.3−3.2 (br) (H of five-membered ring); 4.00 (br d), 4.61 (br s), 4.80 (br s), 5.70 (br), 5.95−6.15 (br) (sugar group), 5.50−5.50 (br, olefinic proton). ^{13}C NMR ($CDCl_3$) δ 174.1−173.3, 173.2 (carbonyl), 134.9−134.6, 133.7−132.5, 131.4−131.2, 129.9, 129.1, 129.0−128.2, 126.2, 125.6 (olefinic carbon), 113.3, 109.4 (isopropylidene), 101.5−100.4, 85.2, 82.3, 79.4, 73.0, 67.0 (sugar group), 49.2, 47.6−48.4, 45.5-46.2, 39.7−43.0, 37.0−38.0, 35.3−36.5, 30.4 (five-membered ring), 27.1, 26.0, 25.2, 24.8 (isopropylidene).

Synthesis of Block Copolymers. Block copolymers were prepared by sequentially adding monomers and were isolated similarly. For block copolymers containing **6**, samples for GPC were prepared after the purification procedure by washing with chilled pentane.

Hydrolysis Procedure. Poly(**2**) (monomer/catalyst = 30, 180 mg) was added to a stirred solution consisting of CF_3CO_2H/H_2O (9/1, v/v, 1.5 g), and the reaction mixture was stirred for 15 min at room temperature. The homogeneous pale blue solution was poured dropwise into a vigorously stirred THF solution (∼70 mL) at 0 °C. The pale blue to white precipitate was collected by filtration, washed with THF (∼20 mL), hexanes (∼100 mL), and ether (∼50 mL) and then dried in vacuo to afford poly(**2′**) as a white powder (140 mg, 88%); ^{13}C NMR spectra were measured in D_2O in the presence of a small amount of tetrahydrofuran as an internal standard.

Tetrablock copolymers containing **1** or **2** were hydrolyzed in the same manner. The polymer (190 mg) was used for the reaction, and 150 mg (89% yield) was collected as a white powder. ^{13}C NMR spectra were measured in D_2O in the presence of a small amount of tetrahydrofuran as an internal standard.

Poly(**1**): Poly(**1**)$_{30}$ (250 mg) was added to a stirred solution consisting of CF_3CO_2H/H_2O (9/1, v/v, 1.8 g), and the reaction mixture was stirred for 15 min at room temperature. The homogeneous pale blue solution was poured dropwise to a vigorously stirred THF solution (∼18 mL) at ca. −30 °C, and stirred for ∼3 min to give a pale blue solution and a white precipitate. Hexane (∼3 mL) was added to the stirred solution and the pale blue to white precipitate of poly (**1′**) was filtered off, washed with cold hexane (∼30 mL) and ether (∼20 mL), and dried in *vacuo*; yield 195 mg (87%).

The proton NMR spectrum of poly(**1′**) was similar to that of poly(**1**) except that resonances at δ 1.31−1.48 due to the cyclic acetal were not seen and several broad peaks (3.4−5.0 ppm) were observed; IR (Nujol) 3424 (broad, OH), 1728 cm^{-1} (carbonyl). The characteristic broad absorption at ∼920 cm^{-1} due to the typical carboxylic acid was not observed.

Poly(2′). ^{1}H NMR (D_2O) 1.32 (br), 1.90 (br), 2.64 (br), 2.85 (br), 3.21 (br) (protons of five-membered ring); 5.15−5.30 (br), 5.32−5.50 (br) (olefinic protons); 3.35 (br), 3.50 (br), 3.70 (br s), 4.10 (br s), 4.42 (br s), 5.10 (br s), 3.60−3.90 (br), 3.90−4.30 (br). The spectrum pattern was similar to that of poly(**2**) except that resonances at δ 1.30−1.47 due to the cyclic acetal were not seen and that several broad peaks (3.3−5.2 ppm) were observed. ^{13}C NMR (D_2O) 174.2−174.3, 173.4−173.5 (carbonyl), 133.3, 132.3−132.5, 130.3−131.1, 129.9, 128.3, 125.6 (olefinic carbon), 96.4, 92.1, 72.3, 71.6, 69.1, 68.7, 68.4, 68.0, 67.2, 63.8−64.2, 63.3−63.7 (sugar group), 51.0−52.4, 45.3−46.0, 43.0−44.4, 37.0-38.5 (carbons of five-membered ring); IR (Nujol) 3424 (broad due to OH) and 1728 cm^{-1} (carbonyl). A broad characteristic absorption band at ∼920 cm^{-1} due to the typical carboxylic acid was not observed.

Tetrablock Copolymer of 1 and 2 (after Hydrolysis). ^{13}C NMR (D_2O) 174.3−174.8, 173.5−174.0 (carbonyl), 131.8−134.0, 129.0−131.3 (olefinic carbon), 96.4, 92.1, 72.4, 71.6, 71.3, 68.7−69.2, 68.7, 68.5, 63.2−64.3 (sugar group), 51.3−52.0,

45.4, 43.2, 41.3, 40.5, 38.0, 37.9, 37.3, 35.1 (carbons of five-membered ring).

Acknowledgment. R.R.S. thanks the Navy for supporting research on ring-opening metathesis polymerization and K.N. thanks the Sumitomo Chemical Co., Ltd. for support.

Supporting Information Available: Proton NMR spectrum of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose, carbon NMR spectrum of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose, proton NMR spectrum of **1** in $CDCl_3$, carbon NMR spectrum of **1** in $CDCl_3$, proton NMR spectrum of poly(**1**) in $CDCl_3$, carbon NMR spectrum of poly(**1**) in $CDCl_3$, carbon NMR spectrum of **2** in $CDCl_3$, carbon NMR spectrum of poly(**2**) in $CDCl_3$, carbon NMR spectrum of hydrolyzed poly(**2**) in D_2O, carbon NMR spectrum of **4** in $CDCl_3$, carbon NMR spectrum of poly(**4**) in $CDCl_3$, FT-IR spectrum of poly(**1**) in Nujol, FT-IR spectrum of hydrolyzed poly(**1**) in Nujol, FT-IR spectrum of poly(**2**) in Nujol, and FT-IR spectrum of hydrolyzed poly(**2**) in Nujol (14 pages). Ordering information is given on any current masthead page.

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MA9512519