Synthesis of Isoxazolino Norbornene Derivatives Containing Sugar Residues by 1,3-Dipolar Cycloaddition and Their Application to the Synthesis of Neoglycopolymers by Living Ring-Opening Metathesis Polymerization

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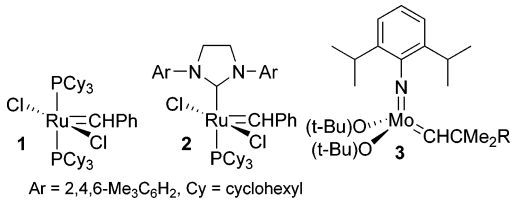
ABSTRACT: The in situ generation and subsequent cycloaddition of glycosyl nitrile oxides to norbornadiene (NBD) afforded monomeric isoxazolino norbornenes bearing xylose, glucose, and mannose residues in high yields. Ring-opening metathesis polymerization (ROMP) of the norbornene derivatives containing acetyl-protected sugar residues initiated by $Ru(CHPh)(Cl)_2(PCy_3)_2$ (**1**) and $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(O^tBu)_2$ (**3**) proceeded in a living manner with quantitative initiation, affording polymers with narrow molecular weight distributions ($M_w/M_n = 1.11-1.35$). The living nature of this polymerization by **1** was further demonstrated by the preparation of diblock copolymers in a precise manner by the sequential polymerization of norbornene and its carbohydrate derivatives. Polymers bearing multiple sugar units bearing free sugars were prepared by the deacetylation of the glycopolymers under basic conditions, and olefinic double bonds in these ROMP polymers were hydrogenated exclusively by *p*-toluenesulfonhydrazide in chlorobenzene without cleavage of the sugar functionality.

Introduction

The synthesis of carbohydrate-functionalized oligomers/polymers has attracted considerable attention recently due to their ability to mediate a wide range of recognition events via lectin−ligand attachments.[1] These unexpected specific and strong affinities can be explained as resulting from the clustering of lectins with multivalent arrays that lead to a greater affinity and specificity than the corresponding monovalent interactions, which are extremely weak. Numerous cellular recognition processes thus depend on protein−carbohydrate interactions, and these attachments are critical in fertilization, cell signaling, pathogen identification, and the inflammatory response.[1,2] Previous methods of preparing these polymers bearing multiple sugar units were by free radical, coordination, and cationic/anionic polymerization,[3] and the reports using ring-opening metathesis polymerization (ROMP) have also been seen recently after the initial findings of Kiessling et al.[4a] describing the synthesis of multivalent arrays of sugar epitopes.[3a,4,5] These ROMP polymers displayed increased activity compared to that of their corresponding monomeric counterparts as inhibitors of a cell surface lectin[3a,4,5] because Kiessling et al. demonstrated that relatively linear polymers prepared by ROMP possessed structural properties that favor clustering.[4g] This ROMP technique has benefited greatly from the synthesis of the well-defined ruthenium carbenes, $Ru(CHPh)(Cl)_2(PCy_3)_2$ (**1**, Cy = cyclohexyl), $Ru(CHPh)(Cl)_2(IMesH_2)(PCy_3)$ (**2**, $IMesH_2$ = 1,3-dimesityl-4,5-dihydromidazol-2-ylidene), developed by Grubbs and co-workers[6,7] (Chart 1), because of their functional group tolerance, high reactivity, and their ability to produce well-defined polymers with controlled architectures and terminal functionalities.[6] Moreover, these ruthenium initiators, especially **1**, are also known to facilitate living polymerizations of norbornene derivatives containing sugars in some cases,[8] enabling molecular weight control and the synthesis of block copolymers.[8b] The molybdenum-alkylidene initiator, $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(O^tBu)_2$ (**3**, Chart 1) was also illustrated as a more effective initiator for the precise preparation of sugar-functionalized polymers[9] because the polymerization of substituted norbornenes and norbornadienes generally proceeds in a living manner with quantitative initiation efficiency,[10,11] and the absence of chain-transfer and termination reactions in such polymerizations allows for the production of homopolymers and block copolymers with narrow molecular weight distributions, as well as enabling the control of terminal groups in both the initiation and the termination sites.[9c,10,11]

Chart 1



We recently reported that isoxazoline-functionalized monomers containing phenyl and ester substitutents,[12] prepared by the cycloaddition of nitrile oxides[13] to norbornadiene, could be polymerized by using the ruthenium initiators **1** and **2**.[6] Norbornene derivatives, in particular those containing sugar (or peptide) functionalities for the ROMP, have been prepared in most cases by (i) use of the norbornene imide template derived from the carboxylic acid anhydride via Diels−Alder addition, and (ii) esterification of a carboxylic acid chloride with a hydroxyl/amino group.[4−6,8] Since we previously demonstrated that glycosyl nitrile oxides may be generated by the dehydration

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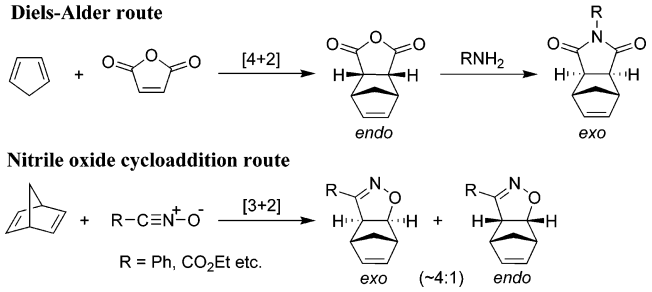
Scheme 1



of the corresponding nitromethyl compound (RCH_2NO_2)[14] (Scheme 1), we therefore decided to explore the application of this technique to prepare norbornene derivatives containing carbohydrate functionalities. This is because, we believe, the present approach may introduce a new synthetic strategy to prepare norbornene derivatives as well as ROMP polymers containing sugars in a controlled manner, not only because the polymerization by $Ru(CHPh)(Cl)_2(PCy_3)_2$ (**1**) and $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)(O^{t}Bu)_2$ (**3**) should take place in a living manner if the hydroxyl groups are protected by acetyl groups in advance,[8b,9] but also because the deprotection of sugar functionality should be easier due to the *C*-glycosidic linkage compared to ester/amide or imide linkages.[15] Moreover, the present approach produces polymers in which the carbohydrates are attached to the polymer via *C*-glycosidic bonds, which are resistant toward both chemical and biological assault in vivo. Additionally, the sugar functionalities may be thus stable without decomposition, even upon the hydrogenation of the resultant ROMP polymers.[4d,5b]

In this paper, we would thus like to introduce the synthesis of norbornene derivatives containing sugars by the 1,3-dipolar cycloaddition reaction of glycosyl nitrile oxides to norbornadiene and their ROMP by using ruthenium (**1**,**2**) and molybdenum (**3**) initiators. We also wish to present that the present method introduces the controlled synthesis of neoglycopolymers by the living ROMP technique, exclusive deprotection, and even hydrogenation of the olefinic double bond in the polymers.

Results and Discussion

1. Synthesis of Carbohydrate Containing Monomers. As described above, we previously demonstrated that glycosyl nitrile oxides should be generated by the dehydration of the corresponding nitromethyl compound (RCH_2NO_2),[14] and we therefore applied this technique to prepare norbornene derivatives containing carbohydrate functionalities. The xylose nitrile oxide (**5a**), derived from 2′,3′,4′-tri-*O*-acetyl-*β*-xylopyranosylnitromethane (**4a**), was reacted with norbornadiene, resulting in 2′,3′,4′-tri-*O*-acetyl-*β*-D-xylopyranosyl-3a,4,7,7a-tetrahydro-4,7-methano-benzo[*d*]isoxazole (**6a**), which was isolated after flash column chromatography as a mixture of exo (63%) and endo (15%) cycloadducts (Scheme 2) in a diastereomeric ratio of 62:38 (illustrated in the inset of Scheme 2). A series of 1D and 2D (COSY and HETCOR) NMR experiments were performed, from which a full assignment of the structure of **6a** was possible. For this exo-adduct, the isoxazoline protons H^{3a} (δ_H 3.42) and H^{7a} (δ_H 4.94, $J_{3a,7a}$ = 9.0 Hz) have small couplings to the adjacent bridgehead protons H^4 and H^7 of 1.9 and 1.5 Hz, respectively, with signals for the protons of the xylose ring at 3.86−5.24 ($H^{1'}$-$H^{5'}$) and the acetate protecting groups at 2.04−2.06 ppm ($COCH_3$). This protection strategy was adopted due to their facile cleavage of the acetyl group under basic conditions according to the established procedure.[16]

The glucose and mannose analogues were also chosen because these saccharides are known to act as potent inhibitors of *Concanavalin A* (Con A)-induced cell agglutination.[4a] The glucose analogue, 3-(2′,3′,4′,5′-tetra-*O*-acetyl-*β*-D-glucopyranosyl)-3a,4,7,7a-tetrahydro-4,7-methanobenzo[*d*]isoxazole (**6b**), could be prepared in moderate yield by reaction of the glucose nitromethane (**4b**) with norbornadiene, and **6b** was isolated as the exo-adducts (59%) contaminated with a 15% trace of the endo-isomers (in a diastereomeric ratio of 55:45, estimated from the ^{13}C NMR spectrum). The flexibility of this approach was further highlighted by the preparation of the mannose analogue **6c** in good yield (65%) as a diastereoisomeric mixture of exo and endo cycloadducts. These norbornenyl monomers **6a**−**c** were recrystallized from a mixture of hexane and ether under nitrogen atmosphere before polymerization to ensure optimum purity because monomer purity is an especially important requirement in the present living polymerization system, especially due to the high sensitivity of the molybdenum initiator (**3**) to moisture and oxygen.

2. Ring-Opening Metathesis Polymerization (ROMP) of Norbornenes Containing Xylose (6a), Glucose (6b), and Mannose (6c) Initiated by the Ruthenium (1, 2) and Molybdenum (3) Complexes. Polymerizations of **6a** initiated by the ruthenium complex (**1**) were conducted in dichloromethane under various monomer/initiator molar ratios (**6a**/**1**, molar ratio), and the reactions were terminated by using ethyl vinyl ether, a method that is widely employed in systems of this general type.[6] As shown in Table 1, these polymerizations took place efficiently, affording **7a** in high yields (84−96%), and the M_n value increased upon increasing the molar ratio (runs 1−8). A linear relationship between the M_n value and the feedstock ratio of monomer (**6a**) to the initiator (**1**) was observed (Figure 1), and the resultant polymers possessed low polydispersity indexes (M_w/M_n = 1.11−1.35).[8,9] These results clearly indicate that ring-opened polymers containing carbohydrate residues can be prepared in a living manner under these conditions, although the preparation of glycopolymers longer than 50 monomer repeated units with **1** under certain conditions had been problematic in a previous report.[17,18]

The ^1H NMR spectra for the resultant polymers showed broad resonances at 5.32−5.60 ppm due to the olefinic protons in the ring-opened structure, and the resonances ascribable to the sugar group were relatively sharp, consistent with a relatively homogeneous environment of the side chains. Almost certainly the resultant polymers do not have regular structures, but are probably a mixture of cis and trans double bonds and a mixture of regioisomers, head-to-head, head-to-tail, and tail-to-tail arrangement of the repeat unit. This assumption was also suggested by the reaction of **6a** with **1** (**6a**/**1** = 1.0, Table 1, entry 1) in $CDCl_3$, monitored by ^1H NMR spectroscopy,[12,19] because the main propagating species **8a** and **8a′** (Chart 2) revealed two poorly resolved resonances in the ^1H NMR spectrum at ca. δ_H 19.6 ppm, which would be explained partly as mixture of regioisomers, along with a sharp singlet at 19.9 ppm attributable to the hydrogen of the initiator (in addition to some broad features are evident at lower frequency, ca. 18.8 and 19.1 ppm, which may be attributed to the propagating species in which only one phosphine is bound to the ruthenium center).[19c]

In the same manner, polymerization of **6c** with **1** (**6c**/**1** = 30 and 50) afforded **7c** in high yields (>91%), and the resultant polymers possessed molecular weights analogous to the calculated values (M_n = 1.47 and 2.41 × 10^4) with narrow molecular weight distributions (M_w/M_n = 1.13−1.22). The dependence of

Scheme 2. Reagents: (i) $MeNO_2$/NaOMe, MeOH; (ii) H_2O, Reflux; (iii) Ac_2O/CF_3SO_3H; (iv) Toluene Diisocyanate (TDI)/ Triethylamine Toluene, Reflux; (v) norbornadiene; (vi) Quench with $H_2NCH_2CH_2NH_2$; (vii) 1 or 2, CH_2Cl_2, 25 °C; (viii) $EtOCH{=}CH_2$.

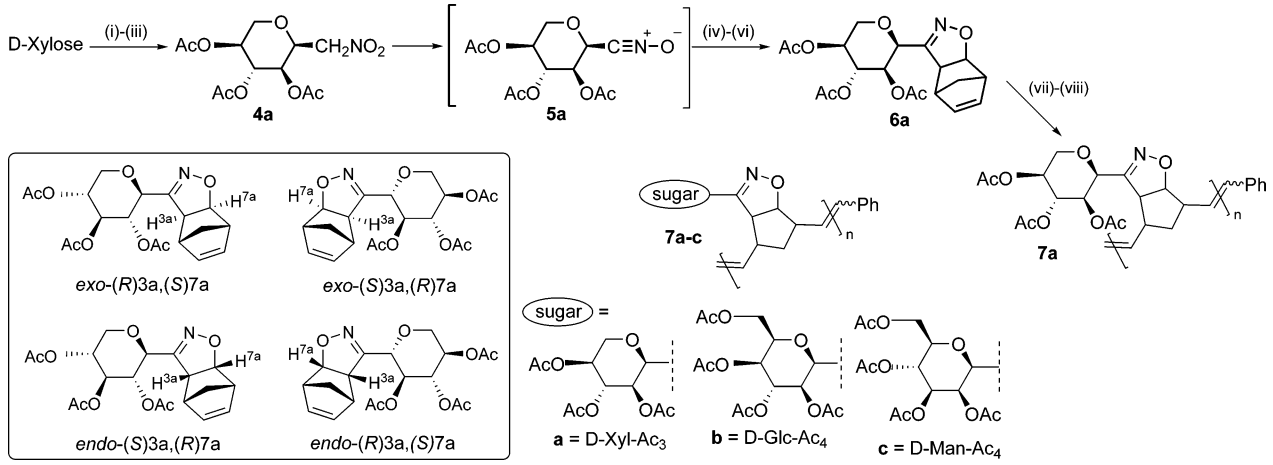


Table 1. Homopolymerization of 6a−c with Ruthenium Initiators 1−2 in CH_2Cl_2[a]

run no.	monomer	[M]/[I][b]	initiator	time/min	$M_{n(calcd)}$[c] × 10^{-4}	$M_{n(obs)}$[d] × 10^{-4}	M_w/M_n[d]	yield[e]/%
1	**6a**	1	**1**	15	0.04	0.04[f]		88
2	**6a**	3	**1**	15	0.12	0.12	1.15	86
3	**6a**	10	**1**	15	0.39	0.54	1.35	84
4	**6a**	20	**1**	20	0.80	0.82	1.14	96
5	**6a**	30	**1**	30	1.18	1.21	1.15	87
6	**6a**	40	**1**	40	1.58	1.64	1.11	93
7	**6a**	50	**1**	50	1.96	2.43	1.34	92
8	**6a**	85	**1**	100	3.34	3.96	1.24	85
9	**6a**	30	**2**	60	1.18	47.05	1.64	75[g]
10	**6b**	30	**2**	60	1.40	8.37	1.84	71[g]
11	**6c**	30	**1**	30	1.40	1.47	1.13	93
12	**6c**	50	**1**	50	2.33	2.41	1.22	91

[a] Conditions: complex **1** or **2** 8.0 μmol, CH_2Cl_2 (total 2.0 mL) at 25 °C. [b] Initial monomer/initiator molar ratio. [c] Calculated on the basis of the monomer/initiator molar ratio. [d] Measured by GPC in THF vs polystyrene standards. [e] Isolated yields as methanol insoluble fraction. [f] Estimated from ^{1}H NMR spectrum. [g] Formation of oligomers ($n < 5$) were also confirmed as methanol soluble fraction.

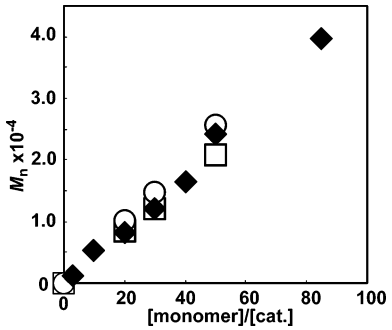
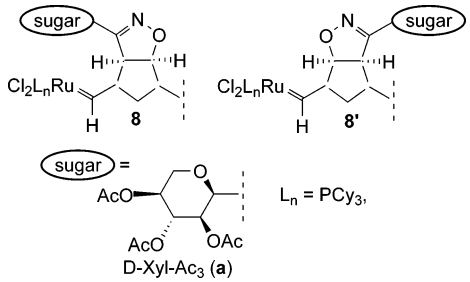


Figure 1. Dependence of the number-average molecular weights (M_n) on the initial [monomer]/[initiator] molar ratios (results based in Table 1). ◆: **7a** by **1**; □: **7a** by **3**; ○: **7c** by **3**.

Chart 2



the molecular weight of **7c** on the initial feedstock ratios, coupled with the narrow molecular weight distribution, illustrated that the polymerization of **6c** with **1** also occurred in a living manner.

The polymerization of **6a** with **2** (**6a**/**2** = 30) afforded **7a** (75%, isolated yield) with a $M_n = 47.05 \times 10^4$, and this M_n value was larger than that prepared by **1** ($M_n = 1.21 \times 10^4$) under the same conditions. The broad molecular weight distribution ($M_w/M_n = 1.64$) may be attributed to a rapid propagation rate versus slow initiation[6] and partial cross metathesis with the internal olefins during/after the polymerization. The breadth of the signals in the ^{1}H and ^{13}C NMR spectra of **7a** produced with both **1** and **2** inhibited an exact estimation of the cis/trans content, which may be attributable to the many different conformations of the repeat unit.[12] The reactivity of **6b** with **2** was gauged by the polymerization of the glucose analogue (**6b**/**2** = 30), affording **7b** (71%), which revealed a $M_n = 8.37 \times 10^4$. Reasons for low isolated yields for **7a** and **7b** prepared by **2** (75%, 71%, respectively) were due to the formation of low-molecular-weight oligomers (less than 5 mer) confirmed by ^{1}H NMR spectra as a methanol soluble fraction, and the results may suggest that partial cross metathesis with internal olefins occurred after the ROMP. Although the molecular weight distributions were somewhat broad, these results demonstrate that synthesis of high-molecular-weight ROMP polymer can be achieved with rapid propagation by **2**, as reported previously.[8b]

Living ROMP of Isoxazolino Norbornenes with the Mo Alkylidene 3. Mo(CHCMe$_2$Ph)(*N*-2,6-^{i}Pr$_2$C$_6$H$_3$)(O^{t}Bu)$_2$ (**3**) was chosen as the initiator because it appears to be the mildest among the well-defined molybdenum initiators, especially for the ROMP,[10] and most examples for the synthesis of these types of polymers were successful by **3**.[9] The polymerizations were performed in toluene at 25 °C, were terminated by adding

Table 2. Homopolymerization of 6a and 6c with Molybdenum Initiator 3 in Toluene[a]

run no.	monomer	[M]/[I][b]	time/min	$M_{n(calcd)}$[c] $\times 10^{-4}$	$M_{n(obs)}$[d] $\times 10^{-4}$	M_w/M_n[d]	yield[e]/%
13	**6a**	20	20	0.81	0.85	1.17	96
14	**6a**	30	30	1.19	1.21	1.15	99
15	**6a**	50	50	1.98	2.09	1.12	97
16	**6c**	20	20	0.95	1.01	1.13	95
17	**6c**	30	30	1.41	1.47	1.13	97
18	**6c**	50	50	2.34	2.56	1.19	98

[a] Conditions: complex **3** 8.0 μmol, toluene (total 2.0 mL) at 25 °C. [b] Initial monomer/initiator molar ratio. [c] Calculated on the basis of the monomer/initiator molar ratio. [d] Measured by GPC in THF vs polystyrene standards. [e] Isolated yield.

Table 3. Copolymerization of 6a, 6c with NBE by 1 in CH_2Cl_2[a]

run no.	monomer[a] n/m	initiator	[n]/[m][b]	time/min 1st/2nd	$M_{n(calcd)}$[c] $\times 10^{-4}$	$M_{n(obs)}$[d] $\times 10^{-4}$	M_w/M_n[d]	yield[e]/%
19	**6a**/NBE	**1**	20:20	20/20	0.93	0.94	1.28	98
20	**6a**/NBE	**1**	30:20	30/20	1.38	1.72	1.22	96
21	**6a**/NBE	**1**	50:20	60/20	2.16	2.25	1.19	98
22	**6c**/NBE	**1**	20:20	20/20	1.13	1.19	1.21	94
23	**6c**/NBE	**1**	30:20	30/20	1.59	1.64	1.17	97
24	**6c**/NBE	**1**	50:20	60/20	2.52	2.57	1.20	96

[a] Conditions: complex **1** 8.0 μmol, CH_2Cl_2 [total 2.0 (1st) + 1.0 mL (2nd polymerization)] at 25 °C. [b] Initial monomer/initiator molar ratio. [c] Calculated on the basis of the monomer/initiator ratio. [d] Measured by GPC in THF vs polystyrene standards. [e] Isolated yield.

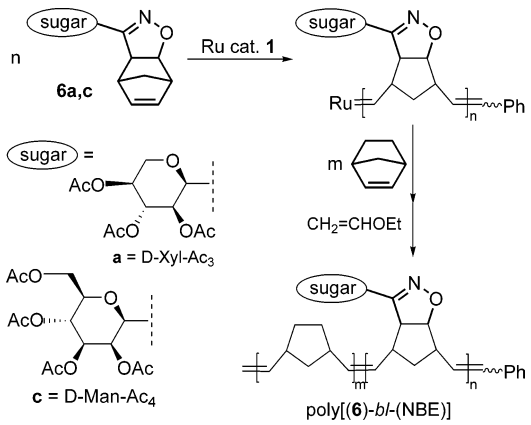
PhCHO, and the results are summarized in Table 2. At varying initial feedstock ratios (**6a**/**3**) of 20:1, 30:1, and 50:1, the polymers formed revealed molecular weights (M_n) observed by GPC, in close correlation to those calculated (Table 2, runs 13−15, Figure 1) with narrow molecular weight distributions (M_w/M_n = 1.12−1.17). ^{1}H and ^{13}C NMR spectra for resultant polymers, **7a** and **7c**, showed that these polymers possessed ring-opened structure in all cases and were comprised of both cis and trans olefinic double bonds.

Similarly, the reaction of the mannose derivative **6c** with **3** at identical feedstock ratios produced polymers with valencies dependent on the initial concentrations (runs 16−18) while maintaining narrow polydispersities (M_w/M_n = 1.13−1.19, Figure 1). These results demonstrate that isoxazoline NBEs bearing carbohydrates can be polymerized by using the molybdenum-alkylidene **3** to afford polymers bearing multiple sugar units of carbohydrates in high yield (95−99%) in a precisely controlled manner.

3. Preparation of Copolymers Using the Ruthenium Initiator 1. Having established that sugar containing isoxazoline NBEs (**6a**,**c**) are readily polymerized with the ruthenium complex **1**, and that the polymerization was strongly suggested to proceed in a living manner, we investigated the possibility of **6a,c** as comonomers for the preparation of diblock copolymers.[8b,9,20] As shown in Table 3 (runs 19−21), various block ROMP copolymers, poly[(**6a**)-*bl*-(NBE)]s, consisting of NBE and the xylose-substituted NBE **6a**, were prepared in high yields (>96%) by sequential addition and the subsequent termination with ethyl vinyl ether (Scheme 3). The M_n values for the resultant copolymers were dependent on the initial feedstock ratio (Figure 2), and the M_w/M_n values were low in all cases, and these results clearly indicate that the polymerization proceeded in a living manner. Similarly, the mannose derivative **6c** was copolymerized with NBE (runs 22−24) affording poly[(**6c**)-*bl*-(NBE)]s in a precise manner in high yields (94−97%) with narrow molecular weight distributions (M_w/M_n = 1.17−1.21). These facts strongly suggest that well-defined carbohydrate functionalized copolymers can be accessed with isoxazoline norbornenes.[21,22]

4. Deacetylation of Neoglycopolymers and Hydrogenation of Homopolymers. Carbohydrate oligomers that modulate cell surface events have sugar residues containing hydroxyl groups;[1−5] therefore, we investigated a postpolymerization deprotection strategy for preparing a deprotected sugar polymer. The acetyl

Scheme 3



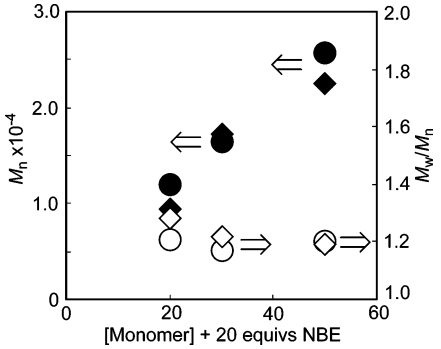


Figure 2. Plots of the molecular weight (M_n) of the copolymers vs the initial [comonomers]/[**1**] ratio. Poly[(**6a**)-*bl*-(NBE)] (◆: M_n; ◇: M_w/M_n), poly[(**6c**)-*bl*-(NBE)] (●: M_n; ○: M_w/M_n).

groups of **7a** were removed by stirring with triethylamine in a THF/MeOH (1:1, v/v) mixture, affording the water-soluble neoglycopolymer in good yield (84% sample in run 5). From the resulting NMR data, the signals for the acetate protecting groups at δ_H 1.92−1.97 ppm ($COCH_3$) and δ_C 20.9−21.6 ($COCH_3$), 169.9−170.6 ppm ($COCH_3$) were completely removed. The high yield and the presence of key resonances for xylose pyranoses connected to a ring-opened poly(norbornene) via isoxazoline linkages at 3.39−4.11 ($H^{1'-5'}$, H^{3a}, and 3 × OH), 4.80 ppm (H^{7a}) in the ^{1}H NMR spectrum, and 47.6 (C^{3a}), 61.2−81.8 ($C^{1'-5'}$), 91.8 (C^{7a}), and 157.1 ppm (C^3) in the ^{13}C NMR data confirmed the structure of the deacetylated polymer.

We previously demonstrated that isoxazoline-bearing polymers could be hydrogenated by refluxing with *p*-toluenesulfonhydrazide in chlorobenzene.[12] Thus, the hydrogenation of **7a** was investigated (Table 1, run 6), as this would potentially impart increased flexibility in the polymer backbone. The ^{1}H NMR spectrum of the reduced analogue showed the absence of terminal vinylic protons at 6.38 and 6.55 ppm and also the complete removal of olefinic protons at 5.32−5.60 ppm and the appearance of a broad multiplet at 0.88 ppm assigned for the chain methylenes, indicated that the reduction had gone to completion. The ^{13}C NMR revealed the absence of olefinic resonances in the region 131.5−133.8 ppm, and the appearance of new peaks at 31.9 and 34.1 ppm attributable to the methylene groups of the hydrogenated polymer chain, and 20.8 (CH_3) and 29.6 ppm (CH_2Ph) due to the polymer termini. Characteristic signals were also present at 169.9 and 169.5 ($COCH_3$), 159.6 (C^3), 92.6 (C^{7a}), 58.8 (C^{3a}), and 20.7 ppm ($COCH_3$), demonstrating that the isoxazoline moiety is stable to the diimide reduction conditions.

Concluding Remarks

The above results demonstrate that isoxazolino norbornenes can be polymerized with the metathesis initiators **1**−**3**, affording neoglycopolymers containing *C*-glycosidic linkages in a living manner. We are currently investigating the potential of these monomers for the preparation of graft polymer architectures according to our established repetitive ROMP procedure.[23]

Experimental Section

General Procedure. All chemicals used were of reagent grade and were purified by standard procedures. Polymerization-grade dichloromethane was distilled from calcium hydride and stored over molecular sieves. $Ru(CHPh)(Cl)_2(PCy_3)_2$ (**1**) and $Ru(CHPh)(Cl)_2(IMesH_2)(PCy_3)$ (**2**) were purchased from Strem Chemicals and used without further purification. Polymerizations mediated by the Ru carbenes **1** and **2** were performed in a glovebag or in a drybox under an atmosphere of nitrogen. Polymerizations adopting the Schrock-type alkylidene, $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}{}^iPr_2C_6H_4)(O^tBu)_2$ (**3**),[11] were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by using standard Schlenk techniques, and the reactions were terminated by benzaldehyde. Polymerization-grade toluene was distilled from sodium and benzophenone, stored over sodium/potassium alloy in a drybox, and was then passed through an alumina short column prior to use.[9]

Melting points were measured on a Gallenkamp capillary apparatus and were uncorrected. Merck aluminum-backed plates coated with Kieselgel GF_{254} (0.2 mm) were used for analytical TLC; detection was by UV or charring with sulfuric acid. Dry flash chromatography was carried out by using Kieselgel GF_{254} and eluted under water pump vacuum. The ^{1}H and ^{13}C NMR spectra were recorded with Brücker WP200SY, AX250, WH360, and Varian VXR600 spectrometers (University of Edinburgh) or on a JEOL JNM-LA400 spectrometer (^{1}H, 399.65 MHz; ^{13}C, 100.40 MHz) (NAIST, Japan) on solutions in $CDCl_3$ (unless otherwise stated) at 25 °C, and all chemical shifts are given in ppm with Me_4Si as an internal standard. Electron impact (EI) and high-resolution mass spectra were obtained on a Kratos MS50TC instrument. Gel permeation chromatography molecular weight measurements were recorded on a Perkin-Elmer system using a 5μ (500 Å) column and a 5μ mixed-bed Perkin-Elmer PL column, calibrated using low-dispersity polystyrene standards (Perkin-Elmer), 860−2.43 × 10^6 Da, connected in series at a flow rate of 0.5 mL/min at ambient temperature (22 °C) on solutions in THF (University of Edinburgh). GPC was also performed at 40 °C on a Shimadzu SCL-10A by using a RID-10A detector (Shimadzu Co. Ltd.) in THF (containing 0.03 wt % 2,6-di-*tert*-butyl-*p*-cresol, flow rate 1.0 mL/min). GPC columns (ShimPAC GPC-806, 804, and 802, 30 cm × 8.0 mm^2 ϕ) were calibrated versus polystyrene standard samples (NAIST, Japan). In both cases, HPLC-grade THF was used, which was degassed prior to use.

Synthesis of *exo*-3-(2′,3′,4′)-Tri-*O*-acetyl-β-D-xylopyranosyl-3a,4,7,7a-tetrahydro-4,7-methano-benzo[*d*]isoxazole (6a). A solution of 2′,3′,4′,-tri-*O*-acetyl-β-D-xylopyranosylnitromethane[24] **4a** (0.27 mmol) in toluene (50 cm^3) was stirred under nitrogen atmosphere, and norbornadiene (1.35 mmol) was added. Triethylamine (0.1 cm^3), catalytic, and tolylene diisocyanate (0.81 mmol) were added, and the reaction was heated at reflux for 7 days, over which period polymeric urea formed. The reaction was cooled to 0 °C, and diaminoethane (0.81 mmol) was slowly added dropwise with vigorous stirring. After 1 h, the reaction was filtered through a Celite pad to remove the polymeric urea present. The pad was washed with chloroform (2 × 50 cm^3), and the combined organics were evaporated. The resultant oil was triturated with pentane to remove the final traces of toluene, and then the crude product (78%) was subjected to flash chromatography (ether/hexane, gradient elution) to afford a mixture of the exo-/endo-diastereomers as white prisms (63%) in a 62:38 ratio (mp 127−128 °C) (from hexanes−ether). ^{1}H NMR ($CDCl_3$): δ 1.54−1.55 (bs, H^8), 2.04, 2.05, 2.06, (3 × s, 3 × $COCH_3$), 3.00 (bs, H,[4] $J_{4,5}$ = 3.2 Hz), 3.14 (bs, H,[7] $J_{7,6}$ = 3.0, $J_{7,7a}$ = 1.5 Hz), 3.42 (d, H^{3a}, $J_{3a,4}$ = 1.9, $J_{3a,7a}$ = 9.0 Hz), 3.86, 3.90 (m, $H^{5ax'}$, $H^{5eq'}$, $J_{5eq',4}$ = 5.7, $J_{5eq',5ax'}$ = 11.4 Hz), 4.59 (d, $H^{1'}$, $J_{1',2'}$ = 9.8 Hz), 4.71−4.75 (m, $H^{2',4'}$, $J_{2',3'}$ = 8.8 Hz), 4.94 (dd, H^{7a}), 5.24 (t, $H^{3'}$), 5.96 (dd, H,[5] $J_{5,6}$ = 5.7 Hz), 6.19 (dd, H^6). ^{13}C NMR ($CDCl_3$): δ 20.9−21.5 (3 × $COCH_3$) 42.8 (C^8), 44.5 (C^4), 49.6 (C^7), 58.4 (C^{3a}), 65.3 ($C^{5'}$), 66.5 ($C^{2'}$), 66.9 ($C^{4'}$), 68.3 ($C^{3'}$), 70.0 ($C^{1'}$), 88.4 (C^{7a}), 135.2 (C^5), 139.9 (C^6), 154.0 (C^3), 169.7, 169.8, 170.0 (3 × $COCH_3$). EIMS *m*/*z*: calcd for $C_{19}H_{23}NO_8$ [M^+ + H] 393.142, found 393.142.

Synthesis of 3-(2′,3′,4′,5′)-Tetra-*O*-acetyl-β-D-glucopyranosyl-3a,4,7,7a-tetrahydro-4,7-methano-benzo[*d*]isoxazole (6b). Reaction of 2′,3′,4′,5′-tetra-*O*-acetyl-β-D-glucopyranosylnitromethane[24] **4b** (0.27 mmol) with norbornadiene (1.35 mmol) was carried out as described above. The crude product (76%) was chromatographed to afford a mixture of the exo diastereomers in a 45:55 ratio, contaminated with a 15% trace of a mixture of the endo adducts as white crystals (59%) (mp 156−157 °C). ^{1}H NMR ($CDCl_3$): δ 1.49−1.54 (m, H^8), 1.99, 2.00, 2.03, 2.06, (4 × s, 4 × $COCH_3$), 3.11 (bs, H,[4,7] $J_{4,5}$ = 3.8, $J_{7,7a}$ = 1.6 Hz), 3.28 (d, H^{3a}, $J_{3a,4}$ = 1.9 Hz), 3.67 (ddd, $H^{5'}$, $J_{5',6a'}$ = 2.9, $J_{5',6b'}$ = 6.9 Hz), 4.13 (dd, $H^{6a'}$, $J_{6a',6b'}$ = 12.2 Hz), 4.24 (dd, $H^{6b'}$), 4.39 (d, $H^{1'}$, $J_{1',2'}$ = 9.9 Hz), 4.74 (d, H,[7a] $J_{7a,3a}$ = 8.3 Hz), 5.02−5.21 (m, $H^{2',4'}$, $J_{4',5'}$ = 9.8 Hz), 5.63 (dd, $H^{3'}$), 5.96 (dd, H,[5] $J_{5,6}$ = 7.2 Hz), 6.16 (dd, H,[6] $J_{6,7}$ = 3.8 Hz). ^{13}C NMR ($CDCl_3$): δ 20.5−21.3 (4 × $COCH_3$), 42.8 (C^8), 45.1, 46.8 (C^4), 49.0, 49.3 (C^7), 56.3, 57.1 (C^{3a}), 61.8, 62.0 ($C^{6'}$), 68.0, 68.2, 68.7, 69.2 ($C^{2',4'}$), 73.2, 73.7 ($C^{3'}$), 74.2, 74.3 ($C^{1'}$), 75.7, 75.9 ($C^{5'}$), 89.3, 89.6 (C^{7a}), 135.2, 135.0, (C^6), 140.0, 140.1 (C^5), 153.4, 153.6 (C^3), 169.2, 169.3, 169.4, 169.7, 169.9, 170.1, 170.4 (4 × $COCH_3$). EIMS *m*/*z*: calcd for $C_{22}H_{27}NO_{10}$ [M^+ + H] 465.16350, found 465.16317.

Synthesis of 3-(2′,3′,4′,5′)-Tetra-*O*-acetyl-β-D-mannopyranosyl-3a,4,7,7a-tetrahydro-4,7-methano-benzo[*d*]isoxazole (6c). Reaction of nitromethyl mannose **4c**[24] (100 mg, 0.27 mmol, 1 equiv) with norbornadiene (125 mg, 1.35 mmol, 5 equiv) was carried out according to the general procedure. The crude product (81%), was subjected to flash chromatography (ether/hexane, 60:40) and recrystallized (ether/hexane) to afford a mixture of the exo diastereomers in a 52:48 ratio contaminated with a 4% trace of the endo adducts as white crystals (65%). ^{1}H NMR ($CDCl_3$): δ 1.19−1.26 (m, H^8), 1.53−1.63 (bs) (bs, H,[4] $J_{4,5}$ = 3.5 Hz), 1.99−2.20 (4 × s, $COCH_3$), 3.14 (m, H,[7] $J_{7,7a}$ = 1.6 Hz), 3.35 (d, H^{3a}, $J_{3a,4}$ = 2.8 Hz), 3.73, 4.47 (2 × bs, $H^{5'}$, $J_{4',5'}$ = 9.6 Hz), 4.08 (dd, $H^{6a'}$, $J_{6a',6b'}$ = 11.9 Hz), 4.15 (dd, $H^{6b'}$), 4.82 (d, H,[7a] $J_{7a,3a}$ = 9.4 Hz), 5.12 (d, $H^{1'}$), 5.25 (m, $H^{2',4'}$), 5.65 (dd, $H^{3'}$), 6.04 (dd, H,[5] $J_{5,6}$ = 6.0 Hz), 6.24 (dd, H,[6] $J_{6,5}$ = 7.0 Hz, $J_{6,7}$ = 2.8 Hz). ^{13}C NMR ($CDCl_3$): δ 20.6−20.8 ($COCH_3$), 42.9, 43.0, 44.8, 45.2, 49.4, 49.5 ($C^{4,7,8}$), 58.0, 58.6 (C^{3a}), 62.2, 62.7 ($C^{6'}$), 65.8, 65.9, 68.1, 68.7 ($C^{2',4'}$), 69.3, 71.7 ($C^{3'}$), 73.2, 73.4 ($C^{1'}$), 75.2, 76.4 ($C^{5'}$), 88.8, 88.9 (C^{7a}), 135.4 (C^6), 140.1 (C^5), 153.8, 154.0 (C^3), 169.6−170.6 ($COCH_3$).

Typical Polymerization Procedure Using 1. A solution of initiator **1** (8.0 μmol) in dichloromethane (1.0 mL) was added in one portion to a rapidly stirred dichloromethane solution (1.0 mL) containing the prescribed amount of sugar monomer **6** at 25 °C, and the reaction mixture was stirred for the prescribed time. The polymerization was terminated by the addition of ethyl vinyl ether (excess to **1**) and stirred for 1 h for completion. The solvent was then removed in vacuo and the resultant tar residue was dissolved in the minimum amount of dichloromethane and added dropwise to methanol containing 2,6-di-*tert*-butyl-4-methylphenol (5 mg) to afford a precipitate, which was filtered, washed with methanol, and dried, affording the polymer. Polymerizations by **2** were performed according to the same procedure except that **2** was used as the initiator in place of **1**.

Typical Polymerization Procedure Using 3. A toluene solution of Mo(CHCMe$_2$Ph)(*N*-2,6-^{i}Pr$_2$C$_6$H$_3$)(O^{t}Bu$_2$)$_2$ (**3**, 2.58 μmol/0.7 mL of toluene) was added in one portion to a rapidly stirred toluene solution (4 mL) containing the prescribed amount of the sugar containing monomer at room temperature, and the solution was stirred for the prescribed time. The polymerization was quenched by adding benzaldehyde ($\sim$10 mg) and stirred an additional 1 h for completion. The solvents were then removed in vacuo, and the resultant solid was dissolved in the minimum amount of THF. The solution was poured dropwise into cyclohexane to afford pale-white precipitates, and the homopolymer was collected by filtration and dried in vacuo.

7a: Yield 84−96%. ^{1}H NMR (CDCl$_3$): δ 1.18, 1.36, 1.67, 1.84 (br, protons of five-membered ring), 1.92−1.97 (m, 3 × COCH$_3$), 2.51, 2.82 (br d, protons of five-membered ring), 3.29 (m, H$^{5'}$), 3.56 (m, H^{3a}), 4.11 (m, H$^{5'}$), 4.28 (m, H$^{1'}$), 4.72 (m, H^{7a}), 5.02, 4.85 (m, H$^{2',4'}$), 5.18 (m, H$^{3'}$), 5.32−5.60 (m, olefinic protons), 6.38, 6.55 (m, CH═C*H*$_2$), 6.91, 6.78 (m, PhHC═C), 7.27−7.29 (m, PhCH), 7.31 (s, C*H*═CH$_2$). ^{13}C NMR (CDCl$_3$): δ 20.9, 21.1, 21.6 (3 × CO*C*H$_3$), 39.0, 47.0, 51.3 (five membered ring), 59.0 (C^{3a}), 67.3, 69.4, 69.6, 73.6, 75.2 (C$^{1'-5'}$), 92.0 (C^{7a}), 131.5−133.8 (olefinics), 156.6 (C^3), 169.9, 170.2, 170.6 (3 × *C*OCH$_3$).

7b: Yield 71%. ^{1}H NMR (CDCl$_3$): δ 1.72, 1.63, 1.23 (br, protons of five-membered ring), 1.95 (4 × COCH$_3$), 2.83, 2.60 (br d, protons of five-membered ring), 3.52 (m, H$^{5'}$), 3.73 (m, H^{3a}), 4.03 (m, H$^{1'}$), 4.23 (m, H^{7a}), 4.65 (m, H$^{6'}$), 5.24, 5.05 (m, H$^{2',4'}$), 5.32 (m, H$^{1'-6'}$), 5.57−5.66 (m, olefinic protons). ^{13}C NMR (CDCl$_3$): δ 20.5, 20.6, 20.7 (4 × CO*C*H$_3$), 39.0, 42.4, 46.6, 51.8 (five-membered ring), 59.5 (C^{3a}), 62.6, 65.6, 67.7, 71.8, 76.5 (C$^{1'-6'}$), 91.2 (C^{7a}), 129.0−134.2 (olefinics), 155.3 (C^3), 169.5 170.0, 170.5 (4 × *C*OCH$_3$).

7c: Yield 91−93%. ^{1}H NMR (CDCl$_3$): δ 1.40, 1.61 (2H, m, protons of five-membered ring), 1.99−2.12 (12H, 4 × bs, COCH$_3$), 2.59−2.83 (2H, m, protons of five-membered ring), 3.49 (1H, br, H^{3a}), 3.64 (br), 3.75 (br), 4.19 (br), 4.31(br), 4.50 (br), 5.09 (br), 5.33 (br) (7H, protons of sugar group), 4.72 (1H, br, H^{7a}), 5.64, 5.72 (2H, br, olefinic protons). ^{13}C NMR (CDCl$_3$): δ 20.7, 20.9 (4 × CO*C*H$_3$), 39.2, 42.8, 45.6, 50.4 (five-membered ring), 57.9 (C^{3a}), 62.6, 66.4, 68.1, 71.9, 76.5 (C$^{1'-6'}$), 90.7 (C^{7a}), 128.6−133.4 (olefinics), 156.2 (C^3), 169.9, 170.7 (4 × *C*OCH$_3$).

A random copolymer[21] was prepared in an analogous manner except that a solution of the initiator **1** was added to the comonomer mixture **6a** and **6b**. Block copolymers (shown in Table 3) were also prepared in a similar fashion with the exception that the second comonomer dissolved in dichloromethane (1.0 mL) was added after consumption of the first monomer, confirmed by independent homopolymerization runs (analyzed by GPC and ^{1}H NMR spectroscopy).[8b]

Deacetylation of Neoglycopolymer (7a). The acteylated neoglycopolymer, **7a** (0.25 mmol) was dissolved in 2 mL MeOH/THF (1:1, v/v), and to this was added triethylamine (0.16 mmol), and the reaction was stirred for 36 h in a nitrogen atmosphere.[16] The reaction mixture was then poured into a solution of THF/H$_2$O (10 mL, 1:1, v/v) containing an excess of 2 M HCl. The mixture was then allowed to stir for 60 min, and then the solvents were removed in vacuo. The resultant solid was washed with water and with ethyl acetate and dried in vacuo. The deacetylated polymer was afforded as a fine white powder, yield 84%. ^{1}H NMR (DMF-d_7): δ 1.78−1.82, 1.97, 2.01, 2.57−2.65 (br m, protons of five-membered ring), 3.39−3.59 (br m), 3.91 (m), 4.11 (br), (H$^{1'-5'}$ and H^{3a} and 3 × −OH), 4.80 (br s, H^{7a}), 5.63−5.88 (br d, olefinic protons), 7.42−7.34, 6.96−6.88 (m, phenyl end group). ^{13}C NMR (DMSO-d_6): δ = 26.8, 31.7, 45.3, 47.8 (five-membered ring), 47.6 (C^{3a}), 61.2, 65.3, 68.7, 72.1, 73.1, 77.2, 81.8 (C$^{1'-C5'}$), 91.8 (C^{7a}), 125.1, 129.4, 132.4, 133.2 (olefinics), 157.1 (C^3).

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(22) We investigated the possibility of preparing a random copolymer based on **6a** and **6b** (**6a**/**6b**/**1** = 70:70:1, molar ratio), and the resultant copolymer yielded poly[(**6a**)-*co*-(**6b**)] with a molecular weight observed by GPC ($M_n = 5.43 \times 10^4$), which was in good correlation with the calculated value ($M_n = 5.75 \times 10^4$). The segment ratio (m:n = 1.00) determined by ^{1}H NMR was exactly the same as the calculated value (m:n = 1.00), demonstrating that the random copolymerization occurred with precise control over the sugar density in the resultant copolymer.
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