Synthesis of End-Functionalized Polynorbornenes and Polynorbornanes via Metathesis: Novel Macromonomers for Polycondensation Reactions

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In recent years, there have been significant advances in finely controlled polymer synthesis via metathesis,[1] where well-defined transition metal initiators allow control over many aspects of the polymer assembly, including molecular weight,[2] molecular weight distribution,[2] alkene backbone configuration,[3] and, in some cases, tacticity.[4]

An important further development has been the controlled introduction of functionalized end groups to metathesis polymers.[5−7] For example, Grubbs has reported that ring-opening metathesis polymerization (ROMP) of cyclooctadiene (COD) with [$RuCl_2(PCy_3)_2$-(=CHCH=CPh_2)] in the presence of 1,4-$(AcO)_2$-*cis*-but-2-ene, after hydrolysis, leads to hydroxytelechelic polybutadiene in which the polymer is bound by terminal diol functionalities. The acyclic alkene acts as a chain transfer agent (CTA), leading to incorporation of the functional end groups as well as causing the molecular weight to be reduced. Such telechelic polymers are potentially useful precursors for subsequent polycondensation, chain extension, and block copolymer syntheses to give materials of potential commercial relevance.[8]

Although the above methodology works well for relatively unstrained monocyclic monomers with acyclic chain transfer agents, where the rate of chain transfer is of the same order of magnitude as the rate of propagation, it does not work well for highly strained bicyclic monomers such as norbornene and its derivatives where the rate of propagation may be several orders of magnitude greater than the rate of chain transfer to the acyclic CTA. To circumvent this limitation, we outline here a *pulsed addition* approach[7] which allows access to low molecular weight, narrow distribution end-difunctionalized polynorbornenes and polynorbornanes suitable for use as condensation macromonomers.

To ensure the presence of functional end groups on every polymer chain, the benzylidene initiator was first converted to the acetate functionalized initiator **3**.[9] The polymerization and chain transfer were then carried out according to Scheme 1.

First, 100 equiv of the *tert*-butylester functionalized norbornene **2** (3:1 mixture of *endo*:*exo*) were treated with initiator **3** in dichloromethane at room temperature followed (after 3 h) by addition of 20 equiv of the chain transfer agent **1**. This mixture was then stirred for a further 3 h to allow complete chain transfer after which a further 400 equiv of norbornene **2** were introduced. The GPC trace obtained on the poly(norbornene) product is shown in Figure 1a. Two narrow distributions, with M_p's of 31 000 and 115 000[13] are observed corresponding to a 100 mer and a 400 mer, respectively. The

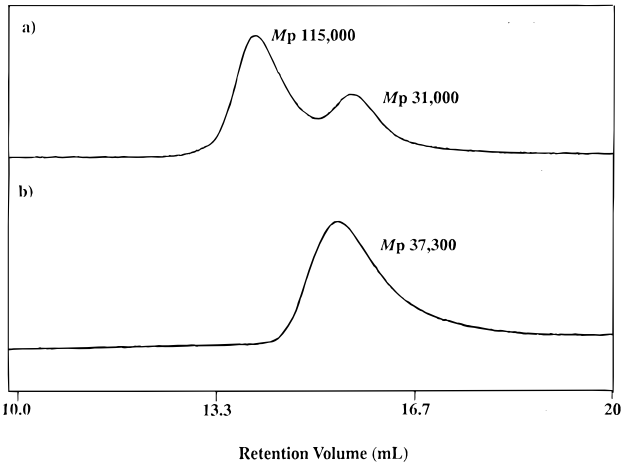
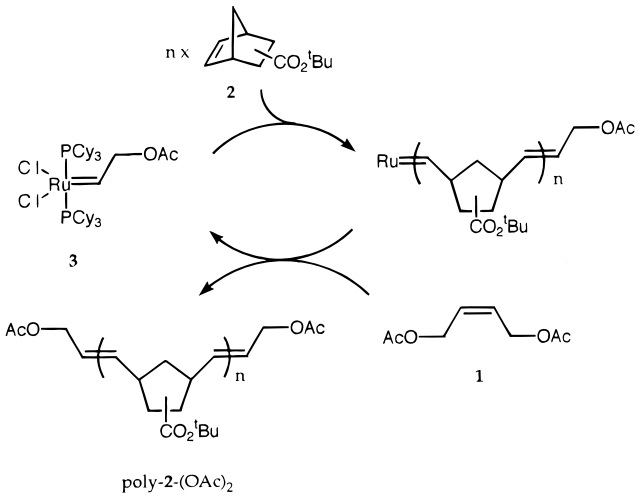


Figure 1. (a) GPC trace of the product arising from treatment of intiator **3** with 100 equiv of monomer **2** followed by 20 equiv of chain transfer agent **1**, and then a further 400 equiv of **2**. (b) GPC trace of the product arising from pulsed (×8) addition of 100 equiv of monomer **2**.

Scheme 1



narrowness of these two distributions and the absence of 500-mer indicates that chain transfer and reinitiation of the second polymerization chain had occurred smoothly. The impressive level of control derives from the two distinct well-controlled steps: (1) living ring-opening polymerization until all monomer is consumed to give size-controlled propagating carbene, and (2) quantitative transfer of the polymeric carbene to the CTA to afford end-functionalized poly-**2**-$(OAc)_2$ and initiator **3**. The quantitative regeneration of **3** then makes possible the controlled polymerization of a new batch of monomer.

Encouraged by this success, 100 equiv of monomer **2** were then added to initiator **3** in the presence of 20 equiv of **1**, followed at intervals of 5 h by 8 more separate 100 equiv batches of monomer **2**. The GPC trace of the resultant polymer (Figure 1b) reveals a product M_n of 22 800 (M_n(calc) 19 400), M_w of 30 400, and PDI of 1.33, consistent with a 100 mer, with a tail to low molecular weight due to a small amount of chain transfer during each propagation step. A similar experiment employing 50 equivalent aliquots of **2** gave a product M_n of 13 900 (M_n(calc) = 9800), M_w of 20 200,

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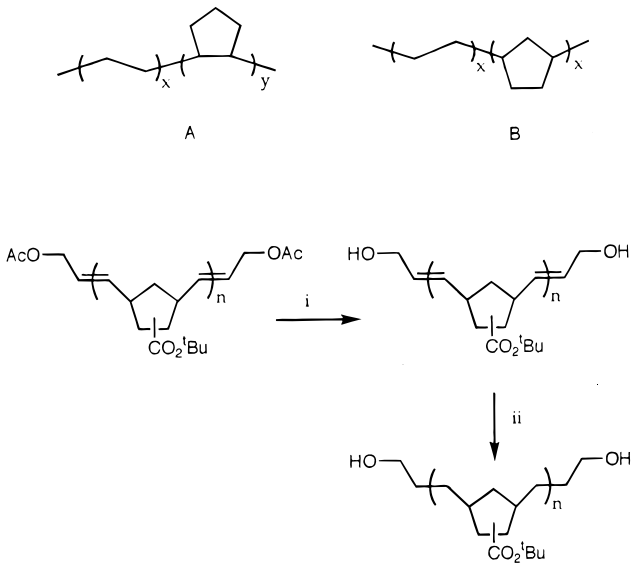
Scheme 2[a]



[a] Reagents and conditions: (i) K_2CO_3/MeOH, THF, 16 h; (ii) p-toluenesulfonhydrazide, toluene, 100 °C, 16 h.

and PDI of 1.45. The ^{1}H NMR spectrum of the resultant poly-**2**$(OAc)_2$ reveals a characteristic multiplet at δ 4.51 attributable to the methylene protons of the $AcOCH_2$ end groups and typical broadened signals in the regions δ 5.2−5.4 (olefin), δ 2.2−3.0 (allylic and adjacent ring CH), and δ 1.5−2.0 (methylene and methylene bridgehead protons) due to the polynorbornene backbone. A sharp resonance at δ 1.3 is due to the *tert*-butyl hydrogens of the ester group. The chain length can also be estimated from integration of the olefinic resonances vs the methylene hydrogens of the end groups, giving a molecular weight of 16 900 (87 mer) for the product from the 100 equiv experiment. The acetate end groups were then converted to hydroxyls by a standard procedure[6] using K_2CO_3/MeOH (Zemplèn conditions) to obtain the polynorbornenediol (M_n, 23 600; M_w, 30 400; PDI 1.29). The hydrogens adjacent to the hydroxyl end groups are clearly observable as a multiplet at δ 4.08 in the ^{1}H NMR spectrum; the hydroxyl protons are not observable, possibly being obscured by the broadened polymer signals.

Polynorbornenes can be hydrogenated to give saturated polymers reminiscent of cycloolefin copolymers (COC's) which find uses in optical applications where high T_g combined with noncrystallinity and clarity are important.[10] COC's are usually obtained via the statistical copolymerization of ethylene with a cyclic monomer such as cyclopentene to give [1,2] incorporation of the cyclic monomer (A, Scheme 2).[11] The principal difference with a COC material generated by hydrogenation of a polynorbornene is the effective [1,3] enchainment of the five-membered ring (B, Scheme 2) as well as perfect C_2/C_5 ring alternation along the polymer backbone. An attractive advantage of the ROMP approach lies in the possibility for synthesizing COC materials with functional groups along the polymer backbone which, at present, are not generally accessible via addition polymerization routes.

Thus, with a view to accessing a family of telechelic polyolefin-like macromonomers, the dihydroxy functionalized polynorbornene, poly-**2**-$(OH)_2$, was treated with *p*-toluenesulfonhydrazide[12] according to Scheme 2 to give the polynorbornane (M_n 25 600, M_w 33 800, PDI 1.32). The absence of olefinic resonances at around δ 5.3 in the ^{1}H NMR spectrum showed that the hydrogenation had gone to 100% completion. The methylene hydrogens of the hydroxymethyl end groups are shielded (δ 3.64) compared to those of poly-**2**$(OAc)_2$ (δ 4.51) and poly-**2**$(OH)_2$ (δ 4.08).

These results show that a *pulsed addition* approach can be used to access controlled molecular weight acetoxy and hydroxy end-functionalized polynorbornenes. A simple hydrogenation procedure affords telechelic polyolefin-like products. The use of these macromonomers in the synthesis of polycondensation products is presently under investigation.

Supporting Information Available: Text detailing the preparation of monomer **2**, its polymerization, end-group modification, and subsequent polymer hydrogenation. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) The molecular weights and polydispersities were determined by gel permeation chromatography in chloroform solvent (Gynkotek 300 HPLC pump, flow rate 1.00 mL min^{-1}, Viscotek DG-700, 2 × PSS SDV 10 μL columns, Knauer differential refractive index detector). The columns were calibrated against polystyrene standards (Polymer Laboratories) ranging from 3700 to 295 000 amu. Data were analyzed using TriSEC GPC Software Version 3.

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