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Main-Chain Chiral Polymers from β-Citronellene via Tandem Diene Metathesis Cyclization/Ring-Opening Metathesis Polymerization

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The synthesis of non-naturally occurring optically active polymers that possess main-chain chirality remains a topic of current interest.[1] In this regard, the polymerization of enantiomerically-enriched chiral monomers in which stereogenic centers of the monomer become those of the polymer backbone guarantees that complete control of the absolute and relative configurations of centers within the main chain, and hence, the "handedness" and tacticity, respectively, of the new material, can be achieved.[2,3] Accordingly, through this strategy, the potential exists to produce not only new materials with maximum optical rotatory power but also those with well-defined backbone conformations, especially in cases where torsional interactions between backbone substituents limits the conformational space that can be probed by the polymer chain.[4] Related to this, we have been interested in further delineating the factors which control the polymerizability of cyclic olefins via olefin metathesis, and in particular, of exo- and endo-substituted cyclopentenes where we have previously shown that the relief of torsional strain can drive the polymerization process irreversibly forward.[5] Thus, as a natural extension of these studies, we were intrigued with the idea of generating new classes of optically active polymers and copolymers from readily available, torsionally-strained, chiral cyclic monomers through "living" ring-opening metathesis polymerization (ROMP).[6] Herein, we now report the first results regarding the realization of this goal which include (1) the large scale syntheses of isomerically pure (3*R*)- and (3*S*)-3-methylcyclopentene (3-MCP) (**1**) via diene metathesis cyclization (DMC)[7] of (−)- and (+)-β-citronellene (**2**), respectively, and (2) the first unequivocal demonstration of the ROMP of (3*R*)- and (3*S*)-3-MCP to yield polymers and copolymers with high optical rotatory power.

Scheme 1

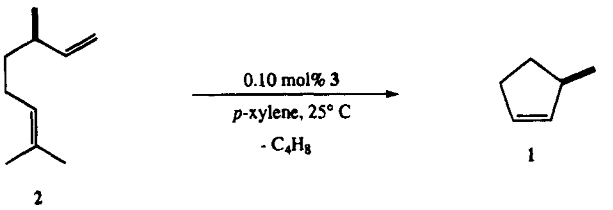

Table 1. ROMP of (3*R*)-1 at −30 °C[a]

entry	initiator	M/I	solvent	yield (%)	M_n[b]	M_w/M_n[b]	% trans[c]	$[\alpha]_D^{20}$ (deg)[d]
1	**3**	390:1	DME	52	38 695	1.56	74	−52
2	**4**	380:1	toluene	64	31 506	1.68	61	−54
3	**4**	380:1	DME	66	31 662	1.61	74	−45

[a] Polymerizations were carried out with a 5 M solution of (3*R*)-**1** for 18 h.[12] [b] Determined by gel permeation chromatography (GPC) at 35 °C using tetrahydrofuran as the eluent and polystyrene standards.[12] [c] Approximated from ^{13}C NMR spectra. [d] *c* = 0.002.

3-Methylcyclopentene (**1**) is notoriously difficult to obtain in isomerically and optically pure form, and previously, this has only been accomplished by a lengthy multistep stereoselective synthesis which provided less than 100 mg of the final product.[8] Given this, we envisioned the production of large amounts of (3*R*)- and (3*S*)-**1** via the DMC of commercially available (−)- and (+)-β-citronellene (**2**),[9] according to Scheme 1. As this scheme indicates, the DMC of **2** could indeed be accomplished in high yield by employing Schrock's molybdenum imido alkylidene complex, $[(CF_3)_2CH_3CO]_2Mo[CHC(Me)_2Ph][N(2,6\text{-}i\text{Pr}_2C_6H_3)]$[10] (**3**), which has previously been used for the DMC of a variety of other α,ω-dienes.[7,11,12] In the present example, however, several important features can be noted. First, on a small scale, using 2 mol % of **3**, this cyclization reaction, which is 0.75 M in (+)-**2** (of 95% optical purity),[12,13] proceeds quantitatively in toluene at room temperature within 30 min to provide isomerically pure (3*S*)-**1** as followed by ^{1}H NMR spectroscopy. More importantly, the DMC of *technical grade* (−)-**2** (85% optically pure)[12] of 90% chemical purity can be carried out in *p*-xylene on a preparative scale (50 g) in 1 h at room temperature using only 0.10 mol % of **3** (276 mg) to provide (3*R*)-**1**, which is still isomerically pure, in a 60% isolated yield.[12,14] Since no isomerization of either **1** or **2** appears to occur under the dilute conditions used for cyclization, we assume that the optical purity of **1** is identical to that of the starting material **2**. This assumption is supported by comparing the $[\alpha]_D^{20}$ value of −155.8° (*c* = 0.012, benzene) [or −163.4° when corrected for the optical purity of (+)-**2**] obtained for (3*S*)-**1** with the $[\alpha]_D^{20}$ value of +157.5° (*c* = 0.012, benzene) previously reported for enantiopure (3*R*)-**1**.[8] In contrast, by employing concentrated solutions of **2** (~50% wt), an isomeric mixture of all three methylcyclopentenes is produced, presumably due to the formation, under these particular conditions, of reduced molybdenum species which can potentially serve as catalysts for the isomerization process.[15] Apparently, this is the first time that isomerization accompanying a DMC catalyzed by **3** has been observed. This suggests that, although simplistic in nature, care should be exercized in utilizing **3** for the DMC of other α,ω-dienes that are to be investigated in the future.

Concerning the ROMP of 3-methylcyclopentene, only two reports, which are contradictory in nature, have appeared in the literature.[16−18] Thus, Günther and coworkers[16] make a brief reference regarding the polymerizability of 3-MCP using a classical Ziegler−Natta cocatalyst system while Dall'Asta[17] states that this result could not be reproduced. Given this sparse and controversial history then, it is surprising to find that most reviews of ROMP treat the polymerizability of 3-MCP as indisputable.[6a,19] However, with a large quantity of isomerically pure **1** now available by the process of Scheme 1, this question can at least be unequivocally settled. As Table 1 shows, **1** can, in fact, be polymerized at −30 °C using either the complex **3** or the commercially available complex $[(CH_3)_3CO]_2Mo[CHC(Me)_2Ph][N(2,6\text{-}i\text{Pr}_2C_6H_3)]$[20] (**4**) as initiator. Due to thermodynamic considerations, the modest yields that are obtained for the ROMP of **1** presumably arise from the living nature of the ROMP process which establishes a monomer/polymer equilibrium even at this low temperature through polymerization/depolymerization mechanisms.[21] In keeping with this, the polydispersities, obtained for the ROMP of **1** are uniformly larger than those expected for the case where irreversible formation of a living

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polymer occurs.[21] Furthermore, inspection of the resulting polymers by NMR spectroscopy reveals that this ROMP of **1** occurs exclusively in a head-to-tail fashion, and by default for enantiopure **1**, with an isotactic relationship of all the stereogenic centers. Consistent with this stereoregular structure, these polymers exhibit a significantly large optical rotation (Table 1). As previously observed, however, the stereochemistry of the double bonds of the polymer backbone is dependent upon the choice of solvent and the nature of the ancillary ligands (Table 1).[6a,22] Not surprisingly, the optical rotation values of these polymers also appear to be dependent upon the *trans* content of the backbone (entries 2 and 3, Table 1) and efforts are underway to identify conditions and initiators that can provide exclusively either all *trans* or all *cis* backbone double bond geometries.

In conclusion, the DMC of (−)- and (+)-β-citronellene (**2**) provides access to large quantities of (3*R*)- and (3*S*)-**1**, respectively, making these compounds perhaps the most readily available chiral monomers that can be utilized for the production of optically active polymers. Indeed, by taking advantage of the apparent living nature of the ROMP process, we are currently pursuing the design and synthesis of novel block copolymers that incorporate segments of (+)- and (−)-poly-**1**.[23] In addition, given the availability of chiral molybdenum alkylidene complexes,[24] the next logical step, which is now under investigation, is to synthesize enantiomerically-enriched **1** via the kinetic resolution of (±)-**2**. The results of these studies will be reported in due course.

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Supplementary Material Available: Text detailing information regarding the synthesis and characterization of (3*R*)-**1**, (−)-poly-**1**, and a (−)-poly-**1**/polynorbornene copolymer (7 pages).

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(11) After submission of this paper, it was brought to our attention through a personal communication with W. A. Nugent and J. Feldman (Central Research and Development, DuPont) that they have achieved a similar DMC of **2** by employing a different catalyst system and that the preliminary results of this work were presented at the April 1994 National American Chemical Society meeting in San Diego, CA.

(12) Full experimental details are provided in the supplementary material.

(13) Enantiopure **2** can be obtained from the corresponding (+)- and (−)-β-citronellols.

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