Poly(1,4:2,2-butanetetrayl). A Novel Polyspirane via Metallocenium-Catalyzed Ring-Opening−Zipping-Up Polymerization of Methylenecyclopropane

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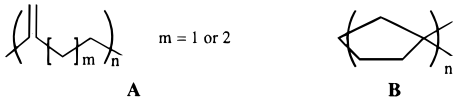
Electrophilic d^0/f^n metallocene centers are highly efficient catalysts for a variety of carbon−carbon bond-forming and bond-breaking transformations.[1−3] We recently reported the d^0/f^n metallocene-mediated ring-opening Ziegler polymerization of strained methylenecycloalkanes in which sequential double bond insertions and β-alkyl shift ring-openings afford polymers of architecture **A**.[4] We wish to communicate here the delineation of a sequential metallocenium-catalyzed ring-opening−"zipping-up" Ziegler polymerization of methylenecyclopropane which yields, in high chemo- and stereoselectivity, a saturated polyspirane having structure **B**, poly(1,4:2,2-butanetetrayl),[5] as well as some of the interesting structural and thermal properties of this new material.



A **B**

Polymerization of methylenecyclopropane[6] catalyzed by $(Me_5Cp)_2ZrMe^+MeB(C_6F_5)_3^-$ [2h] was carried out in dilute toluene solutions under rigorously anhydrous/anaerobic conditions. At temperatures from −10 °C to −30 °C, rapid and complete consumption of the monomer is observed by NMR using the monomer:catalyst ratios shown in Table 1. Interestingly, at room temperature, the reaction pauses before monomer is completely consumed. That this loss of activity is not due to poisoning of the catalyst by adventitious impurities is confirmed by the observation that activity is completely restored on exposure to H_2.[7] The resulting polymers were isolated by removal of the solvent, followed by washing with ethanol. The polymeric product was then characterized by a combination of elemental analysis,[8a] 1-D and 2-D NMR techniques, laser and field desorption mass spectrometry,[8b] GPC, X-ray diffraction, and DSC. Both ^1H and ^{13}C spectra (Figure 1; solution phase and CPMAS solid state ^{13}C spectra are essentially identical) indicate that the polymer chains have saturated hydrocarbon backbones. DEPT ^{13}C and ^1H-coupled ^{13}C experiments show that the three major resonances, C_a, C_b, and C_c at δ 55, 51, and 42 ppm, respectively, are secondary, quaternary, and secondary carbon atoms, respectively. The relative intensity ratio of C_a, C_b, and C_c is 1:1:2.[9] Two-dimensional HETCOR experiments[10] reveal that the major components of the proton spectrum, H_a

Table 1. Polymerization of Methylenecyclopropane Using $(Me_5Cp)_2ZrMe^+MeB(C_6F_5)_3^-$ as Catalyst

entry	catalyst amount (mg)	methylene-cyclo-propane (mg)	reaction temp (°C)	reaction time (h)	polymer yield (mg)	M_n[d] (M_w/M_n)
1[a]	6.5	398	−30	2.5	340	6200 (2.82)
2[b]	5.0	250	−20	0.4	220	
3[b]	5.0	70	−10	4.0	50	5100 (2.63)
4[a,c]	10.2	230	25	4.0	160	

[a] Toluene (15 mL) as the solvent. [b] Reaction in an NMR tube, toluene-d_8 as the solvent. [c] Hydrogen gas was used to re-initiate the polymerization at 20 min intervals. Total reaction time, 4 h. [d] Apparent data *vs* polystyrene by GPC in 1,2,4-trichlorobenzene at 145 °C using refractive index detection.

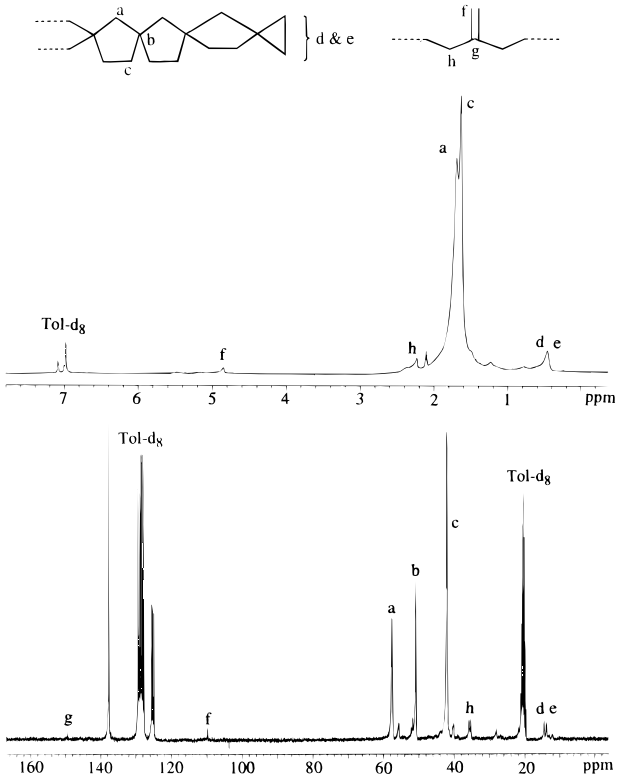


Figure 1. ^1H and ^{13}C NMR spectra (400 and 100 MHz, respectively; toluene-d_8, 95 °C) of the methylenecyclopropane polymerization product (Table 1, entry 3).

(1) For recent reviews of metallocenium d^0 catalysis, see the following and references therein: (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143−1170. (b) Möhring, R. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1−29. (c) Kaminsky, W. *Catal. Today* **1994**, *20*, 257−271. (d) Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57−65. (e) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325−387.

(2) For representative recent discussions of metallocenium d^0 catalysis; see: (a) Deck, P. A.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 6128−6129. (b) Wu, Z.; Jordan, R. F.; Petersen, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 5867−5874. (c) Lancaster, S. J.; Robinson, O. B.; Bochmann, M.; Coles, S. J.; Hursthouse, M. B. *Organometallics* **1995**, *14*, 2456−2462. (d) Erker, G.; Ahlers, W.; Frohlich, R. *J. Am. Chem. Soc.* **1995**, *117*, 5853−5854. (e) Coates, G. W.; Waymouth, R. M. *Science* **1995**, *267*, 217−219. (f) Flores, J. C.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1995**, *14*, 1827−1833. (g) Pellecchia, C.; Pappalardo, D.; Oliva, L.; Zambelli, A. *J. Am. Chem. Soc.* **1995**, *117*, 6593−6594. (h) Yang, X.; Stern, C.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015−10031.

(3) For representative recent discussions of f^n catalysis see: (a) Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 283−362. (b) Fu, P.-F.; Brard, L.; Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 7157−7168. (c) Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623−4640. (d) Molander, G. A.; Hoberg, J. O. *J. Org. Chem.* **1992**, *57*, 3266−3268. (e) Heeres, H. J.; Renkema, J.; Booji, M.; Meetsma, A.; Teuben, J. H. *Organometallics* **1988**, *7*, 2495−2502. (f) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51−55. (g) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111−8118.

(4) (a) Yang, X.; Jia, L.; Marks, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 3392−3393. (b) Yang, X.; Seyam, A. M.; Fu, P.-F.; Marks, T. J. *Macromolecules* **1994**, *27*, 4625−4626.

(5) We thank Dr. W. V. Metanomski of Chemical Abstracts Service for assistance with the nomenclature.

(6) Methylenecyclopropane was synthesized according to a literature procedure and purified by trap-to-trap distillation: Köster, R.; Arora, S.; Binger, P. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 205−206.

(7) Similar observations were made in the case of organolutetium-catalyzed methylenecyclopropane polymerization[4b] and are associated with the formation (supported by D_2O quenching studies) of η^3-allyl species.

(8) (a) Anal. Calcd for $(C_4H_6)_n$: C, 88.82; H, 11.18. Found: C, 87.50; H, 11.28. (b) Fisons VG Tofspec and 70-VSE spectrometers were used for UV laser desorption and field desorption mass spectrometry, respectively. A FDMS spectrum is included in the supporting information.

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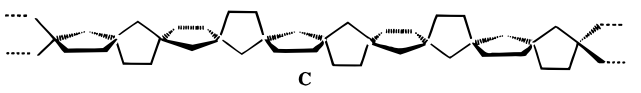
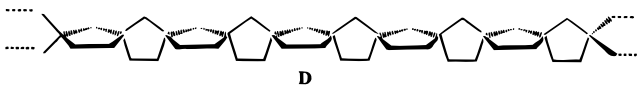
and H_c at δ 1.5−1.7 ppm, are directly attached to C_a and C_c. The linkage pattern between the carbon atoms is then determined to be $C_a-C_b-C_c$ by INADEQUATE 2-D ^{13}C NMR. The only chain structure compatible with the above observations is structure **B**. Indeed, the NMR parameters exhibited by **B** are rather similar to those of 3-7 ring polyspiranes recently reported by Trost and Shi.[11] In the present case, the sharpness of the ^{13}C NMR signals suggests high stereospecificity in the spirocyclization process; however, it is not possible to rigorously distinguish between the two simplest possible tacticity motifs, **C** (rodlike) and **D** (helical), with the data in hand. Control of



C



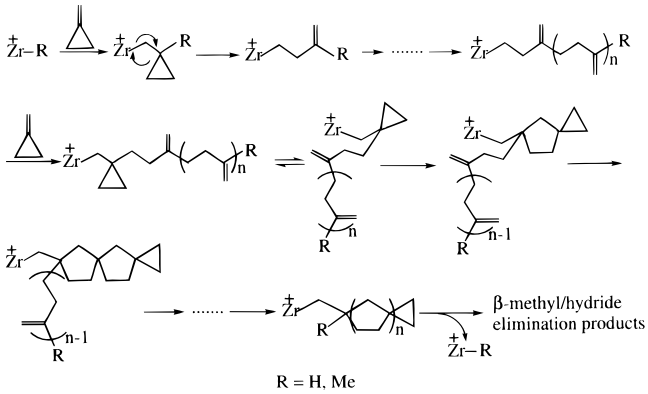
D

the stereochemistry during the zipping-up process is apparently tightly fixed by the relative conformation of the adjacent ring that forms in the preceding step (chain end control; see proposed mechanism below). Polymer **A** ($m = 1$) is a minor product of the room temperature polymerization and can be partially separated by extraction with a 2:1 mixture of toluene and ethanol. The selectivity of polymerization toward polymer **B** increases and the percentage of polymer **A** decreases at lower temperatures (∼8% at 20 °C, ≲1% at −30 °C). Interestingly, the minor unzipped polymer fraction **A** undergoes complete ring closure on storage in the solid state over a period of several weeks at 25 °C, to afford polymer **B** in the absence of a coordination catalyst. In contrast, solution phase zipping-up is not observed in the absence of a metallocene catalyst.[12]

Laser and field desorption mass spectrometry[8b] were employed to characterize the molecular weight of **B**. Both spectroscopies of the polymer in entry 1 of Table 1 exhibit broad envelopes (with maxima at ∼2300 and ∼2800 g/mol, and full widths at half-maximum of ∼1000 and ∼1900 g/mol, respectively), corresponding to macromolecular masses in approximate agreement with an NMR end group analysis based on cyclopropyl residues (∼1900 g/mol, vide infra). GPC-derived polydispersities (Table 1) are expected to be reliable; however, absolute GPC-derived molecular weights await a suitable calibration standard.[13]

A θ-2θ X-ray powder diffraction scan (Ni-filtered Cu Kα radiation) of polymer **B** at room temperature[10] exhibits a single sharp reflection at $2\theta = 16.0°$, with a full width at half-maximum of 1.6°, indicating relatively high crystallinity in the solid state, with an average particle size/coherence length of ∼190 Å. DSC scans (5 deg/min; sample of entry 1, Table 1) using temperature modulation reveal a glass transition-like feature at ∼181 °C, apparently reflecting substantial rigidity of the polymer backbone. Heating **B** to temperatures >300 °C induces a small exotherm, and a large exotherm is observed at ∼425 °C, corresponding to the decomposition temperature. At this point, the polymer is insoluble in toluene.

Scheme 1



The formation of structure **B** can be rationalized on the basis of an established ring-opening mechanism,[4] followed by a zipping-up process (Scheme 1). The reaction begins with the ring-opening polymerization of methylenecyclopropane. At some stage, competing intramolecular C═C bond insertion is initiated, and the spirocyclization process proceeds along the chain. Although the initiation of zipping-up could, in principle, follow several plausible pathways, NMR examination of the polymer end groups provides important insight. Unopened cyclopropyl structures (a broad signal for $H_{d,e}$ at δ 0.5 ppm in the ^1H spectrum is correlated with two signals, C_d and C_e at δ 14.1 and 14.4 ppm, respectively, in the ^{13}C spectrum by GHMQC; $J_{C-H} = 162$ Hz)[9] are assigned to end groups on the basis of the absence of large quantities of uncyclized structure **A**.[14] The presence of cyclopropyl end groups suggests that the zipping-up process is initiated when monomer insertion is followed by intramolecular, ring-closing $C{=}CH_2$ insertion before β-alkyl shift ring-opening[4] can occur, thus leading to sequential spirocyclization along the entire chain (Scheme 1). NMR observation of two inequivalent adjacent CH_2 fragments of the cyclopropyl groups supports the expected local symmetry at the chain end (Scheme 1). In support of the sequential ring-opening−zipping up pathway is the observation that samples of **A** prepared using an organolanthanide catalyst[4b] undergo reaction with $(Me_5Cp)_2ZrH^+HB(C_6F_5)_3^-$ [2h] to produce **B**-rich samples in which zipping-up appears by NMR to be initiated randomly along the **A** chain.

In summary, these results describe the synthesis of a new polyspirane via the chemo- and stereoselective ring-opening-zipping-up polymerization of methylenecyclopropane catalyzed by a cationic d^0 zirconocenium catalyst. Efforts to obtain additional structural and mechanistic information are underway.

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Supporting Information Available: NMR spectra, field desorption mass spectrum, and X-ray powder diffraction pattern (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(9) The gated inverse decoupling mode was chosen to suppress NOE effects and to thus obtain accurate integrals: Levy, G. C.; Lichter, R. L.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Spectroscopy*; Wiley: New York, 1982; pp 38−44.

(10) See supporting information.

(11) (a) Trost, B. M.; Shi, Y. *J. Am. Chem. Soc.* **1993**, *115*, 9421−9438. (b) Dispirane and trispirane structures have also been produced by organoscandium catalysts: Bunel, E. E., Ph.D. Thesis, California Institute of Technology, 1989. We thank Prof. J. E. Bercaw for making us aware of this result.

(12) This behavior is reminiscent of that of CO−olefin copolymers: Jiang, Z.; Sen, A. *J. Am. Chem. Soc.* **1995**, *117*, 4455−4467 and references therein.

(13) GPC in 1,2,4-trichlorobenzene *vs* polystyrene. We consider the molecular weights to be "apparent" pending suitable calibration.

(14) In principle, ring-unopened cyclopropyl groups could be located either in the middle of the backbone or at the chain end. If in the middle, the zipping-up reaction affording five-membered rings would presumably be halted at cyclopropyl group "kinks", and as a result, large quantities of structure **A** would remain unzipped. This is not observed, and the cyclopropyl group location is most reasonably assigned to the polymer chain end.