Communications to the Editor

Diastereoselectivity in the Homogeneous Cyclopolymerization of 1,5-Hexadiene[†]

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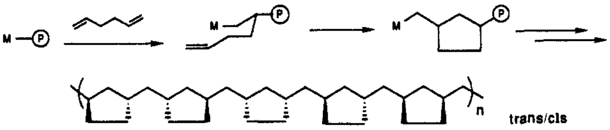
The advent of homogeneous stereospecific olefin polymerization catalysts[1] has stimulated a renaissance in Ziegler–Natta chemistry. Key discoveries by Ewen[2] and Kaminsky[3] and mechanistic studies by Pino[4] and Zambelli[5] have ushered in an era where polyolefin microstructures can be rationally controlled by choice of the appropriate homogeneous transition metal catalyst precursors. Herein we report our results on the stereoselective cyclopolymerization of nonconjugated diolefins[6-9] in the presence of achiral metallocene catalysts[10,11] (eq 1).



(1)

Presented in Table I are results for the cyclopolymerization of 1,5-hexadiene in the presence of catalysts derived from Cp_2ZrX_2 derivatives (X = Cl, Me) or $Cp^*_2ZrCl_2$ and methyl aluminoxane.[12] Cyclopolymerization of 1,5-hexadiene in toluene solution with catalysts derived from Cp_2ZrCl_2 or Cp_2ZrMe_2 proceeded with conversions of 11 and 25% after 1 h to give a solid polymer (M_w = 27 000 and 20 000 vs polystyrene; M_w/M_n = 2.2 and 2.1, respectively). Resonances corresponding to uncyclized monomer units were barely detectable by ^1H or ^{13}C NMR; thus, under these conditions, greater than 99% cyclization had taken place. Polymerization in bulk monomer proceeded with 100% conversion after 1 h; in this case, 59% of the polymer was insoluble in benzene, suggesting that some cross-linking may have occurred. However, the benzene-soluble fraction contained no detectable uncyclized monomer units in the polymer.

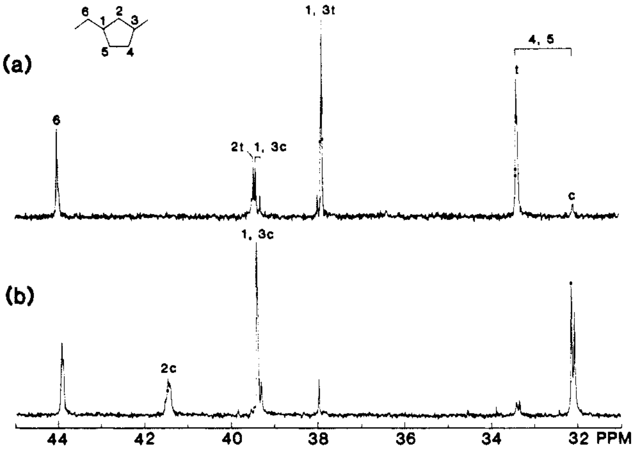


Figure 1. ^{13}C NMR spectra (100 MHz) (resolution-enhanced) in tetrachloroethane-d_2 at 80 °C; reference vs HMDS = 2 ppm; t = trans ring, c = cis ring. (a) Sample **1** prepared at −80 °C with Cp_2ZrMe_2. (b) Sample **2** prepared at −25 °C with $Cp^*_2ZrCl_2$.

Polymerization of 1-hexene under the same conditions with Cp_2ZrMe_2 proceeded with similar conversion of monomer but yielded only low-molecular-weight oligomers (Dp = 6).[13] Thus, under similar conditions, *1,5-hexadiene produces a much higher molecular weight polymer than 1-hexene.* We attribute the higher molecular weight to a lower termination rate in the polymerization of 1,5-hexadiene, due to the higher strain energy of the liberated olefin (methylenecyclopentane endgroups). Consistent with this analysis, cyclopolymerization of 1,6-heptadiene with Cp_2ZrMe_2 yielded only oligomers (Dp = 5–10); the lower molecular weight in this case is consistent with the lower strain energy of methylenecyclohexane (1.9 kcal/mol) relative to methylenecyclopentane (6.3 kcal/mol).[14]

Stereochemistry. In the presence of the metallocene derivatives Cp_2ZrX_2 (X = Cl, Me), we observe an unprecedented trans selectivity in the cyclopolymerization of 1,5-hexadiene. At a polymerization temperature of 80 °C, ^{13}C NMR analysis[9] indicates that there is a 1:1 ratio between trans and cis five-membered rings. At a polymerization temperature of 22 °C, approximately 80% of the cyclopentane rings in the polymer are trans, as evidenced by the ratio of the resonances at 33.4 and 32.1 ppm. Polymerization at −78 °C afforded the first example of poly(methylene-*trans*-1,3-cyclopentane) (Figure 1a, 91% trans by ^{13}C NMR, sample **1**).

In the presence of the more sterically hindered $Cp^*_2ZrCl_2$ (Cp* = pentamethylcyclopentadienyl) as the catalyst precursor, a high-cis polymer is obtained.[15] At a polymerization temperature of 20 °C, approximately 70% of the cyclopentane rings are cis, while at −25 °C, the cis-ring content is 86% (Figure 1b, sample **2**).

[†] This manuscript is dedicated to the memory of Professor Piero Pino.

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(1) The development by Brintzinger of chirai ansa metallocenes was a key breakthrough in this area. (a) Wild, F. R. W. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1985**, *232*, 233; (b) **1985**, *288*, 63. (c) Collins, S.; Kurtz, B. A.; Ward, D. G. *J. Organomet. Chem.* **1988**, *342*, 21.

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(5) (a) Longo, P.; Grassi, A.; Pellecchia, C.; Zambelli, A. *Macromolecules* **1987**, *20*, 1015. (b) Grassi, A.; Zambelli, A.; Resconi, L.; Albizzati, E.; Mazzocchi, R. *Macromolecules* **1988**, *21*, 617.

(6) Cyclopolymerization of 1,5-hexadiene was first reported by Marvel and Stille[7] and further investigated by Makowski.[8] Using catalysts derived from $TiCl_4/Al$-*i*-Bu_3 and $TiCl_4/AlEt_3$, respectively, both groups reported low activities and incomplete cyclization of the diolefin. More recently, Cheng[9] reported the cyclopolymerization of 1,5-hexadiene using a $TiCl_3/AlEt_2Cl$ catalyst. ^{13}C NMR analysis of the resulting polymer indicated complete cyclization and a 1:1 ratio of *trans*- and *cis*-cyclopentane rings in the polymer.

(7) Marvel, C. S.; Stille, J. K. *J. Am. Chem. Soc.* **1958**, *80*, 1740.

(8) (a) Makowski, H. S.; Shim, K. C.; Wilshinsky, Z. W. *J. Polym. Sci., Part A* **1964**, *2*, 1549. (b) Makowski, H. S.; Shim, B. K. C.; Cain, W. P. U.S. Patent 3,357,961, 1967. (c) Olson, S. G. U.S. Patent 3,435,020, 1969.

(9) Cheng, H. N.; Khasat, N. P. *J. Appl. Polym. Sci.* **1988**, *35*, 825.

(10) (a) The cyclopolymerization of nonconjugated diolefins in the presence of chiral metallocenes will be the subject of a forthcoming paper. Resconi, L.; Waymouth, R., manuscript in preparation. (b) For these polymers, there are four structures of maximum order (ref 11). Of these, the trans diisotactic polymer is chiral. We are currently investigating the synthesis of optically active polymers with this microstructure.

(11) Farina, M. *Top. Stereochem.* **1987**, *17*, 1–111.

(12) Sherex (30% in toluene), $\langle M_w \rangle$ = 1400.

(13) Degree of polymerization (Dp) determined by endgroup analysis by ^1H NMR.

(14) Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377.

(15) Preliminary endgroup analysis of polymer **2** suggests that the polymer is methyl-terminated, indicating that transfer to Al is the major chain-transfer process.

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Table I. Cyclopolymerization of 1,5-Hexadiene in Toluene[a]

metallocene	(μmol)	T, °C	time, min	conversn, %	trans,[b] %
Cp_2ZrCl_2	(4.8)	21	60	11.1	80
Cp_2ZrMe_2	(4.8)	22	60	25.0	79
Cp_2ZrMe_2	(6.7)	0	270	56.0	84
Cp_2ZrMe_2	(14.3)	−78	420	0.6	91
$Cp^*_2ZrCl_2$	(3.4)	20	180	46.0	30
$Cp^*_2ZrCl_2$	(9.2)	−25	330	65.0	14

[a] Conditions: 5 mL of 1,5-hexadiene, Al/Zr = 2500. [b] From $C_{4,5}$ cis/trans ratio.

The trans selectivity in the presence of the Cp_2ZrX_2 catalysts can be rationalized by a preference of the growing polymer chain to adopt an equatorial position in a pseudo-chair transition state in the cyclization. However, inspection of molecular models suggests that a chair-type transition state is not readily accommodated in the presence of the more sterically hindered Cp* ligands. A twist-boat conformation could be accommodated, but placement of the polymer chain in the equatorial position in this case would lead to a cis ring.

In conclusion, homogeneous Ziegler–Natta catalysts are efficient for the cyclopolymerization of nonconjugated diolefins. High-molecular-weight polymers can be readily obtained from monomers which form strained olefins upon β-hydrogen elimination, and polymers with a range of microstructures can be obtained by choice of the appropriate catalyst precursor.

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Registry No. Cp_2ZrCl_2, 1291-32-3; Cp_2ZrMe_2, 12636-72-5; $Cp^*_2ZrCl_2$, 54039-38-2; 1,5-hexadiene (homopolymer), 25067-96-3; polylmethylene-1,3-cyclopentanediyl, 40022-21-7; 1-hexene (homopolymer), 25067-06-5.

Supplementary Material Available: Polymerization procedures and ^{13}C NMR spectral data of polymer samples **1** and **2** (1 page). Ordering information is given on any current masthead page.

Doped Glassy Carbon Materials (DGC): Low-Temperature Synthesis, Structure, and Catalytic Behavior

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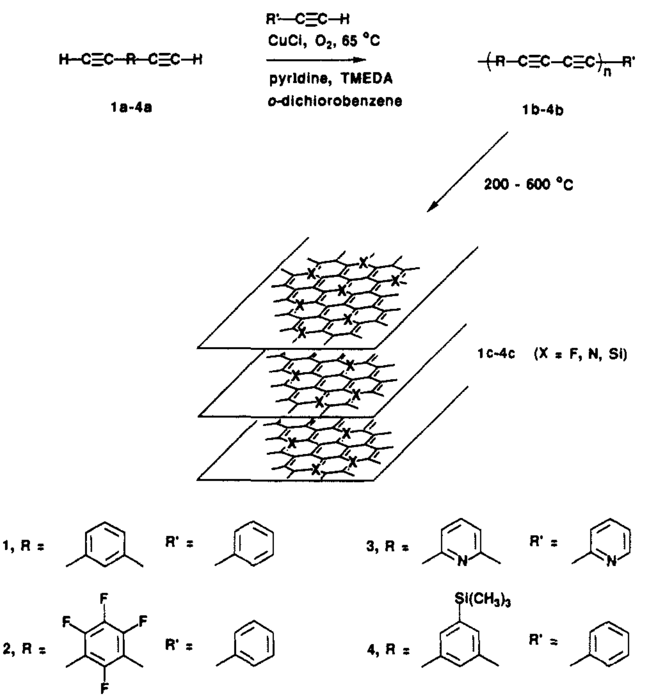
Glassy carbon has unique properties including chemical and thermal inertness, hardness, impermeability to gases and liquids, and electrical conductivity.[1] Current approaches to glassy carbon (GC) materials require high-temperature treatment (1000–3000 °C) of nonvolatilizing organic materials.[1-3] The extreme temperature requirements for these syntheses yield glassy carbon with <0.5% of any element other than carbon, independent of the precursor material.[4] Carbon electrodes are involved in a significant fraction of the more than $35 billion/year of U.S. products directly resulting from electrochemistry.[5] We felt that the homogeneous introduction of dopants would alter the electrochemical behavior of glassy carbon by modifying the adsorption of molecules to the electrode surface and by promoting catalytic activity.

Scheme I



As part of our program in the preparation and study of highly cross-linked organic solids, we have discovered a low-temperature route (600 °C) to doped (0–15 atom %) glassy carbon (DGC).[6] We report here the preparation, characterization, and catalytic properties of these doped glassy carbon materials. We chose four precursor diethynyl aromatics to demonstrate the versatility of our approach: 1,3-diethynylbenzene (**1a**),[7] the nondoped parent system; 1,3-diethynyl-2,4,5,6-tetrafluorobenzene (**2a**),[8] to ultimately generate a fluorinated glassy carbon surface; 2,6-diethynylpyridine (**3a**),[7,9] to incorporate a potential binding site in glassy carbon for metal complexes;[7] and 1,3-diethynyl-5-(trimethylsilyl)benzene (**4a**),[9] to probe the sensitivity of the thermal conversion reaction to an alkyl side chain. We prepared diacetylenes **1a–4a**, oxidatively coupled[10-12] these monomers in the

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[‡] AT&T Bell Laboratories.

(1) Jenkins, G. M.; Kawamura, K. *Polymeric Carbons-Carbon Fibre, Glass and Char*; University Press: Cambridge, 1976.

(2) A wide variety of organic materials can be converted to glassy carbon including phenol–formaldehyde polymers, furfuryl alcohol resins, polyphenylene oxide, polyphenylene sulfide, cellulose, polyacrylonitrile, and polyvinyl chloride.

(3) Kinoshita, K. *Carbon: Electrochemical and Physicochemical Properties*; Wiley: New York, 1988.

(4) Fitzer, K.; Mueller, K.; Schaefer, W. *Chem. Phys. Carbon* **1971**, *7*, 237.

(5) Alkire, R. C., Ed. *New Horizons in Electrochemical Science and Technology*, NMAB Publication 438-1; National Academy Press: Washington, DC, 1986.

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(9) Spectral data for 1,3-bis[(trimethylsilyl)ethynyl]-5-(trimethylsilyl)benzene: mp 73–75 °C; IR (melt) 2942, 2882, 2143, 1570, 1369, 1273, 1246, 1160, 1130, 970, 799, 790, 755 cm^{-1}; ^1H NMR ($CDCl_3$, δ) 7.54 (s, 1 H), 7.50 (s, 2 H), 0.24 (s, 9 H), 0.23 (s, 18 H); ^{13}C NMR ($CDCl_3$, δ) 141.0, 136.4, 135.7, 122.7, 104.5, 94.7, −0.1, −1.3; HRMS, *m/z* 342.1613 (M^+, calcd for $C_{19}H_{30}Si_3$ 342.1655). Spectral data for **4a**: IR (neat) 3280, 3025, 2950, 2875, 2080, 1565, 1380, 1245, 1130, 870, 835, 805, 750 cm^{-1}; ^1H NMR ($CDCl_3$, δ) 7.60 (s, 3 H), 3.06 (s, 2 H), 0.25 (s, 9 H); ^{13}C NMR ($CDCl_3$, δ) 141.4, 137.0, 135.7, 121.9, 83.0, 77.7, −1.40; HRMS, *m/z* 198.0872 (M^+, calcd for $C_{13}H_{14}Si$ 198.0865). Spectral data for **3b**: IR (KBr) 3050, 2200, 2140, 2100, 1720, 1620, 1560, 1545, 1430, 1240, 1195, 1155, 980, 810 cm^{-1}. Anal. Calcd: C, 85.53; H, 2.72; N, 11.47. Found: C, 77.18; H, 3.39; N, 10.63. Spectral data for **4b**: IR (KBr) 3020, 2942, 2880, 2200, 1562, 1375, 1248, 1130, 870, 835, 750, 680, 620 cm^{-1}; ^1H NMR ($CDCl_3$, δ) 7.66 (s), 0.30 (s); ^{13}C NMR ($CDCl_3$, δ) 142.0, 137.9, 136.0, 132.6, 131.0, 128.5, 128.0, 121.7, 81.1, 74.6, −1.4. Anal. Calcd: C, 80.35; H, 6.07; Si, 13.59. Found: C, 79.30; H, 6.11; Si, 14.04.

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