Macromolecules **2001,** *34,* 6167−6168

Methylenation of an Optically Active γ-Polyketone: Synthesis of a New Class of Hydrocarbon Polymers with Main-Chain Chirality

Kyoko Nozaki,*[†,‡] Naoyuki Kosaka,[†] Vera M. Graubner,[†] and Tamejiro Hiyama[†]

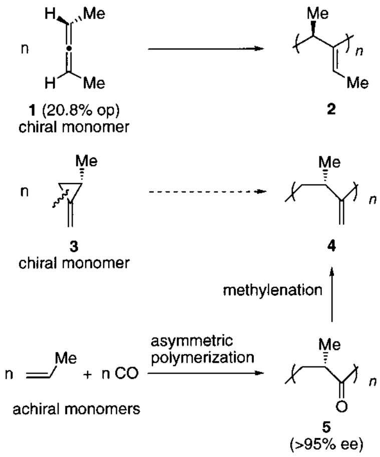
Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan; and PRESTO, JST, Tokyo, Japan

Received May 4, 2001

Since Natta synthesized isotactic polypropene,[1] stereocontrol has been one of the most important technologies in polymer synthesis.[2] Efforts have been devoted not only to tacticity control but also to chirality control when chirotopic centers are included in the main chain. Optically active polymers are commonly produced either by polymerization of chiral monomers or by asymmetric polymerization of achiral monomers.[3] An example of the former approach is the polymerization of the chiral allene **1**, affording a helical polymer, **2** (Scheme 1), as reported by Porri.[4] However, no method is available for polymerizing a chiral monomer that would add one more methylene to the repeating unit, e.g., the ring-opening polymerization of optically active methylenecyclopropane **3** to polymer **4**.[5] As an alternative route to the chiral polymer **4**, we now report the methylenation of an optically active polyketone **5**, which is easily available by asymmetric polymerization of the achiral monomers, propene and carbon monoxide.[6−8] Almost complete conversion has been performed in spite of the fact that polymer reactions often suffer from retarded reactivity and impossible separation of the unreacted moieties from the products. Because the methylenation takes place without losing the enantiopurity of the chirotopic carbons of **5**, the present study should provide a route to a new class of optically active hydrocarbon polymers **4** that cannot be prepared by any other means.[9]

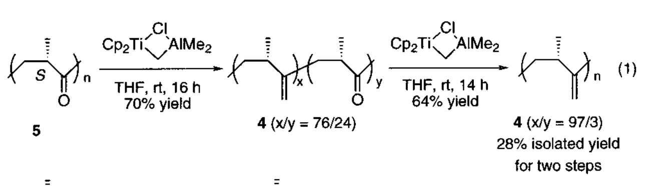
The polyketone **5** ($M_n = 19500$, $M_w/M_n = 1.38$, $[\alpha]_D^{25}$ $-56.6°$) was prepared via the asymmetric alternating copolymerization of propene and carbon monoxide according to our previous report.[6] Although many precedents appeared for the functionalization of the carbonyl groups of a polyketone, mainly poly(ethene-*co*-CO), no example has ever been reported for the methylenation.[10] First, we treated **5** with 1.5 equiv of the Tebbe reagent (1-dicyclopentadienyl-μ-chloro-μ-methylene-2-dimethyl-2-aluminum-1-titanium, $Cp_2Ti(\mu\text{-}Cl)(\mu\text{-}CH_2)(AlMe_2)$ at 23 °C for 16 h (eq 1).[11,12] After workup with aqueous NaOH and removal of the inorganic residues by filtration, a polymer **4** that contains both the methylene and ketone moieties was obtained. The methylene/ketone ($=x/y$) ratio was determined to be 76/24 by ^1H NMR analysis. Polymer **4** thus obtained was again treated with the Tebbe reagent (5 equiv to carbonyl) to improve the x/y ratio up to 97/3. The crude product was contaminated by organic residues from the Tebbe reagent and was therefore purified by silica gel column chromatography and then by size exclusion chromatography. Polymer **4** was obtained in its pure form in 28% overall isolated yield from polyketone **5**.

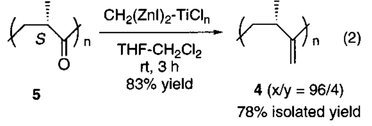
Scheme 1

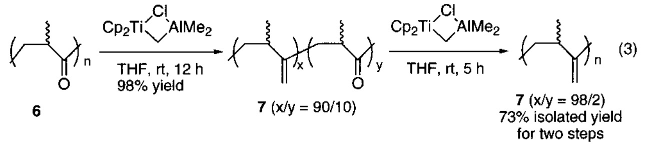


Next, we employed another methylenation reagent, the combination of $CH_2(ZnI)_2$ and low valent titanium species $TiCl_n$ ($n = 2$ or 3)[13,14,15] (eq 2). According to the literature method,[13] a dichloromethane solution of polyketone **5** was added to a suspension of bis(iodozincio)methane ($CH_2(ZnI)_2$) and $TiCl_n$ in THF. The reaction was quenched with aqueous HCl, and the polymer was extracted with chloroform. The polymer **4** ($x/y = 96/4$) was obtained in its pure form in 78% isolated yield by reprecipitation from chloroform into methanol. Thus, under these conditions, the reaction reached synthetically satisfactory levels of yield and purity.

The high stereoregularity of the polymer **4** was confirmed by comparing its ^{13}C NMR spectrum with that of atactic polymer **7**. An atactic and exclusively head-to-tail polyketone **6** was prepared using a Pd(II) complex of 1,2-bis(dicyclohexylphosphino)ethane[7] and was then repeatedly treated with the Tebbe reagent to afford an atactic methylenated polymer **7** ($x/y = 98/2$) in 73% yield (eq 3). Figure 1 shows the ^{13}C NMR signals due to the sp[2] carbons in the main chain. Each of the four partial spectra corresponds to the isotactic polyketone **5** (a), its methylenated product **4** with $CH_2(ZnI)_2-TiCl_n$ (b), the atactic polyketone **6** (c), and its methylenated product **7** (d).[16] The sharp peak at 153.3 ppm observed with polymer **4** in Figure 1(b) is assigned to a like (*S,S* or *R,R*) diad, and the other peaks around 152.9−153.2 ppm in Figure 1(d) are due to an unlike







[†] Kyoto University.

[‡] PRESTO, JST.

10.1021/ma0107713 CCC: $20.00

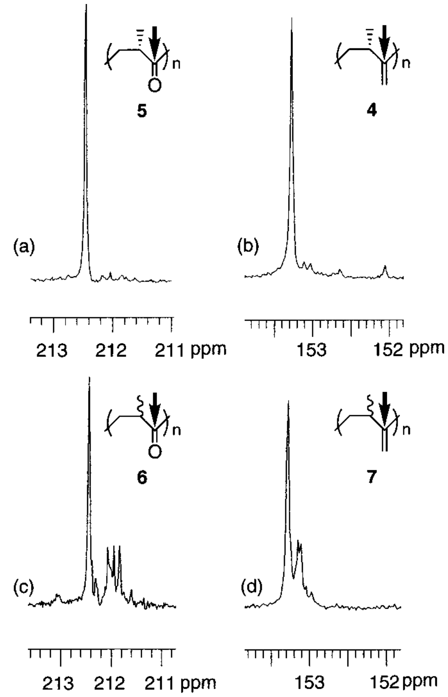


Figure 1. Partial ^{13}C NMR spectra for the sp^2 carbons in the main chain of (a) isotactic polyketone **5**, (b) isotactic **4** obtained with $CH_2(ZnI)_2-TiCl_n$, (c) atactic polyketone **6**, and (d) atactic **7**. The peaks at 153.3 ppm in parts b and d are assigned to a like (*S*,*S* or *R*,*R*) diad, and the other peaks around 152.9–153.2 ppm in part d are due to an unlike (*S*,*R* or *R*,*S*) diad or a $-C(=CH_2)-$ group neighboring on a carbonyl group. The peak at 153.3 ppm contains over 85% of all the peak areas in part b.

(*S*,*R* or *R*,*S*) diad or a $-C(=CH_2)-$ group neighboring on a carbonyl group. The fact that the peak at 153.3 ppm contains over 85% of the total peak area in Figure 1b indicates that polymer **4** is highly isotactic. This agrees well with the reports that no epimerization was observed during methylenation with $CH_2(ZnI)_2-TiCl_n$ [13] or the Tebbe reagent.[17]

The chiral polymer **4** ($x/y = 96/4$) obtained with $CH_2(ZnI)_2-TiCl_n$ exhibited a specific rotation of $[\alpha]_D^{25}$ −15.7 (*c* 0.99 in $CHCl_3$). This value may be compared to the rotation value $[\alpha]_D$ +13.29 of (*S*)-(+)-2,3-dimethylpent-1-ene.[18] The opposite sign for the same *S*-isomers might be attributed to the existence of neighboring C=C double bonds in polymer **4**. Polymer **4** is soluble in chloroform, dichloromethane, THF and diethyl ether when the polymer is contaminated with a trace amount of THF, while the polyallene **2** prepared from the monomer with 31% optical purity is reportedly insoluble in most common organic solvents.[4]

In conclusion, treatment of optically pure α-methyl-γ-polyketone **5** with the $CH_2(ZnI)_2-TiCl_n$ reagent produced the methylenated polymer **4** in 78% isolated yield and in a ratio of methylene/carbonyl = 96/4. No epimerization took place under these reaction conditions. Thus, a new route was established for preparing of a novel optically active hydrocarbon polymer with main-chain chirality. The present study also shows that the modern tools of "organometallic chemistry oriented to organic synthesis", the CH_2 dianion species in this case, is now applicable to the modification of macromolecules with molecular weights near 20 000.

Acknowledgment. We thank Prof. K. Osakada (Tokyo Institute for Technology) for the helpful discussions. The work was partially supported by the Grant-in-Aids for COE Research on Elements Science, No. 12CE2005, from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

Supporting Information Available: Text giving the experimental details for the preparation of polymers **4**, **6**, and **7** and figures showing the ^{13}C NMR spectra of polymers **4** obtained with the Tebbe reagent and with $CH_2(ZnI)_2-TiCl_n$, **5**, **6**, and **7** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Natta, G.; Pino, P.; Corradini, P.; Danusso, F.; Mantica, E.; Mazzanti, G.; Moraglio, G. *J. Am. Chem. Soc.* **1955**, *77*, 1708. (b) Natta, G. *J. Polym. Sci.* **1955**, *16*, 143.
(2) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223.
(3) Okamoto, Y.; Nakano, T. *Chem. Rev.* **1994**, *94*, 349.
(4) Porri, L.; Rossi, R.; Ingrosso, G. *Tetrahedron Lett.* **1971**, 1083.
(5) Ring-opening polymerization of unsubstituted methylenecyclopropane: (a) Jia, L.; Yang, X.; Seyam, A. M.; Albert, I. D. L.; Fu, P.-F.; Yang, S.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 7900. Recently, Osakada reported the ring-opening polymerization of racemic 1-methylene-2-phenylcyclopropane using a Pd complex to give head-to-tail and atactic $-[CH_2CHPhC(=CH_2)]_n-$: (b) Kim, S.; Takeuchi, D.; Osakada, K. Pacifichem 2000, Symposium 149, No. 198, Dec 14–19, 2000, Honolulu, HI, and private communications.
(6) Nozaki, K.; Sato, N.; Tonomura, Y.; Yasutomi, M.; Takaya, H.; Hiyama, T.; Matsubara, T.; Koga, N. *J. Am. Chem. Soc.* **1997**, *119*, 12779.
(7) Jiang, Z.; Sen, A. *J. Am. Chem. Soc.* **1995**, *117*, 4455.
(8) (a) Jiang, Z.; Adams, S. E.; Sen, A. *Macromolecules* **1994**, *27*, 2694. (b) Bronco, S.; Consiglio, G.; Hutter, R.; Batistini, A.; Suter, U. W. *Macromolecules* **1994**, *27*, 4436. (c) Brookhart, M.; Wagner, M. I.; Balavoine, G. G. A.; Haddou, H. A. *J. Am. Chem. Soc.* **1994**, *116*, 3641. (d) Nozaki, K.; Sato, N.; Takaya, H. *J. Am. Chem. Soc.* **1995**, *117*, 9911.
(9) Synthesis of optically active hydrocarbon polymers, for example. Asymmetric cyclopolymerization of 1,5-hexadiene: (a) Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 6270. (b) Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 91. An optically active polystyrene: (c) Wulff, G.; Dhal, P. K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 196. Asymmetric polymerization of 1,3-pentadine: (d) Natta, G.; Porri, L.; Valenti, S. *Makromol Chem.* **1963**, *67*, 225.
(10) A short review for the functionalization of polyketone was reported by Sen: (a) Sen, A. *CHEMTECH* **1986**, 48. Recent examples: (b) Jiang, Z.; Sanganeria, S.; Sen, A. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 841. (c) Green, M. J.; Lucy, A. R.; Lu, S.; Paton, R. M. *J. Chem. Soc., Chem. Commun.* **1994**, 2063. (d) Nozaki, K.; Kosaka, N.; Muguruma, S.; Hiyama, T. *Macromolecules* **2000**, *33*, 5340.
(11) (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (b) Pine, S. H. *Org. React.* **1993**, *43*, 1.
(12) Insoluble polymeric materials but not polymer **4** were produced by the Wittig reaction using CH_3PPh_3I in combination with bases such as BuLi or *t*-BuOK.
(13) Matsubara, S.; Mizuno, T.; Otake, T.; Kobata, M.; Utimoto, K.; Takai, K. *Synlett* **1998**, 1369.
(14) (a) Matsubara, S.; Oshima, K.; Utimoto, K. *J. Organomet. Chem.* **2001**, *617–618*, 267. (b) Hashimoto, Y.; Mizuno, U.; Matsuoka, H.; Miyahara, T.; Takakura, M.; Yoshimoto, M.; Oshima, K.; Utimoto, K.; Matsubara, S. *J. Am. Chem. Soc.* **2001**, *123*, 1503.
(15) About the valency of the titanium, see: (a) Naula, S. P.; Sharma, H. K. *Inorg. Synth.* **1985**, *24*, 181. (b) Hermes, A. R.; Giriolami, G. S. *Inorg. Synth.* **1998**, *32*, 309.
(16) The ^{13}C NMR spectrum of **4** obtained with the Tebbe reagent in eq 1 is quite similar to Figure 1b.
(17) Brown-Wensley, K. A.; Buchwald, S. L.; Cannizzo, L.; Clawson, L.; Ho, S.; Meinhardt, D.; Stille, J. R.; Straus, D. Grubbs, R. H. *Pure Appl. Chem.* **1983**, *55*, 1733.
(18) Lardicci, L.; Rossi, R.; Pucci, S.; Aglietto, M.; Botteghi, C.; Pino, P. *Chem. Ind. (Milan)* **1968**, *50*, 227.

MA0107713