Methylenation of Optically Active γ -Polyketones

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ABSTRACT: Reaction of poly[(*S*)-1-oxo-2-methylpropylene] (**1**) with a dizinc-titanium reagent, CH₂(ZnI)₂–TiCl₃, afforded the corresponding completely methylenated polymer, poly[(*S*)-1-methylene-2-methylpropylene] (**3**), in 78% isolated yield. It was confirmed that no significant epimerization took place under the reaction conditions by comparing ¹³C NMR spectrum of **3** with an atactic analog. Also, poly[(*S*)-1-oxo-2-butylpropylene] (**2**) was converted to the methylenated polymer **4**. The exo-methylene/ketone ratio of **4** did not exceed 85/15 even by the repeated treatment with CH₂(ZnI)₂–TiCl₃, possibly due to the steric hindrance of side-chain butyl group. In polymer **4**, the main chain was suggested to be less flexible based on the smaller peak area and shorter relaxation time (*T*₁) of the main chain protons in ¹H NMR.

KEY WORDS Enantioselective Alternating Copolymerization / Polyketone / Methylenation / *gem*-Dizinc Reagent / Tebbe Reagent / Hydrocarbon Polymer / Asymmetric Center /

Physical properties of synthetic polymers are highly dependent upon stereoregularity of the main chain. Since Natta synthesized isotactic polypropylene,¹ many researchers have taken interest in stereocontrol of the main chain,² and efforts have been devoted not only to tacticity control but also to chirality control of chirotopic centers in the main chain.³ However, appeared are few examples of syntheses of optically active hydrocarbon polymers with main chain chirality, the only four examples are, asymmetric polymerization of 1,3-pentadiene,⁴ asymmetric cyclopolymerization of 1,5-hexadiene,⁵ syntheses of optically active polystyrenes with chiral templates,⁶ and polymerization of optically active allene.⁷ These methods can be classified as asymmetric polymerization of prochiral monomers or polymerization of optically active monomers. Here we report another method of producing optically active hydrocarbon polymers with main chain chirality, methylenation of optically active polyketones. Polyketones **1** and **2** are given by asymmetric alternating copolymerization of carbon monoxide with olefins, propene and 1-hexene, respectively (Scheme 1). These are γ -polyketones which have an asymmetric carbon at the α -position of each carbonyl group.^{8–11} The carbonyl groups can be transformed into various functional groups, and therefore chemical modification of the carbonyl groups would provide new classes of chiral polymers.^{9,12} Although many examples were reported for the functionalization of polyketones, mainly

poly(ethene-*co*-CO) or achiral poly(propene-*alt*-CO), no report has ever appeared for the nucleophilic addition of carbanions to the carbonyl groups.¹³ Carbanions may possibly cause side reactions, such as the enolate formation and the following aldol reaction, due to their strong basicity. In spite of its nucleophilic nature, however, methylenation of carbonyl groups is known to proceed without any enolate formation using appropriate reagents.^{14,15} In such a case, the methylenation of optically active polyketones with one of these reagents should provide optically active hydrocarbon polymers without epimerization at the chirotopic centers. Here we report the methylenation of the polyketones **1** and **2** using the Tebbe reagent or alternatively dizinc-titanium reagent, CH₂(ZnI)₂–TiCl₃, to give the corresponding methylenated polymers **3** and **4**, respectively.¹⁶ It was confirmed that the reaction proceeded without any significant epimerization by comparison of ¹³C NMR of the methylenated polymer **3** with an atactic analog. The products, a new class of hydrocarbon polymers with main-chain chirality, are attainable only by this transformation but not by any other meth-

Scheme 1.

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ods, such as ring-opening polymerization of 2-alkyl-1-methylenecyclopropanes.¹⁷

EXPERIMENTAL

Materials

The Tebbe reagent ($\text{Cp}_2\text{Ti}(\mu\text{-CH}_2)(\mu\text{-Cl})\text{AlMe}_2$) and 1,2-bis(dicyclohexylphosphino)ethane were purchased from Tokyo Chemical Industry and Strem Chemicals, respectively. Most of reagents were available from Wako Pure Chemical Industries Ltd. or Nacalai Tesque Ltd. Ozone was generated by an apparatus of O-3-2 of Nihon Ozone Co., Ltd. All of solvents used for the reactions were distilled under argon after drying over appropriate drying agents. For silica-gel column chromatography, Wako-gel C-200 was used.

Wittig Reaction of Isotactic Poly(CO-*alt*-propene) (**1**)

Poly(CO-*alt*-propene) (**1**) was prepared by the procedure previously reported.⁸ Potassium *tert*-butoxide (0.19 g, 1.7 mmol) was added to the solution of $\text{CH}_3\text{PPh}_3\text{I}$ (0.35 g, 0.86 mmol) in THF (15 mL) at 0°C. A solution of the polyketone **1** (0.030 g, 0.43 mmol) in CH_2Cl_2 (1.8 mL) was added to the mixture at the same temperature, and the resulting mixture was stirred for 20 h at room temperature. The reaction mixture was filtered through a Celite pad and the filter cake was washed with chloroform (100 mL) but no polymeric material was extracted.

Methylenation of Isotactic Poly(CO-*alt*-propene) (**1**) with $\text{CH}_2(\text{ZnI})_2\text{-TiCl}_3$

A THF solution of $\text{CH}_2(\text{ZnI})_2$ (0.87 M, 1.7 mL, 1.5 mmol) was added to a suspension of TiCl_3 (0.18 g, 1.2 mmol) in THF (23 mL) at room temperature. To the mixture was added a solution of isotactic polyketone (**1**) (0.052 g, 0.74 mmol) in CH_2Cl_2 (2 mL) *via* cannula and the resulting mixture was stirred for 3 h at room temperature. The reaction was quenched by the addition of 1 M HCl aq. (50 mL) and chloroform (40 mL) at 0°C. The separated aqueous layer was extracted with chloroform (3 $\times$ 30 mL). The combined organic layers were dried over anhydrous magnesium sulfate, filtered and concentrated to afford the crude polymer **3** (83% yield, 96/4 of methylene/carbonyl). The methylene/carbonyl ratio and the yield were determined by ^1H NMR using methoxyacetone nitrile as an internal standard. The crude polymer **3** was purified by the reprecipitation from $\text{CHCl}_3/\text{CH}_3\text{OH}$ to give polymer **3** in its pure form (0.040 g, 0.56 mmol, 78% yield). **3**: ^1H NMR (CDCl_3) δ 1.00 (d, J = 6.4 Hz, 3H), 1.76–2.06 (m, 1H), 2.11–2.40 (m, 2H), 4.74 (s, 1H), 4.82 (s, 1H); ^{13}C NMR (CDCl_3) δ 19.4, 37.5, 41.9, 108.8, 153.3; IR

(CH_2Cl_2): 3080, 3060, 1710 (unreacted C=O), 1640, 890 cm^{-1} ; $[\alpha]_{\text{D}}^{25}$ -15.7° (c 0.99, CHCl_3).

Methylenation of Optically Active and Isotactic Poly(CO-*alt*-propene) (**1**) with the Tebbe Reagent

To a suspension of **1** (0.049 g, 0.70 mmol of unit) in THF (10 mL) was added the Tebbe reagent (0.5 M in toluene, 2.1 mL, 1.1 mmol) at 0°C. The resulting mixture was stirred at room temperature for 16 h. Dry Et_2O (15 mL) and then 0.1 M NaOH aq. (0.4 mL) were added. The mixture was dried over anhydrous sodium sulfate and filtered through a Celite pad. The filter cake was washed with Et_2O (70 mL) and CHCl_3 (100 mL). The solution was concentrated to afford crude polymer **3** (70% yield, 76/24 of methylene/carbonyl, determined by ^1H NMR). Crude polymer **3** thus obtained (corresponds to 0.12 mmol of carbonyl) was dissolved in THF (10 mL) and again treated with the Tebbe reagent to yield **3** in 64% for the second step (estimated by ^1H NMR). The residue was purified first by silica-gel column chromatography (CHCl_3 then Et_2O) and then by size exclusion chromatography for separation (CHCl_3) to afford the polymer **3** (0.013 g, 0.20 mmol, in 28% overall yield from polyketone **1**). Polyethylene (15 wt%) which originated from the Tebbe reagent contaminated the product.

Preparation of Atactic Poly(CO-*alt*-propene) (**5**)

A solution of 1,2-bis(dicyclohexylphosphino)ethane (0.022 g, 0.052 mmol) in benzene (1.5 mL) was added to a solution of $\text{Pd}(\text{CH}_3)(\text{Cl})(\text{cod})$ (0.014 g, 0.052 mmol) in benzene (1.5 mL). The solution was stirred at room temperature for 2 h and then concentrated *in vacuo*. The residue was dissolved in CH_2Cl_2 (5.5 mL), and to the solution, was added a solution of $\text{NaB}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_4$ (0.046 g, 0.052 mmol) in CH_3CN (2.5 mL). After the mixture was stirred at room temperature for 1 h, the solvents were removed. The residue was dissolved in CH_2Cl_2 (6 mL) and the solution was transferred into a 100 mL autoclave and charged with propene (3 atm). The mixture was stirred under CO (20 atm) at 40°C for 4 days. The crude polymer was reprecipitated from $\text{CHCl}_3/\text{CH}_3\text{OH}$ and washed with CH_3OH to afford atactic poly(CO-*alt*-propene) **5** (0.20 g): M_n = 9000, M_w/M_n = 1.34; ^1H NMR (CDCl_3) δ 1.00–1.10 (br d, 3H), 2.43–2.62 (m, 1H), 2.82–3.15 (m, 2H); ^{13}C NMR (CDCl_3) δ 16.1–17.5 (m), 39.4–41.8 (m), 43.0–45.8 (m), 211.2–213.3 (m).

Methylenation of Atactic Poly(CO-*alt*-propene) (**5**) with the Tebbe Reagent

A suspension of atactic poly(CO-*alt*-propene) (**5**)

(0.049 g, 0.70 mmol of the repeating unit) in THF (10 mL) was added the Tebbe reagent (2.1 mL, 1.1 mmol) at 0°C and the mixture was stirred at room temperature for 12 h. The same work-up as above described afforded the crude polymer **6** (98% yield (^1H NMR), 90/10 of methylene/carbonyl). The crude polymer **6** (corresponds to 0.070 mmol of carbonyl) was again treated with the Tebbe reagent (0.70 mL, 0.35 mmol) at room temperature for 5 h. Purification by silica-gel column chromatography (chloroform then ether) and size exclusion chromatography (chloroform) gave the atactic methylenated polymer **6** (0.035 g, 0.51 mmol, 73% yield from polyketone **5**). ^1H NMR (CDCl_3) δ 1.00 (d, J = 6.2 Hz, 3H), 1.75–2.08 (m, 1.3H), 2.08–2.40 (m, 1.7H), 4.74 (s, 1H), 4.82 (s, 1H); ^{13}C NMR (CDCl_3) δ 19.2–20.1 (m), 36.8–38.2 (m), 41.0–42.2 (m), 107.4–110.8 (m), 152.9–154.6 (m).

Methylenation of Isotactic Poly(CO-alt-1-hexene) (2) with $\text{CH}_2(\text{ZnI})_2\text{-TiCl}_3$

Poly(CO-alt-1-hexene) (**2**) was prepared by the procedure previously reported.¹¹ A THF solution of $\text{CH}_2(\text{ZnI})_2$ (0.44 M, 2.6 mL, 1.2 mmol) was added to a suspension of TiCl_3 (0.14 g, 0.89 mmol) in THF (3 mL) at room temperature. To the mixture was added a solution of isotactic polyketone (**2**) (0.050 g, 0.45 mmol) in THF (10 mL) *via* cannula and the resulting mixture was stirred for 3 h at room temperature. The reaction was quenched by the addition of 1 M HCl aq. (30 mL) and chloroform (30 mL) at 0°C. The separated aqueous layer was extracted with chloroform (2 $\times$ 25 mL). The combined organic layers were dried over anhydrous magnesium sulfate, filtered and concentrated to afford the crude polymer **4** (> 95% yield, 47/53 of methylene/carbonyl, determined by ^1H NMR). The crude polymer **4** was again treated with $\text{CH}_2(\text{ZnI})_2$ (0.60 mmol) and TiCl_3 (0.46 mmol) in THF (4 mL) in the manner same as the method of the first treatment to obtain the crude polymer **4** (> 95% yield in the second step, 67/33 of methylene/carbonyl). Third treatment with $\text{CH}_2(\text{ZnI})_2$ (1.0 mmol) and TiCl_3 (0.78 mmol) in THF (10 mL) gave the crude polymer **4** in > 95% yield in the third step. The crude polymer was purified by size exclusion chromatography to afford methylenated polymer **4** (0.040 g, 0.36 mmol, 80% overall yield from polyketone **2**, 85/15 of methylene/carbonyl).

Measurements

Nuclear magnetic resonance spectra were taken with JEOL EX-270 (^1H 270 MHz; ^{13}C 68 MHz) or Varian Mercury 200 (^1H 200 MHz; ^{13}C 50 MHz) spectrometer using tetramethylsilane as an internal standard, and coupling constants are given in Hertz. Infrared spec-

tra were recorded by JASCO IR-810. Optical rotation was measured on a JASCO DIP-360. Molecular weights were estimated by size exclusion chromatography (Shodex, KF-804L, THF as an eluent) using polystyrene as a standard.

RESULTS AND DISCUSSION

Methylenation of Poly(propene-alt-CO)

First, we attempted the Wittig reaction, one of the most common methods of methylenation.¹⁸ Polyketone **1** (M_n = 19500, M_w/M_n = 1.38, $[\alpha]_D^{25}$ = -56.6 (c 1.05, CHCl_3)) was prepared *via* the asymmetric alternating copolymerization of propene and carbon monoxide according to our previous report.⁸ Using $\text{CH}_3\text{PPh}_3\text{I}$ in combination with bases, such as *n*-BuLi and *t*-BuOK, insoluble polymeric materials were given (eq 1). Considering that methylenated polymer **3** is soluble in chloroform, we assume that the polyketone **1** became insoluble because of spiroketalization (vide infra) or intramolecular aldol reaction.¹⁹ It is likely that these side reactions took place due to the strong basicity of the Wittig reagent.

Next, we employed the Tebbe reagent²⁰ that has weaker basicity than the Wittig reagent. We treated polyketone **1** with 1.5 equiv. of the Tebbe reagent (1-dicyclopentadienyl- μ -chloro- μ -methylene-2-dimethyl-2-aluminum-1-titanium, $\text{Cp}_2\text{Ti}(\mu\text{-Cl})(\mu\text{-CH}_2)\text{-AlMe}_2$) at room temperature for 16 h (eq 2). After work-up with aqueous NaOH and removal of the inorganic residues by filtration, polymer **3** that contains both methylene and ketone moieties was obtained. The yield and the methylene/ketone (x/y) ratio were determined by ^1H NMR analysis to be 70% and 76/24, respectively. Polymer **3** thus obtained was again treated with the Tebbe reagent (5 equiv. to carbonyl) to improve the x/y ratio up to 97/3. The yield for the second step was estimated to be 64% by ^1H NMR. The crude product was contaminated by organic residues from the Tebbe reagent, and therefore purified by silica-gel column chromatography and then by size exclusion chromatography. Polymer **3** (x/y = 97/3) was obtained in its pure form in 28% overall isolated yield from polyketone **1**.

For comparison, atactic polyketone **5** was also methylenated with the Tebbe reagent. First, a head-to-tail and atactic polyketone **5** was prepared by the alternating copolymerization of propene with carbon monoxide using Pd-bis(dicyclohexylphosphino)ethane complex as a catalyst.⁹ Treatment of this atactic polyketone **5** with 1.5 equiv. of the Tebbe reagent afforded polymer **6** (x/y = 90/10) in 98% yield (eq 3). The crude polymer was again treated with the Tebbe reagent

and then purification by silica-gel column chromatography and size exclusion chromatography to give atactic methylenated polymer **6** ($x/y = 98/2$) in 73% overall isolated yield from polyketone **5**.

Here we compare the two substrates, isotactic **1** and atactic **5**, in the first treatment with the Tebbe reagent. In the reaction of the atactic polyketone, the methylenated polymer **6** was obtained quantitatively after aqueous work-up and filtration, while the isotactic methylenated polymer **3** was obtained in only 70% yield. The difference may be attributed to the spiroketal formation of the isotactic polyketone **1** (Scheme 2). It is reported that the propene/carbon monoxide alternating copolymer sometimes contains spiroketal units when the polymerization catalyst, a cationic palladium complex, behaves as a Lewis acid.²¹ Under the Tebbe reaction conditions, carbonyl groups should be activated by titanium or aluminium, and then nucleophilic addition reaction by enol and tandem cyclization likely occur to give a spiroketal structure as shown in Scheme 2. Thus, polymer **7** which contains both ketone and spiroketal can be formed. Because spiroketal units in **7** is insoluble in most of the common organic solvents,⁹ the whole polymer becomes insoluble once spiroketal is formed during the methylenation reaction. Isotactic polyketone **1** is known to show higher tendency to be converted to spiroketal compared to atactic polyketone **5**.^{21a} Thus, the formation of spiroketal seems responsible to the lower yield of **3**. Also, polyketone **1** was probably converted into the insoluble spiroketal in the Wittig reaction above mentioned due to the basic conditions (vide supra).

As an improved methylenation reagent, we next employed the combination of $\text{CH}_2(\text{ZnI})_2$ and TiCl_3 (eq 4).^{14, 22} According to the literature method,¹⁴ a

Scheme 2.

dichloromethane solution of isotactic polyketone **1** was added to a suspension of $\text{CH}_2(\text{ZnI})_2$ and TiCl_3 in THF. The reaction was quenched with aqueous HCl , and the polymer was extracted with chloroform. The methylenated polymer **3** ($x/y = 96/4$) was obtained in its pure form in 78% isolated yield by reprecipitation from chloroform/methanol. The methylenation reaction of **1** was accomplished only by the first treatment of $\text{CH}_2(\text{ZnI})_2\text{--TiCl}_3$, while in the Tebbe reaction, the second treatment was necessary for the completion. Furthermore, the reaction with $\text{CH}_2(\text{ZnI})_2\text{--TiCl}_3$ exhibited higher yield than with the Tebbe reagent, which indicates that spiroketal formation of **1** was slower in the $\text{CH}_2(\text{ZnI})_2\text{--TiCl}_3$ system. The difference is likely attributed to the Lewis acidity of the reagents, namely lower Lewis acidity of the Ti(III) species in the $\text{CH}_2(\text{ZnI})_2\text{--TiCl}_3$ reaction than Ti(IV) species in the Tebbe reaction.

Investigation on the Stereoregularity of Polymer **3**

First, we attempted reoxidation of the methylenated polymer **3** to polyketone **1**, in order to compare its stereoregularity with the original polyketone **1**. We employed the combination of OsO_4 and NaIO_4 .²³ When a dioxane- H_2O solution of polymer **3** was treated with 0.1 equiv. of OsO_4 and 2.9 equiv. of NaIO_4 at room temperature for 21 h, however, polymeric materials insoluble in CHCl_3 were obtained, though polyketone **1** is soluble in CHCl_3 . In IR analysis, not carbonyl but hydroxyl group was observed, which indicates that oxidation of C=C with OsO_4 proceeded but further oxidation of the resulting diols with NaIO_4 did not occur. Next, a dichloromethane solution of methylenated polymer **3** was treated with ozone at -78°C for 5 h, and then with dimethyl sulfide. The reaction did not proceed completely, however, and both carbonyl and exo-methylene groups were observed by ^{13}C NMR.

Next, ^{13}C NMR spectrum of isotactic methylenated polymer **3** was compared with that of atactic one **6**. Figure 1 shows the ^{13}C NMR signals due to the sp^2 carbons in the main chain. Each of the five partial spectra corresponds to (a) isotactic polyketone **1**, (b) its methylenated product **3** with the Tebbe reagent, (c) **3** with $\text{CH}_2(\text{ZnI})_2\text{--TiCl}_3$, (d) atactic polyketone **5**, and (e) its methylenated product **6**. The sharp peaks at 153.3 ppm observed with polymer **3** in Figures 1b and 1c are assigned to a *like* (*S-S* or *R-R*) diad, and the other peaks

Figure 1. ^{13}C NMR spectra for the sp^2 carbons in the main chain of: (a) isotactic polyketone **1**, (b) isotactic **3** obtained with Tebbe reagent, (c) isotactic **3** obtained with $\text{CH}_2(\text{ZnI})_2\text{-TiCl}_3$, (d) atactic polyketone **5**, and (e) atactic **6**. The peaks at 153.3 ppm in (b), (c), and (e) are assigned to a *like* (*S-S* or *R-R*) diad, and the other peaks around 152.9–153.2 ppm in (e) are due to an *unlike* (*S-R* or *R-S*) diad or a $-\text{C}(=\text{CH}_2)-$ group neighboring on a carbonyl group. The peak at 153.3 ppm contains over 85% of all the peak area in (b) and (c).

around 152.9–153.2 ppm in Figure 1d are due to an *unlike* (*S-R* or *R-S*) diad or a $-\text{C}(=\text{CH}_2)-$ group neighboring on a carbonyl group. The fact that the peak at 153.3 ppm contains over 85% of the total peak area in Figures 1b and 1c indicates that polymer **3** is highly isotactic. This agrees well with the reports that no significant epimerization was observed during methylenation with $\text{CH}_2(\text{ZnI})_2\text{-TiCl}_3$ ¹⁴ or the Tebbe reagent.¹⁵

Methylenation of Poly(1-hexene-alt-CO)

We also examined methylenation of the isotactic polyketone **2**¹¹ ($M_n = 11800$, $M_w/M_n = 2.07$, $[\alpha]_D^{27} = -74.0$ (c 0.49, CHCl_3)) which is the alternating copolymer of 1-hexene and carbon monoxide. Polyketone **2** was treated with $\text{CH}_2(\text{ZnI})_2\text{-TiCl}_3$ repeatedly three times (eq 5). The corresponding polymer **4** was obtained quantitatively, but the reaction was not completed and the ratio of methylene and ketone (x/y) reached only 85/15. The crude polymer was purified by size exclusion chromatography to afford the methylenated polymer **4** in 80% isolated yield. It seems that the reaction was not completed because the steric hindrance of the butyl group in the side chain lowered the reactivity of the polyketone **2**. Here we compare

the two substrates, methyl substituent polyketone **1** and butyl substituent polyketone **2** in the first treatment with $\text{CH}_2(\text{ZnI})_2\text{-TiCl}_3$ reagent. In the reaction of **2**, the methylenated polymer **4** was obtained quantitatively after aqueous work-up (eq 5), while in the reaction of **1**, the methylenated polymer **3** was obtained in only 83% yield (eq 4). The differences may be explained either that spiroketal was not formed from polyketone **2**, or that spiroketal units from **2** are soluble, unlike **1**, to allow the equilibrium back to the ketone units.

Figure 2 shows ^1H and ^{13}C NMR spectra of methylenated polymer **4**. In ^1H NMR (Figure 2a), integration of the resonances of the main chain and exo-methylene are 1.3 H and 0.6 H, respectively, with respect to the 3 H of the side chain end methyl. Similarly, in ^{13}C NMR (Figure 2b), intensities of signals around main chain are relatively low. These phenomena may be caused that solvent (CDCl_3) does not reach the main chain because of the steric hindrance of the side chain butyl group, and thus the main chain is not completely solvated, in other words, it is not dissolved.

Relaxation times T_1 of methylenated polymers **3** and **4** and polyketones **1** and **2** in ^1H NMR were measured, and summarized in Figure 3. Each of the four figures corresponds to the T_1 values of (a) methylenated polymer **4**, (b) polyketone **2**, (c) methylenated polymer **3**, and (d) polyketone **1**. It should be noted that the T_1 value of main-chain methylene protons of polymer **4** is 0.19 s which is much shorter than that of methyl protons at the side chain end, 0.83 s (Figure 3a). Therefore motion of the main chain is likely restricted compared to the side chain. The T_1 value of this main-chain methylene, 0.19 s, is also smaller than that of the main-chain methylene in polyketone **2** (0.24 s) (Figure 3b) and the methylenated polymer **3** (0.26 s) (Figure 3c). Thus, it is suggested that the main chain of methylenated polymer **4** is placed in its difficult surroundings to move.

Insights of the Higher Order Structure of Methylenated Polymers **3** and **4**

Molecular weights of the obtained methylenated polymer **3** and **4** were measured by GPC with a polystyrene standard. M_n and M_w of methylenated polymer **3** obtained with Tebbe reagent are 5500 and 12800, respectively, the values being much lower than those of the substrate polyketone **1** ($M_n = 19500$, $M_w = 27000$ measured by GPC with a polystyrene

Figure 2. (a) ^1H NMR and (b) ^{13}C NMR spectra of methylenated polymer **4**. In ^1H NMR, number of protons of each peak exhibits relative integration to the methyl signal, 3 H.

Figure 3. Values of relaxation time (T_1) in ^1H NMR of (a) methylenated polymer **4** with butyl substituent, (b) polyketone **2** with butyl substituent, (c) methylenated polymer **3** with methyl substituent obtained with $\text{CH}_2(\text{ZnI})_2\text{-TiCl}_3$, and (d) polyketone **1** with methyl substituent.

standard). Similarly, molecular weight of methylenated polymer **4** obtained with $\text{CH}_2(\text{ZnI})_2\text{-TiCl}_3$ ($M_n = 1200$, $M_w = 7400$) was smaller than the substrate polyketone **2** ($M_n = 11800$, $M_w = 24500$). Meanwhile, absolute molecular weight (M_n) of the polyketone **1** was estimated to be 19100 by ^1H NMR assuming that the alternating copolymerization proceeded in a living manner.⁸ Therefore molecular weight of polyketone **1** measured by GPC ($M_n = 19500$) seems to be reasonable and that of the methylenated polymer **3** seems to be too small. The reason why methylenated polymer **3** and **4** have smaller exclusion volume than polystyrene is not cleared. The C–C bond cleavage in the main-chain is not probable under the reaction conditions.^{20, 22}

A specific rotation of methylenated polymer **3** ($x/y = 96/4$) obtained with $\text{CH}_2(\text{ZnI})_2\text{-TiCl}_3$ was $[\alpha]_D^{25} -15.7$ (c 0.99, CHCl_3). This value may be compared to the rotation value $[\alpha]_D +13.29$ of (*S*)-2,3-dimethylpent-1-ene²⁴ which can be regarded as a model compound of the polymer **3**. Therefore methylenated polymer **3** is not necessary to have stable helical conformation. The

opposite sign for the same *S*-isomer might be attributed to the multiple existence of neighboring C=C double bonds to the asymmetric carbon in polymer **3**. Meanwhile, methylenated polymer **4** exhibited a specific rotation of $[\alpha]_D^{25} -0.63$ (c 1.03, CHCl_3). The small value might be explained that the specific rotation of an exomethylene unit and that of a remaining ketone unit are compensated.

CONCLUSION

Methylenation of optically active γ -polyketones **1** and **2** with the dizinc-titanium reagent, $\text{CH}_2(\text{ZnI})_2\text{-TiCl}_3$ afforded methylenated polymer **3** and **4** in 78% and 80% isolated yield, respectively. No significant epimerization occurred under these reaction conditions, that was confirmed by the comparison of the ^1H NMR spectrum of the polymer **3** with that of atactic polymer **6**. Based on the NMR integration and relaxation time, we speculate that the main chain is less flexible in the methylenated polymer **4** with a butyl side chain. The present study shows a novel synthetic route of the synthesis of hydrocarbon polymer with main chain chirality.

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