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Notes

Synthesis of Isotactic Poly-1,2-(4-methyl-1,3-pentadiene) by a Homogeneous Titanium Catalyst

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Introduction

Polymerization of conjugated dienes performed in the presence of homogeneous transition-metal catalysts has been widely investigated.[1,2] One can obtain polydienes with different microstructures by varyng the catalytic system and other polymerization conditions.[3] However, in the case of 4-methyl-1,3-pentadiene (4-MPD) the attempts to influence the polymer structure by rational choice of the catalyst have been unsuccessful. In the presence of group 4 homogeneous catalysts (e.g., half-sandwich or σ-hydrocarbyl compounds) both 4-MPD and styrene produce syndiotactic 1,2-polymers.[4,5] The geminal methyl groups on the double bond prevent the 1,4-polymerization of 4-MPD. Therefore, its polymerization behavior is more closely related to that of styrene than to that of conjugated 1,3-diolefins. The 2,1-insertion of 4-MPD and syndiotactic arrangement in the polymer chain were previously explained by considering electronic factors and the steric interactions of the incoming monomer with the active species, in analogy to what was reported for the polymerization of styrene.[2] Recently, the polymerization of 4-MPD was performed by some C_2-symmetric *ansa*-zirconocenes activated by methylaluminoxane (MAO).[6] Although *rac*-[CH_2(1-indenyl)$_2$]-$ZrCl_2$, which promotes isotactic polymerization of styrene,[7] is completely inactive, *rac*-[CH_2CH_2(1-indenyl)$_2$]-$ZrCl_2$, which is inactive toward styrene, produces poly-(1,4-4-MPD). Syndiotactic poly(1,2-4-MPD) is obtained in the presence of *rac*-[CH_2(3-*tert*-butyl-1-indenyl)$_2$]-$ZrCl_2$. The authors explain this behavior considering that the "chain-end control" overrides the isotactic stereocontrol due to the symmetry of the catalyst.

Isotactic poly(1,2-4-MPD) was first synthesized by Porri and Gallazzi by heterogeneous titanium and vanadium catalysts activated by $Al(C_2H_5)_3$[8] and was characterized by X-ray diffraction and infrared spectroscopy. However, NMR spectra, recorded in our laboratory on poly(4-MPD) obtained in the presence of $TiCl_3$/$Al(C_2H_5)_3$, showed that the polymer structure has both 1,2- and 1,4-arrangements.[9]

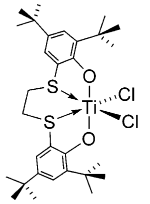

Figure 1. Dichloro{1,4-dithiabutanediyl-2,2′-bis(4,6-di-*tert*-butyl-phenoxy)}titanium (**1**).

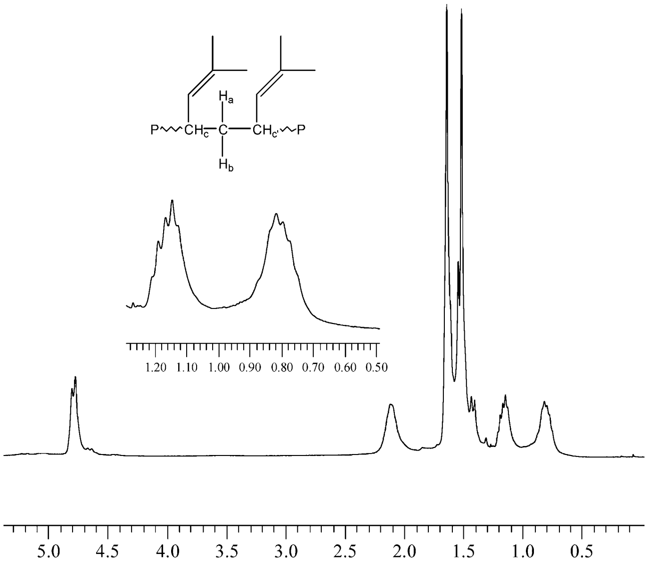

Figure 2. ^{1}H NMR spectrum of isotactic poly-1,2-(4-methyl-1,3-pentadiene). The region between 0.5 and 1.3 ppm is evidenced.

Recently, we developed a new class of group 4 metal catalysts precursors such as complex **1**, which incorporate a tetradentate ligand having two phenoxo units linked through a 1,ω-dithiaalkanediyl bridge $S(CH_2)S_n$ (n = 2 and 3).[10] They possess an octahedral structure with C_2-symmetry (see Figure 1) and, when activated with MAO, are very active in isospecific polymerization of styrene.

In this Note we report that complex **1** activated by MAO produces highly isotactic poly-1,2-(4-methyl-1,3-pentadiene).

Results and Discussion

Figure 2 shows the ^{1}H NMR spectrum of poly(4-MPD) obtained with complex **1** activated by MAO. The expanded region between 0.6 and 1.3 ppm, relative to the methylene proton of the polymeric chain, shows the multiplicity of the signals which are diagnostic of isotactic enchainment. One can observe a couple of multiplets that arise from the geminal coupling between the methylene protons (H_a and H_b) in addition to the

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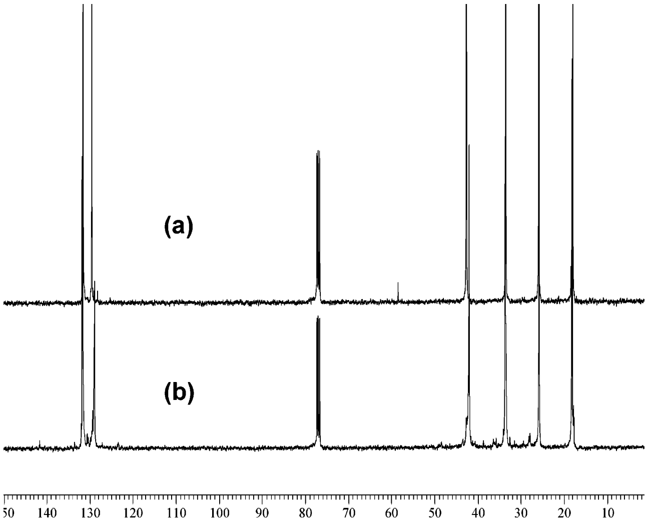
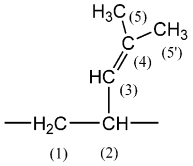


Figure 3. ^{13}C NMR spectra of syndiotactic (a) and isotactic (b) poly-1,2-(4-methyl-1,3-pentadiene).

Table 1. Assignments of the ^{13}C NMR Resonances for Isotactic and Syndiotactic Poly-1,2-(4-methyl-1,3-pentadiene)



carbon	isotactic poly-1,2-(4-methyl-1,3-pentadiene) (ppm)	syndiotactic poly-1,2-(4-methyl-1,3-pentadiene) (ppm)
C(1)	42.00	42.63
C(2)	33.69	33.52
C(3)	131.75	131.54
C(4)	128.86	129.54
C(5)	25.81	25.86
C(5′)	18.11	17.95

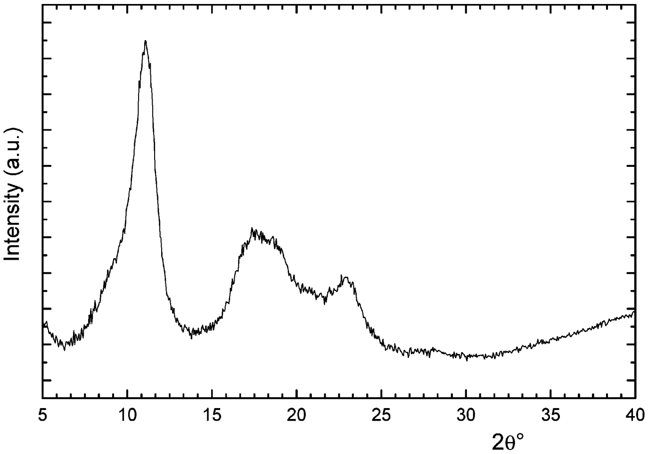


Figure 4. X-ray diffraction pattern of isotactic 4-MPD obtained with catalyst **1**.

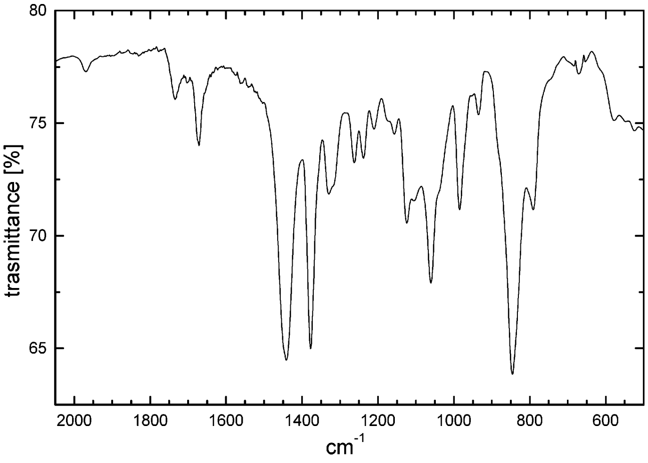


Figure 5. Infrared spectrum of isotactic 4-MPD obtained with catalyst **1**.

vicinal coupling due the methine protons (H_c and $H_{c'}$). These data unambiguously distinguish this polymer from the syndiotactic one, which shows pseudotriplet for the methylene protons.[4,6] The resonances at 1.42 (d), 1.54 (s), and 4.66 ppm (br) are relative to 4-MPD units with 1,4-arrangement.

In addition, Figure 3 shows the ^{13}C NMR spectra of the syndiotactic (a) and isotactic (b) polymers obtained as reported in ref 6 and by **1** in the presence of MAO, respectively. The presence of six sharp resonances indicates that both spectra are highly stereoregular polymers where the monomers are connected predominantly in the 1,2-fashion. One can observe from the assignments listed in Table 1 that the peaks for both polymers almost overlap, except for the signal for C(1) and C(4) which differ by 0.63 and 0.68 ppm, respectively. The small signals observed in Figure 3b centered at 27.2, 36.1, 46.4, 122.5, and 142.6 ppm are relative to 4-MPD units in 1,4-arrangement that can be estimated from the ^{13}C NMR by the amount less than 3%. The X-ray diffraction pattern (Figure 4) and the FT-IR spectrum (Figure 5) performed on poly(4-methyl-1,3-pentadiene) 1,2-isotactic, as obtained, are similar to those reported by Porri et al.[8] of the crystalline modification I. In particular, in the X-ray diffraction pattern, reflections at 2θ 11.0°, 17.5°, and 22.9° are present. In the FT-IR spectrum the characteristic bands for modification I at 525, 580, 931, and the shoulder at 1035 cm^{-1} are observed, which are all absent in the IR spectrum of crystalline modification II. The characteristic bands of the *trans*-1,4 units at 963 cm^{-1} are slightly overlapping with the band at 960 cm^{-1}. *cis*-1,4-Units, detectable in the region of 725−770 cm^{-1}, are absent, confirming again that this polymer prevailingly consists of 1,2-sequences.

Heating and cooling curves from DSC measurements are shown in Figure 6 (curves a and b) together with the heating curve of the sample crystallized from the melt (curve c). The endothermic peak at ≈80 °C ($\Delta H = 6.7$ J/g) is probably due to the transition from the crystalline modification I to the crystalline modification II, while the endothermic peak at 146 °C ($\Delta H = 28.8$ J/g) corresponds to the melting of the more stable form II. The absence of any exothermic peak in the range 60−90 °C could be due to the fact that the transition from form I to the more stable form II occurs directly or the exothermic peak is hidden from the large endothermic peak. On crystallizing from the molten state ($T_c = 110$ °C) only the modification II is obtained, indicated by curve c, in which the endothermic peak at ≈80 °C is absent. In curve c a T_g is clearly apparent at $T = 11.4$ °C. The lower melting temperature (146 °C) with respect to the value of 166 °C observed previously[8] may be due to the incorporation of some 1,4-units which reduces the length of the crystallizable 1,2-sequences in the polymer chains. The GPC analysis of this poly(4-MPD) shows M_w

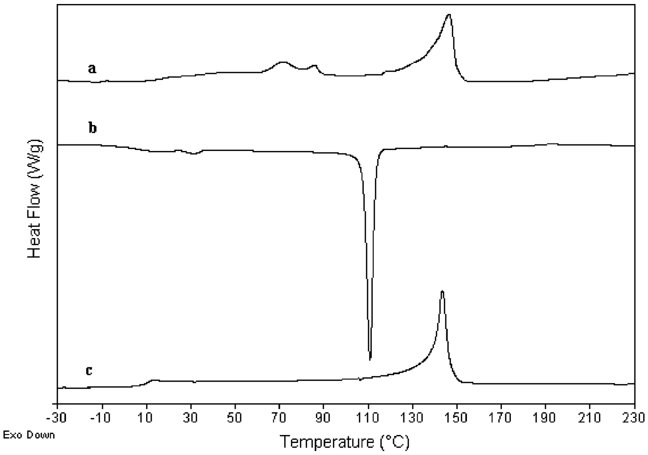


Figure 6. DSC analyses: (a) first heating, (b) cooling, and (c) heating.

= 57 000 Da and a polydispersity of 1.7, as predicted for single site catalyst.

Conclusions

In this paper we have shown that this new homogeneous C_2-symmetric octahedral titanium catalyst promotes the isospecific polymerization of 4-MDP with a high degree of stereocontrol. The isotactic polymer have been fully characterized by NMR, FTIR, X-ray diffraction, and thermal analysis. The polymorphic behavior observed in the polymer is analogous to that described for the isotactic polymer obtained in the presence of heterogeneous Ziegler–Natta catalyst.

Experimental Section

Materials. Toluene (Carlo Erba Analytical Grade) was refluxed 48 h under a nitrogen atmosphere over sodium and benzophenone before using. Toluene and $Al(CH_3)_3$ present in MAO 10% (Witco) solution were removed under reduced pressure. The residual white powder was washed with dry *n*-hexane, dried in a vacuum, and stored in a glovebox under nitrogen. 4-Methyl-1,3-pentadiene was purchased from Fluka (purum 98% GC) and distilled over MAO. Catalyst precursor **1** was prepared as reported previously.[10]

Polymerization. Polymerization of 4-MPD was carried out under a nitrogen atmosphere in a 100 mL glass flask, equipped with a magnetic stirrer and immersed in thermostated oil bath at 25 °C for 1 h. The glass flask was sequentially filled with 4.0 mL of toluene, 300 mg (5.0 mmol) of solid MAO, 1.80 g (22 mmol) of 4-methyl-1,3-pentadiene, and 1.0 mL of catalyst **1** toluene solution (1.0×10^{-2} M). The run was stopped by injecting ethanol. The polymer sample, coagulated with acidified ethanol, was washed several times with ethanol, recovered by filtration, and dried in a vacuum at 60 °C; yield 0.55 g. Syndiotactic poly(4-MPD) was prepared as reported in ref 6.

Instrumentation. The NMR spectra were recorded on an AM 400 Bruker spectrometer operating at 100 MHz in a Fourier transform mode at 295 K. The samples were prepared dissolving in an NMR tube 25 mg of the polymers with $CDCl_3$.

The calorimetric measurements were carried out on a TA 2920 differential scanning calorimeter operating under nitrogen flow and calibrated by the measurement of the melting point of indium. The heating and cooling were performed at a 10 °C/min rate.

Wide-angle X-ray diffraction patterns were obtained with nickel-filtered Cu Kα radiation, using a PW 1710 Philips powder diffractometer.

Infrared spectra were obtained at a resolution of 2.0 cm^{-1} with a Vector 22 FT-IR spectrometer from Bruker. The frequency scale was internally calibrated to 0.01 cm^{-1} using a He–Ne reference laser.

GPC analyses were performed by using a WGE Bures chromatograph operating in $CHCl_3$.

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