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Polymerization of (*Z*)-1,3-Pentadiene with CpTiCl$_3$/MAO. Effect of Temperature on Polymer Structure and Mechanistic Implications

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Much work has been carried out on the polymerization of 1,3-pentadiene with Ziegler–Natta catalysts.[1,2] The *E*-isomer, EP, has been polymerized with various types of catalysts, either homogeneous or heterogeneous, some of which are highly stereospecific.[3-5] In contrast, the *Z*-isomer, ZP, has been polymerized with some heterogeneous systems, but the most common soluble catalysts used for the polymerization of 1,3-dienes were found to be inactive for the polymerization of this isomer.[3-5] Recently, however, it has been reported[6] that the soluble catalyst system CpTiCl$_3$/methylaluminoxanes (MAO) has a good activity for the polymerization of ZP. The polymer obtained at room temperature consists almost exclusively of cis-1,4 units and has a predominantly isotactic structure according to ^{13}C NMR analysis. We have now examined the effect of temperature on the polymerization of ZP with CpTiCl$_3$/MAO and have found that at low temperature (<0 °C) this system gives a poly(ZP) with a 1,2-syndiotactic structure. Such a remarkable effect of the polymerization temperature on polymer structure is surprising and has some interesting mechanistic implications. We report in this paper the results of our preliminary investigations.

Experimental Section. Materials. CpTiCl$_3$ (Strem Chemicals) and MAO (Schering; 30 wt % solution in toluene) were used as received. Toluene (Baker; >99% pure) was refluxed over Na for ca. 10 h, then distilled, and stored over molecular sieves under dry N$_2$. (*Z*)-1,3-Pentadiene (Fluka; >98% pure) was refluxed over calcium hydride for ca. 2 h, then distilled, and stored over molecular sieves under dry N$_2$.

Polymerization. Toluene and ZP were introduced into a 50-mL predried flask, in the amount indicated in Table 1. The solution was brought to the polymerization temperature, and then MAO and CpTiCl$_3$ were added in order. The polymerization was terminated with methanol; the polymer was coagulated and repeatedly washed with a large excess of methanol and then dried in vacuo at room temperature.

Polymer Characterization. Intrinsic viscosities were measured in toluene at 25 °C, using a Desreux-Bishof viscometer. IR spectra were taken on a Perkin-Elmer 457 infrared grating spectrophotometer, using films on KBr disks. ^{13}C NMR and ^{1}H NMR spectra were collected on a Bruker AM 270 instrument using polymer solutions in CDCl$_3$ (polymer concentration from 3 to ca. 10 wt %; TMS as internal standard). DSC measurements were made with a Mettler TA 3000 instrument, under a N$_2$ atmosphere; the scan speed ranged from 15 to 20 K/min. X-ray diffraction spectra were taken with a Siemens D500 diffractometer for unoriented samples.

Results and Discussion. Table 1 reports some data on the polymerization of ZP with CpTiCl$_3$/MAO, at different temperatures. The polymer obtained at +20 °C, of low molecular weight, consisted almost exclusively of cis-1,4 units, as reported in the literature.[6] The polymer obtained at 0 °C consisted of a mixture of cis-1,4 and 1,2 units, the latter being predominant, while that obtained at −28 °C or below was made up almost exclusively of 1,2 units. Surprisingly, the polymerization was found to be faster at −28 °C than at +20 °C, which seems indicative of a different mode of monomer insertion.

Table 1. Polymerization of (*Z*)-1,3-Pentadiene with CpTiCl$_3$/MAO[a]

polymerization			polymer				
temp (°C)	time (h)	conv (%)	cis (%)	1,2 (%)	mp[b] (°C)	[η] (dL·g^{-1})	X-ray exam
20	2	5	≥99			waxy	
0	2	25	28	72	86.6	0.11	cryst
−28	2	53		≥99	100	0.19	cryst

[a] Polymerization conditions: toluene, 4.25 mL; monomer, 2 mL; MAO (as a 30 wt % solution in toluene), 5.75 mL (Al/Ti molar ratio = 500); CpTiCl$_3$, 5 × 10^{-5} mol. [b] Melting points of the acetone-insoluble fraction; determined by DSC.

The ^{13}C NMR spectrum of the polymer obtained at −28 °C (Figure 1) shows five sharp resonances at 13.33, 32.39, 42.54, 122.98, and 137.06 ppm, which were assigned as indicated on the basis of the data reported in the literature for carbons in similar environments and on DEPT ^{13}C NMR experiments.[7,8] The fact that the chemical shift of the methine carbon attached to the methyl group is in the olefinic region proves the 1,2 structure of the polymer. The ^{1}H NMR spectrum of the polymer (Figure 2) is consistent with the previous assignments.[9] Moreover, the resonance of the protons of the methylene group is a triplet (1.143, 1.167, and 1.191 ppm), as expected for a syndiotactic polymer.[10,11] The coupling constant of the olefinic protons (J_{H1-H2} = ca. 10 Hz) indicates that the double bond has a cis structure. This conclusion is confirmed by the IR spectrum of the polymer, which shows a band at 727 cm^{-1}, characteristic of the *cis*-1,2-pentadiene units.[7,12]

The polymer obtained at −28 °C was extracted with boiling acetone to remove the low molecular weight waxy products. The fraction insoluble in acetone, completely soluble in diethyl ether, was found to be crystalline by X-ray (Figure 3), melting point ca. 100 °C. Determination of the crystalline structure of the polymer is now in progress.

A tentative interpretation of the results of Table 1 is as follows.

(1) The formation of cis-1,4 isotactic poly(ZP) is interpretable on the basis of the scheme we have proposed in previous papers[1,2,13] for the cis-1,4 isotactic polymerization of terminally substituted butadienes. In this scheme the last polymerized unit has an anti structure and the incoming monomer is cis-η^4-coordinated. The orientation of the incoming monomer with respect to the last polymerized unit determines the stereospecificity.

(2) The formation of 1,2 syndiotactic poly(ZP) at temperatures below 0 °C is difficult to interpret. Other monomers that are polymerized by CpTiCl$_3$/MAO (e.g., butadiene, (*E*)-pentadiene) give polymers of the same structure either at +20 or −28 °C. As a working hypothesis, we propose the following interpretation for the specific behavior of ZP.

A cis-η^4-coordination likely takes place in two steps, the first of which is the coordination with one double bond only (trans-η^2-coordination), while the second one is the coordination with the other double bond, after rotation around the C$_2$–C$_3$ bond of the monomer (cis-η^4-coordi-

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C(1)	C(2)	C(3)	C(4)	C(5)
42.5_4	32.3_9	137.0_6	122.9_8	13.3_3

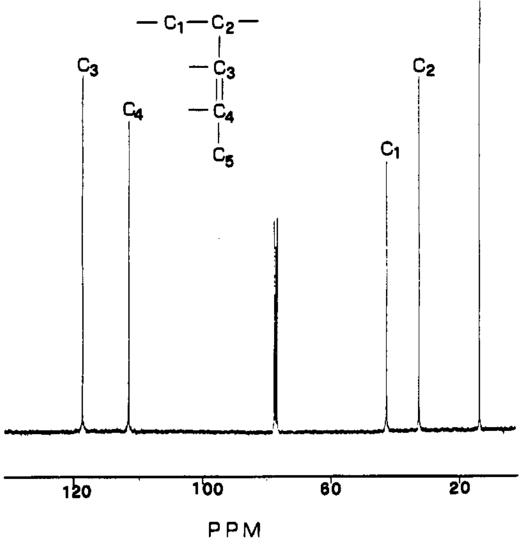

Figure 1. ^{13}C NMR spectrum of poly[(*Z*)-1,3-pentadiene] obtained with $CpTiCl_3$/MAO in toluene at −28 °C ($CDCl_3$; room temperature; TMS as internal standard).

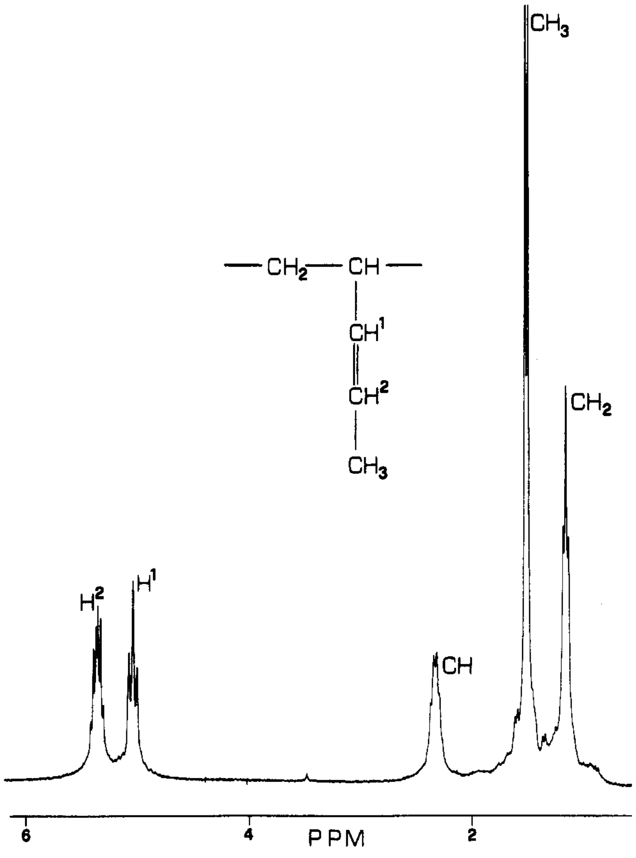

Figure 2. ^1H NMR spectrum of poly[(*Z*)-1,3-pentadiene] obtained with $CpTiCl_3$/MAO in toluene at −28 °C ($CDCl_3$; room temperature; TMS as internal standard).

nation). The two steps are presumably very rapid for diolefins such as butadiene or (*E*)-1,3-pentadiene but not so rapid for monomers such as ZP, for which the cis-η^4-coordination is less favored for steric reasons. It is possible that at low temperature insertion of the trans-η^2-coordinated ZP is more rapid than the trans-$\eta^2 \rightarrow$ cis-η^4 step, and this may be the reason for the formation of a 1,2 unit.

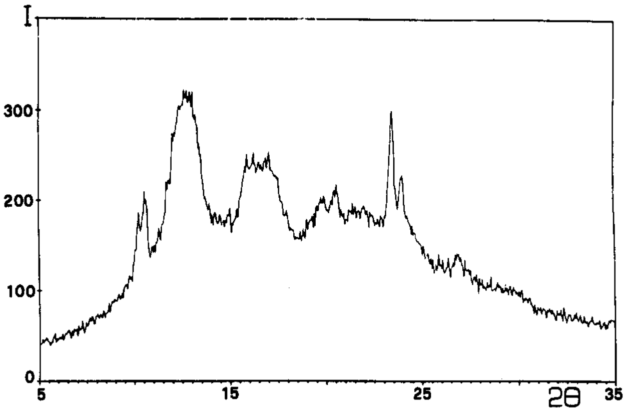

Figure 3. X-ray powder spectrum of poly[(*Z*)-1,3-pentadiene] obtained with $CpTiCl_3$/MAO in toluene at −28 °C (residue to acetone extraction).

A more detailed discussion of the factors that determine the change of stereospecificity with temperature in the polymerization of ZP with $CpTiCl_3$/MAO will be reported in a future paper together with new data on the homopolymerization of 4-methyl-1,3-pentadiene and the copolymerization of this monomer with ZP.

Conclusions. A change of stereospecificity with temperature has been observed in the polymerization of ZP with the homogeneous system $CpTiCl_3$/MAO: a cis-1,4 isotactic polymer is obtained at +20 °C and a 1,2 syndiotactic polymer at −20 °C. This remarkable effect, which has not been observed in the polymerization of other dienes (e.g., butadiene, (*E*)-1,3-pentadiene) with the same catalyst, is presumably attributable to a different mode of coordination of the monomer, which is cis-η^4 at room temperature and may be trans-η^2 at <0 °C.

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