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## STEREOSPECIFIC CYCLOPOLYMERIZATION WITH GROUP 4 METALLOCENES

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### ABSTRACT

Homogeneous Ziegler–Natta catalysts are stereoselective cyclopolymerization catalysts for non-conjugated dienes. Cyclopolymerization of 1,5-hexadiene affords poly(methylene-1,3-cyclopentane) (PMCP), a polymer for which four structures of maximum order are possible. A variety of metallocene catalyst precursors have been investigated; the molecular weight and microstructure of the polymers are sensitive to the structure of the catalyst precursor as well as the reaction conditions. The selectivity for cyclization depends on reaction conditions; decreasing the olefin concentration and increasing the temperature of the reaction favor cyclization. The stereochemistry of cyclopolymers can also be controlled with appropriate choice of catalyst precursor. Diastereoselective cyclopolymerization of 1,5-hexadiene with achiral catalysts yields atactic *trans*-PMCP and *cis*-PMCP, depending on the catalyst precursor. Enantioselective cyclopolymerization with optically active catalysts yields optically active poly(methylenecyclopentane), a novel example of a polymer which is chiral by virtue of its main-chain stereochemistry.

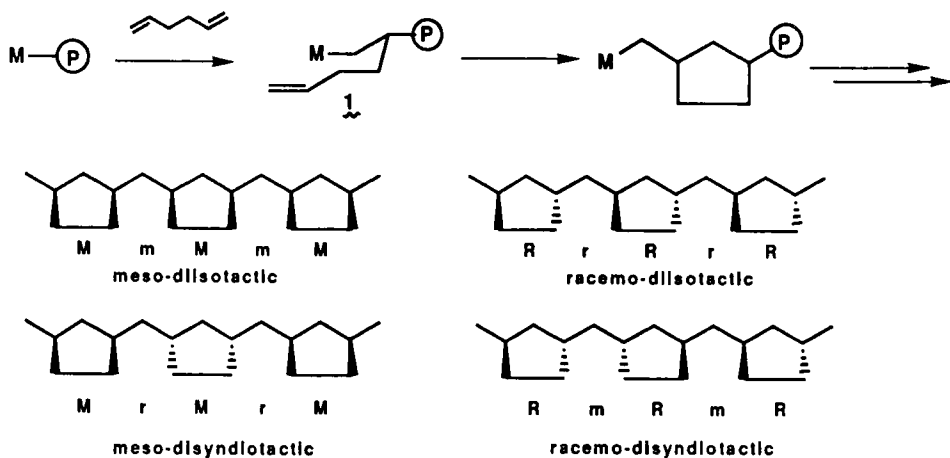
### INTRODUCTION

Homogeneous Ziegler–Natta catalysts exhibit remarkable activity and stereospecificity in the polymerization of  $\alpha$ -olefins [1]. We have been

investigating the stereospecific cyclopolymerization of nonconjugated dienes with group 4 metallocenes [2]. Cyclopolymerization of 1,5-hexadiene with homogeneous Ziegler–Natta catalysts of the Kaminsky-type [3] yields poly(methylene-1,3-cyclopentane) (PMCP), a polymer for which four structures of maximum order [4] are possible (Scheme 1). Of these, the racemo-diisotactic microstructure is a novel example of a polymer which is chiral by virtue of configurational main-chain stereochemistry [4–6].

## EXPERIMENTAL

All experiments were carried out under a dry nitrogen atmosphere, using standard Schlenk-tube techniques. Toluene was distilled from Na/benzophenone, pentane (Aldrich) from  $\text{LiAlH}_4$ . 1,5-Hexadiene (Wiley) was dried over  $\text{CaH}_2$ .  $\text{CDCl}_3$ ,  $\text{D}_2\text{O}$ , and  $\text{Me}_3\text{Al}$  (Aldrich) were used as received; methylaluminumoxane (Schering, 30% toluene solution) was used after removing all volatiles and drying the resulting white powder *in vacuo* (4 h, 21°C, 0.1 mmHg).  $\text{Cp}_2\text{ZrCl}_2$  (Cp = cyclopentadienyl) was obtained from Boulder Scientific,  $\text{Cp}^*\text{ZrCl}_2$  (Cp\* = pentamethylcyclopentadienyl) from Strem, and they were used as received.  $\text{EBIZrCl}_2$  [EBI = ethylenebis(indenyl)],  $\text{EBTHIZrCl}_2$  [EBTHI = ethylenebis(4,5,6,7-tetrahydro-1-indenyl)], and  $\text{EBTHIZrBINOL}$  (BINOL = 1,1'-bi-2-naphtholate) were prepared according to literature procedures [7].



SCHEME 1.

## Polymerization

In a typical procedure the metallocene and the aluminum cocatalysts were placed in a 500-mL round-bottom Schlenk flask at room temperature. Toluene was then added and the resulting yellow solution was thermostated to the appropriate temperature with an external bath. Monomer was added dropwise to the catalyst solution over a period of 3–30 min. Polymerizations were quenched by slow addition of methanol and water (or deuterated water). The polymers were extracted into refluxing toluene for 24 h; in some cases additional fractionation by pentane and chloroform was carried out.

## Characterization

$M_w$ 's were determined on a Waters analytical GPC calibrated to polystyrene.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were run on Varian instruments (GEM-300 at room temperature in  $\text{CDCl}_3$  or XL-400 at  $80^\circ\text{C}$  in  $\text{C}_2\text{D}_2\text{Cl}_4$ ). Optical rotations were measured in chloroform using a Jasco DIP-360.

## RESULTS AND DISCUSSION

A variety of catalyst precursors have been investigated for the cyclopolymerization of 1,5-hexadiene (Table 1). The molecular weight can be controlled by varying the reaction conditions. Chain transfer occurs both by  $\beta$ -H elimination and chain transfer to aluminum with this homogeneous polymerization system. With more active catalysts ( $\text{Cp}_2\text{ZrX}_2$ , EBIMX<sub>2</sub>, EBTHIMX<sub>2</sub>), molecular weights as high as 260,000 (vs polystyrene, Table 1) can be attained;  $\beta$ -H elimination appears to be the predominant chain transfer process under these conditions. In contrast, the molecular weights of polymers obtained from 1-hexene under similar conditions are very low ( $DP = 6$ ). One possible origin of this difference is a lower chain transfer rate for 1,5-hexadiene polymerization, due to the higher strain energy of the olefin liberated upon  $\beta$ -H elimination (methylene cyclopentane = 6 kcal/mol strain energy [8]).

Cyclopolymerization of 1,5-hexadiene with more sterically hindered catalyst precursors such as  $\text{Cp}^*\text{ZrCl}_2$  at  $-25^\circ\text{C}$  leads to a completely saturated polymer of relatively low molecular weight (3000 vs polystyrene). Following acidic workup of the polymer, methylcyclopentane end-

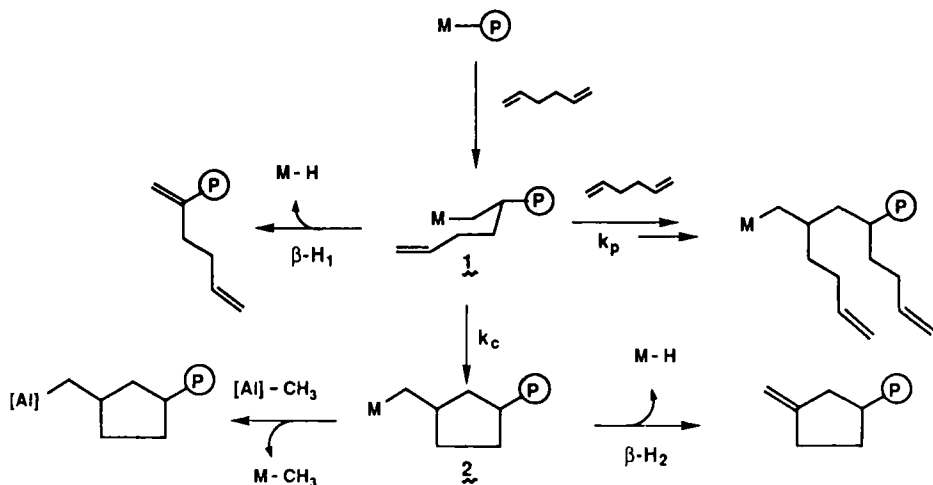
TABLE 1. Cyclopolymerization of 1,5-Hexadiene in Toluene

Metalocene	[Cat] ( $\times 10^4$ M)	[Olefin], M	T, °C	Time, min	Conversion, %	<i>trans</i> , % <sup>a</sup>	<i>M<sub>w</sub></i> <sup>b</sup>
Cp <sub>2</sub> ZrCl <sub>2</sub>	0.5	0.42	21	60	11.1	80	27,000
Cp <sub>2</sub> ZrMe <sub>2</sub>	0.5	0.42	22	60	25.0	79	20,000
"	0.6	0.40	0	270	56.0	84	26,500
"	2.6	0.73	-78	420	0.6	91	
Cp* <sub>2</sub> ZrCl <sub>2</sub>	7.0	8.42	20	180	46.0	30	1,100
"	4.4	2.05	-25	330	65.0	14	3,500
EBIZrCl <sub>2</sub>	0.5	0.40	25	60	81.4	64	48,500
EBIZrCl <sub>2</sub>	0.3	0.40	55	60	98.0	61	40,000
EBTHIZrCl <sub>2</sub>	0.4	0.40	21	60	11.4		61,000
(-)-EBTHIZrBINOL	1.99	0.765	-25	540	47.0	63	
EBTHIZrBINOL	1.95	0.526	0	360	78.8	64	260,000
"	1.95	0.526	25	360	93.0	67	36,000
"	1.95	0.526	50	360	86.3	65	18,000
"	1.95	0.526	80	360	79.6	58	3,000

<sup>a</sup>Determined from C<sub>4,5</sub> *cis/trans* ratio in <sup>13</sup>C NMR (Fig. 2).<sup>b</sup>GPC vs polystyrene.

groups can be detected by  $^{13}\text{C}$ -NMR spectroscopy. Acidic workup with  $\text{D}_2\text{O}$  yields a polymer with deuteriomethyl endgroups. Integration of the methylcyclopentane endgroup  $^{13}\text{C}$ -NMR signal reveals that 50% of the methyl groups are deuterated. These results imply that chain transfer to aluminum is the dominant chain-transfer process under these conditions [9].

The selectivity for cyclization versus intermolecular propagation depends on conditions (catalyst, olefin concentration, temperature). At olefin concentrations  $\leq 0.5\text{ M}$ , cyclization is in general faster than propagation (for 1,5-hexadiene), resulting in very little residual unsaturation in the polymer. However, in the presence of the EBTHIZrBINOL catalyst precursor, there was a significant fraction of uncyclized monomer units. Assuming a two-step mechanism (olefin insertion and olefin cyclization) [10], the selectivity for olefin cyclization can be interpreted in terms of competitive unimolecular cyclization and bimolecular propagation from intermediate **1** ( $k_p[\text{hexadiene}]$  vs  $k_c$ , Scheme 2). These competing processes are influenced by monomer concentration and temperature [11]. Shown in Fig. 1 are the ratios of cyclized and uncyclized monomer units for polymers obtained from 1,5-hexadiene in the presence of EBTHIZrBINOL as a function of temperature. The selectivity for cyclization improves with increasing temperature, as one might expect for competing unimolecular and bimolecular processes [11, 12].

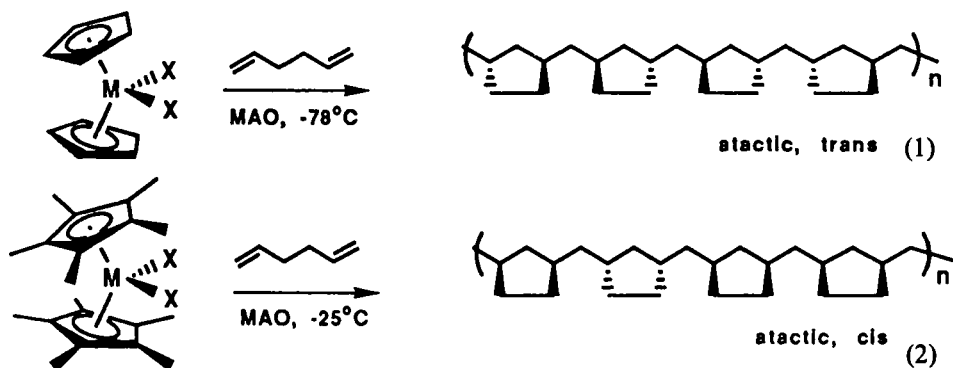


SCHEME 2.

## Stereochemistry

Cyclopolymers contain a rich molecular architecture. For poly(methylene-cyclopentane) there are four structures of maximum order. Of these, the racemodiisotactic microstructure is chiral by virtue of its main-chain stereochemistry [5]. There are two distinct stereochemical events for these cyclopolymerizations: olefin insertion and olefin cyclization (Scheme 1). The enantioselectivity of olefin insertion determines the tacticity of the polymer (the relative stereochemistry of every other stereocenter), and the diastereoselectivity of the cyclization step determines whether *cis* or *trans* rings are formed. Both steps must be controlled in order to prepare any one of the four regular structures.

With homogeneous, achiral catalysts, the *cis/trans* diastereoselectivity can be controlled, leading to the first examples of atactic *trans*-PMCP and *cis*-PMCP [2]. The *trans* polymer is obtained in the presence of  $\text{Cp}_2\text{ZrX}_2$ ; the *cis* polymer is obtained in the presence of the more sterically hindered  $\text{Cp}^*\text{MX}_2$  (Eqs. 1 and 2). Preliminary studies of the physical properties of these polymers reveal substantial differences; for example, the 20:80 *cis/trans* polymer melts at 70°C whereas the 77:23 *cis/trans* polymer melts at 170°C.



To control the tacticity of these cyclopolymers, we have investigated chiral metallocene precursors of the Brintzinger-type [7]  $\text{EBIZrX}_2$  and  $\text{EBTHIZrX}_2$ . Successful interpretation of these experiments requires a method for assignment of the microstructure. To assist in microstructural analysis of these polymers by  $^{13}\text{C}$ -NMR spectroscopy, we are proposing a modification of the Bovey *mr* formalism [13] popular for vinyl polymers. For the cyclopolymers, we propose the use of capital letters

(*M* for meso, *R* for racemic) to denote relative stereochemistry within the rings and lowercase letters (*m* and *r*) to refer to relative stereochemistry between rings (Scheme 1). This notation provides an unambiguous description of all four microstructures.

Shown in Fig. 2 is a portion of the  $^{13}\text{C}$ -NMR spectra of polymers produced from  $\text{Cp}_2\text{ZrMe}_2$  (a) and the chiral precursor EBIZrBINOL (b). The ratio of resonances at 33.4 and 32.1 ppm indicate that both catalysts exhibit a selectivity for the formation of trans rings [14]. Closer analysis reveals fine structure in these resonances which could be attributed to different tacticities of the two samples. The differences in the two spectra imply that the  $^{13}\text{C}$ -NMR chemical shifts are sensitive to differences in tacticity, but do not constitute an unambiguous proof for an isotactic microstructure. Preliminary analysis of the fine structure would imply that the  $^{13}\text{C}$ -NMR spectra are sensitive to triad (*mR*, *rR*; *mM*, *rM*) or perhaps tetrad [15] resolution.

Enantioselective cyclopolymerization of 1,5-hexadiene in the presence of optically active [(+)(S)-EBTHIZrBINOL] ( $[\alpha]_{435} + 1848^\circ, c, 0.52, \text{CHCl}_3$ ) yields optically active PMCP with a molar optical rotation of  $[\Phi]_{405}^{28} - 49.3^\circ (c, 7.9, \text{CHCl}_3)$ . The optically active polymers have similar  $^{13}\text{C}$ -NMR spectra to the racemic polymers. Because isotacticity is a requirement for chirality in these materials, this experiment provides unambiguous evidence for an isotactic microstructure. In addition, this experiment represents the first example of an enantioselective cyclopo-

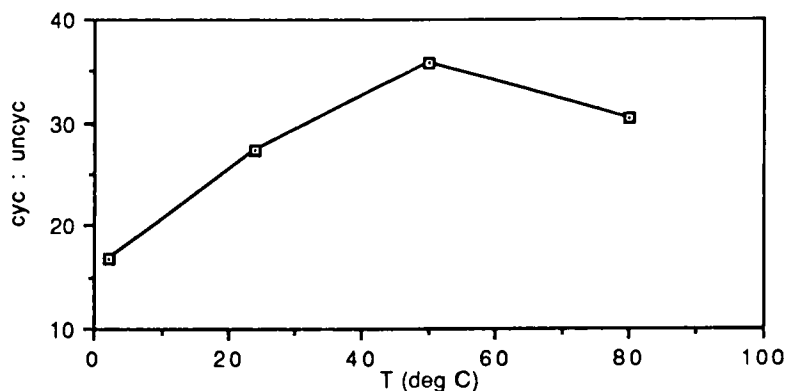


FIG. 1. Temperature dependence of cyclization in cyclopolymerization with EBTHIZrBINOL.



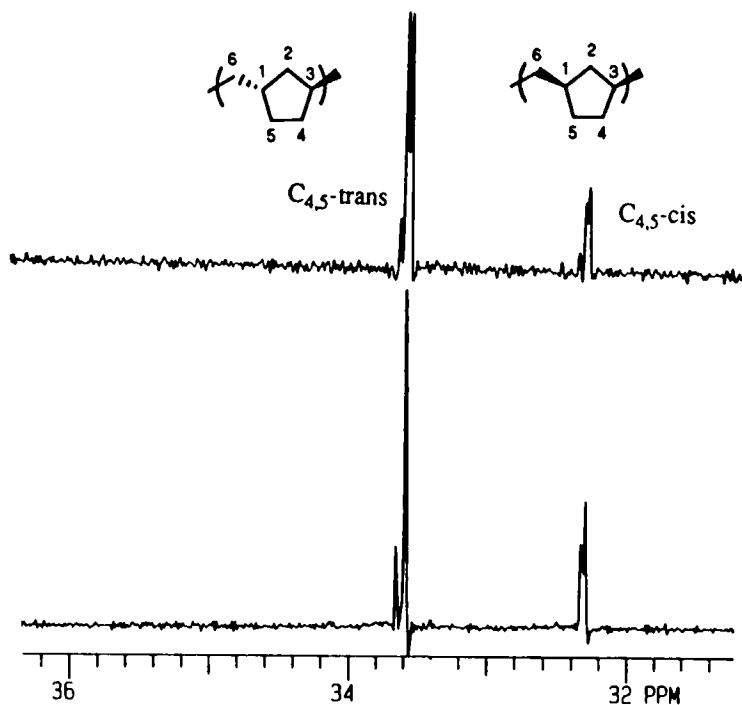


FIG. 2.  $^{13}\text{C}$ -NMR spectrum of  $\text{C}_{4,5}$  of polymethylenecyclopentane: (a)  $\text{Cp}_2\text{-ZrMe}_2$ , (b)  $\text{ETHIZrBINOL}$ .

lymerization. Further studies are underway to study the physical and chiroptical properties of these novel polymers and to develop the scope of enantioselective cyclopolymerization as a route to chiral macromolecules.

### ACKNOWLEDGMENTS

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