The Role of 'Internal' and 'External' Lewis Bases in Controlling the Stereochemistry of Highly Active Ziegler–Natta Catalysts

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Chiral discrimination of the enantiomers of racemic α-alkenes in polymerization with highly active MgCl$_2$-supported Ziegler–Natta catalysts is observed when (−)-menthyl benzoate is used as internal Lewis base; using (−)-menthyl benzoate as an external Lewis base leads to opposite but lower stereoelectivity.†

It is recognised that the preparation of MgCl$_2$-supported Ziegler–Natta catalysts for alkene polymerization involves preliminary treatment of MgCl$_2$ with a Lewis base (internal base = IB). This base is also present during the reaction of MgCl$_2$-supported TiCl$_4$ with the aluminium alkyl. Moreover a second base (external base = EB) is added with the large excess of aluminium alkyl for catalyst activation.[1,2] We have used optically active (−)-menthyl benzoate, [(−)-MtB] as an alternative for both the internal and external Lewis base in the stereoelective[3,4] polymerization of racemic 3,7-dimethyloct-1-ene [(R)-, (S)-DMO] and thus have demonstrated for the first time the different effects of the IB and EB on the stereochemistry of polymerization.†,‡

When (−)-MtB was used as the internal base (IB) substantial stereoelectivity was observed. The recovered monomer shows positive optical rotation indicating excess of the

(S)-enantiomer, whereas the polymer shows negative optical rotation, because of the prevailing insertion of (R)-enantiomer, as expected for a stereoelective process.[3,4] Polymer extraction with boiling solvents shows that production of isotactic polymer (boiling diethyl ether insoluble fraction) is the same as with most conventional stereospecific catalysts[5] and that the stereoelectivity increases with the stereoregularity of the polymer (Table 1).

Different behaviour is observed when IB = EtB and EB = (−)-MtB. In spite of the large excess of (−)-MtB with respect to titanium [(−)MtB/Ti molar ratio = 56], the stereoelectivity of the polymerization is much lower than in the previous case and practically limited to the fractions with low stereoregularity; the isotactic polymer obtained in almost the same yield shows no detectable optical rotation (Table 1).

The enhancement in the stereoelectivity on using (−)-MtB as the internal base is shown by the large difference in values for the ratio of the optical purity of the polymerized monomer to the amount of optically active base per Ti atom used (Table 1). This can be considered as a measure of the efficiency of the system in inducing chiral discrimination into the racemic monomer.§

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† In this communication the term stereoelectivity is used to indicate the preferential polymerisation of a single enantiomer from a racemic mixture (see refs. 3–6);

‡ The MgCl$_2$-supported catalysts were prepared in co-operation with Professor J. C. W. Chien at the Polymer Science and Engineering Department, University of Massachusetts, Amherst, U.S.A. The preparation of the catalyst with ethyl benzoate (EtB) as internal base is already described in ref. 2. The catalyst with (−)-menthyl benzoate [(−)-MtB] as internal base was obtained using the same procedure, replacing EtB with (−)-MtB.

§ No effect of conversion can be claimed as similar data have been obtained in analogous experiments with racemic 4-methyl-1-hexene as the monomer and conversions 13 and 22%, respectively with (−)-MtB as IB and EB (F. Ciardelli, unpublished results).

Table 1. Stereoelective polymerization of racemic DMO by highly-active chirally-modified $MgCl_2$ supported Ziegler–Natta catalysts[a].

IB	EB	(−)-MtB/Ti (mol ratio) (B)	Conversion (%)	Recovered monomer $[\alpha]_D^{25b}$	Low stereoregular polymer		Isotactic polymer		Stereo-electivity[d] efficiency
					%	$[\alpha]_D^{25c}$	%	$[\alpha]_D^{25c}$	
(−)-MtB	MT[b]	1	3.9	+0.03	13.8	−1.5	86.2	−5.1	4.4
EtB	(−)-MtB	56	19.7	−0.01	18.7	+1.3	81.3	~0	0.004

[a] Composition of catalyst: IB, -p-cresol–$AlEt_3$–$TiCl_4$–$AlBu^i_3$–EB; 3600 mol DMO mol^{-1} Ti; 167 mol $AlBu^i_3$ mol^{-1} Ti; ratio EB: $AlBu^i_3$ 1:1; solvent n-heptane, temperature 50 °C. Other details on catalyst preparation and activation are in ref. 2. [b] Neat, pathlength = 10 cm. [c] In cyclohexane solution, pathlength = 10 cm. [d] Evaluated as polymerized monomer optical purity/B.

These data confirm the presence of sites with different stereospecificity and Lewis acidity in the heterogeneous catalytic systems,[4] and that the internal base only affects the stereochemical structure of the active sites producing the isotactic polymer, at least in the case of branched α-alkenes. The lower stereoelectivity for the partially nonstereoregular chains with the optically active external base may be related to solvation of the more exposed sites.[6]

References

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