under vacuum to ~5 mL. Addition of a large excess of methanol (100 mL) gave a precipitate, which was filtered (0.07 g, 20%).

Registry No. **1a**, 99542-62-8; **1b**, 105971-08-2; **1c**, 99542-63-9; **1d**, 105971-09-3; **2a**, 105971-10-6; **2b**, 105971-11-7; **2c**, 105971-12-8; **2d**, 105971-13-9; 4,4'-$HOC_6H_4CO_2C_6H_4O(CH_2)_3CH_3$, 70568-44-4; $Br(CH_2)_6Br$, 629-03-8.

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Stereoselective Copolymerization of Chiral α-Olefins by High-Activity Ziegler–Natta Catalysts

The intrinsically asymmetric structure of the active sites in Ziegler–Natta catalysts makes them able to chirally discriminate between the enantiomers of α-olefins bearing one stereogenic center in the α and β position to the double bond.[1] As a consequence each macromolecule is built up predominantly from a single enantiomer (stereoselective polymerization) as shown for both conventional[2] and supported high-activity[3] catalytic systems.

One application of stereoselectivity, carried out with conventional $TiCl_3/AlR_3$ catalyst, was based on the copolymerization of a racemic α-olefin, (*RS*)-3,7-dimethyl-1-octene [(*RS*)-DMO], with optically active (*S*)-3-methyl-1-pentene [(*S*)-3MP], also having the asymmetric carbon atom α to the double bond. As the active sites discriminate on the basis of chirality rather than chemical structure, a random copolymer of (*S*)-DMO with (*S*)-3MP was obtained together with the homopolymer of (*R*)-DMO[4] (Scheme Ia). This was demonstrated by fractionating the polymer by solvent extraction and measuring optical rotation ($[\alpha]^{25}{}_D$) and IR absorption (D_{763}/D_{732}) of the fractions. It resulted that the more soluble polymer fractions consisted, as expected, of copolymer of *S* monomers, whereas the last fraction was based on poly[(*R*)-DMO] (Table I). The same approach has now been extended to a high-activity Ziegler–Natta catalyst,[5] schematically indicated as $MgCl_2/EtB/PC/AlEt_3/TiCl_4$, where the internal base EtB is ethyl benzoate and PC is *p*-cresol. Experimental conditions are briefly indicated in footnote *a* of Table I.

Scheme I[a]

(a) Simultaneous Addition
$S' + S + R \rightarrow -SSS'SSSS'SSSS'SSSSS'- +$
$-RRRRRRRRRRRRRRRR-$
(b) Two-Step Addition
Step 1
$S' \rightarrow -S'S'S'S'S'S'S'S'-$
Step 2
$-S'S'S'S'S'S'S'S'- + S' + S + R \rightarrow$
$-S'S'S'S'S'S'S'S'SSS'SSSS'SSSSSS- +$
$-RRRRRRRRRRRRRRRR- + -SS'SSS'SSSS'-$

[a] S' = (*S*)-3-methyl-1-pentene, R = (*R*)-3,7-dimethyl-1-octene, and S = (*S*)-3,7-dimethyl-1-octene.

The copolymerization of racemic DMO with (*S*)-3MP in 3.8/1 molar ratio, slightly higher than that used with the conventional catalyst, in the presence of the above high-activity system activated by $Al(i\text{-}Bu)_3$ and *p*-methyl toluate (MT) as external base gave results very similar to the previous ones.[4] This indicates that the chiral recognition of active centers capable of polymerizing these sterically hindered branched olefins remains substantially the same even in the presence of the support ($MgCl_2$) and of the Lewis base.

The practically identical behavior of the two systems is confirmed by the fact that the recovered nonpolymerized DMO was optically active in both cases with the same prevalence of the *R* antipode, indicating that the DMO enantiomer having the same absolute configuration as the optically active comonomer is polymerized at a slightly higher rate[6] (Table II).

A second copolymerization experiment was then performed in two steps, starting with pure (*S*)-3MP and adding, after formation of some homochains, racemic DMO in an amount double of the initial (*S*)-3MP to compensate for the partial homopolymerization of the latter and realize, during the second step, a DMO/3MP ratio similar to that of the previous experiment. Solvent extraction gave, however, very different results. These results cannot be entirely accounted for by the possible higher amount of (*S*)-3MP present during the second step. Indeed, no fraction with negative optical rotation was isolated, indicating either that the stereoselectivity of the centers has been substantially modified by the preliminary interactions with pure (*S*)-3MP or that the extraction is now less efficient due to the presence of less soluble (less random) (*S*)-DMO/(*S*)-3MP copolymer. Taking into account the tendency of the catalyst to give a rather narrow molecular weight distribution,[7] we can explain this result also by assuming that when DMO is added, some (*S*)-3MP chains are still living. Indeed, this would finally lead to the formation on the *S* monomer polymerizing sites of a (*S*)-3MP/(*S*)-DMO copolymer consisting of a long block

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Table I
Physical Properties of Fractions Obtained by Extracting with Boiling Solvents the Polymeric Products Obtained by Copolymerizing (*RS*)-3,7-Dimethyl-1-octene [(*RS*)-DMO] with (*S*)-3-Methyl-1-pentene [(*S*)-3MP][a]

	simultaneous addition of (*RS*)-DMO and (*S*)-3MP (3.8/1 molar ratio)			addition of (*RS*)-DMO to polymerizing (*S*)-3MP (2/1 molar ratio)		
fraction[b]	wt %	$[\alpha]^{25}{}_{D}$,[c] deg	D_{763}/D_{732}[d]	wt %	$[\alpha]^{25}{}_{D}$,[c] deg	D_{763}/D_{732}[d]
1	6.3	+6.0	n.d.	4.8	+12.0	n.d.
2	10.8	+41.3	0.50	8.3	+61.4	0.64
3	51.8	+64.5	0.60	60.4	+71.6	0.62
4	31.0	−20.4	0.32	26.5	+25.7	0.58

[a] Molar ratios α-olefins/Ti, Al(*i*-Bu)$_3$/Ti, and Al(*i*-Bu)$_3$/external base are 3600, 167, and 3, respectively; reaction temperature = 50 °C; solvent = *n*-heptane. [b] Extracted successively with acetone (1), ethyl acetate (2), diethyl ether (3), and cyclohexane (4). [c] In cyclohexane solution; l = 1 dm. [d] D_{763} and D_{732} are the optical densities of the IR bands related to poly(3MP) and poly(DMO), respectively; D_{763}/D_{732} is 13 for poly(3MP) and 0.11 for poly(DMO) (see ref 4).

Table II
Relative Polymerization Rate of the Two Antipodes of (*RS*)-3,7-Dimethyl-1-octene [(*RS*)-DMO] in the Presence of (*S*)-3-Methyl-1-pentene [(*S*)-3MP]

run	(*RS*)-DMO/ (*S*)-3MP[a]	conv, %	nonpolymerized DMO enan purity	nonpolymerized DMO abs conf	k_S/k_R[b]
1 step	3.8	4.6	0.14	*R*	1.06
2 steps	2.0	9.1	1.20	*R*	1.27

[a] Overall (*RS*)-DMO/(*S*)-3MP molar ratio. [b] Relative polymerization rate of the two antipodes, calculated as $(100 + P_p)/(100 - P_p)$, where P_p is the enantiomeric purity of the polymerized DMO (see ref 4).

of (*S*)-3MP units [formed before addition of (*RS*)-DMO] attached to a block of random (*S*)-3MP/(*S*)-DMO copolymer (Scheme Ib). This block copolymer is expected to be less soluble than the analogous random copolymer obtained in the one-step experiment and thus could be not easily separated from the homopolymer of (*R*)-DMO. According to this hypothesis no substantial residue was found after cyclohexane extraction, indicating almost no formation of (*S*)-3MP homopolymer, which is more than 90% insoluble in this solvent.[8] Lack of (*S*)-3MP homopolymer suggests that most chains were living when (*RS*)-DMO was added. Furthermore, the optical rotation of the last fraction, as well as the content of (*S*)-3MP units, is lower than for the previous fractions as expected in the case of a substantially stereoselective process.

It must also be noted that in this latter experiment the recovered nonpolymerized DMO is optically active according again to a preferential polymerization of the *S* enantiomer, with an increase of the k_S/k_R ratio from 1.06 to 1.27 (Table II). Such higher stereoelectivity, which corresponds to an enantiomeric purity 6 times higher, cannot be simply explained by taking into account the larger (*S*)-3MP content (less than 2 times) and the use of (−)-menthyl benzoate [(−)-MtB] as external base. Indeed, (−)-MtB, employed because its high chemical purity allowed us to obtain a good activity with the sterically hindered olefins of the present investigation, is known to give an extremely low stereoelectivity.[9] It is likely that the chiral discrimination of the active sites is affected by the two-step addition either because centers with living (*S*)-3MP homopolymer are more stereoelective or because all *R* and *S* sites are affected by solvation by the optically active olefins.[10]

These preliminary results confirm nicely and simply the stereoselective character of the new generation high-activity Ziegler–Natta catalysts and indicate that the use of chiral monomers, one racemic and the other optically active, constitutes an informative approach for testing the capability of high-activity Ziegler–Natta catalysts to give block or stereoblock copolymers as well as of the monomer to affect the stereochemistry of active sites.

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Registry No. (±)-DMO, 13827-59-3; (*S*)-3MP, 5026-95-9; EtB, 93-89-0; PC, 106-44-5; MT, 99-75-2; ((*S*)-3MP((±)-DMO) (block copolymer), 105931-32-6; MgCl$_2$, 7786-30-3; AlEt$_0$, 97-93-8; TiCl$_4$, 7550-45-0.

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Time-Dependent Ginzburg–Landau Approach for Microphase-Separation Kinetics of Block Polymers

In this communication we present an approach to the interpretation of the qualitative basic phenomena underlying the time evolution of the order parameter of block polymers and mixtures of block polymers with themselves or homopolymers in the process of microphase separation, i.e., the phase transition from the disordered state to the

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