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Isotactic Polymerization of Propene: Initiation at Titanium–Phenyl Bonds

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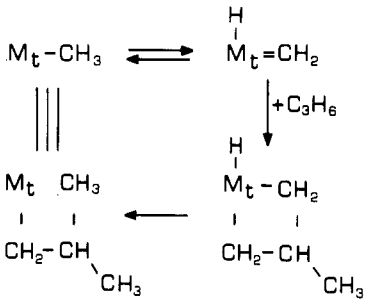
ABSTRACT: The structure of the end groups coming from initiation in the presence of active sites carrying phenyl substituents has been elucidated. Insertion of propene into the phenyl bonds of the isotactic-specific sites appears to be enantioselective.

Heterogeneous Ziegler–Natta catalytic systems for isotactic-specific polymerization of α-olefins are usually prepared by contacting a transition-metal halide and an organometallic compound, e.g., AlR_3, ZnR_2, BeR_2 (where R is an alkyl, aryl, or aralkyl group). According to the literature the isotactic-specific active sites are surface transition-metal atoms carrying one active R group and several halide ligands, i.e., X_nTi–R. Isotactic polymerization involves sequential enantioselective insertions, e.g., of propene into the active Mt–R bonds of the active sites. In fact the isotactic-specific sites are chiral and, depending on the configuration, preferentially attack either one or the other enantioface of prochiral α-olefins. The enantioselectivity of propene insertion has been determined on active sites of different composition (Mt = Ti, X = Cl or I, R = CH_3 or C_2H_5 or i-C_4H_9 or growing polymer chain).[1-3] In particular for X = Cl it has been observed that the enantioselectivity of the insertion of propene into Ti–CH_3 bonds is negligible if it exists.[2,3] The enantioselectivity of the insertion into Ti–CH_2–CH_3 is appreciable and becomes very high for Ti–i-C_4H_9 and Ti–growing chain bonds.[2,3]

These findings, particularly the lack of enantioselectivity of the insertion into Ti–CH_3 bonds, have been rationalized by Corradini and co-workers[4-6] by means of a model of chiral active sites. According to these authors the stereochemical control of the insertion comes from the nonbonded interactions between the methyl of the incoming propene and the carbon of R ligands in the β position with respect to the transition metal. The isospecificity of the reaction should be mainly due to the fixed chiral orientation of the first C–C bond of the growing polymer chain. Therefore, the presence of a bulkier R group bearing two carbons instead of one carbon in the β position could in principle produce a decrease or even a change of the nature of the steric control in the insertion of the first monomer unit.

Scheme I



The lack of enantioselectivity for the insertion of the monomer into Ti–CH_3 bonds could be as well rationalized considering the possibility that the insertion might occur via a mechanism involving reversible migration of H from the α carbon to the transition metal, and carbene metallacyclobutane intermediates as proposed by Ivin[7] and by Casey.[8] (See Scheme I.)

The use of active sites carrying aryl groups could verify (i) the influence of the presence of two β carbons on the steric control of the first monomer insertion and (ii) the likelihood that propene insertion into the metal–aryl bonds

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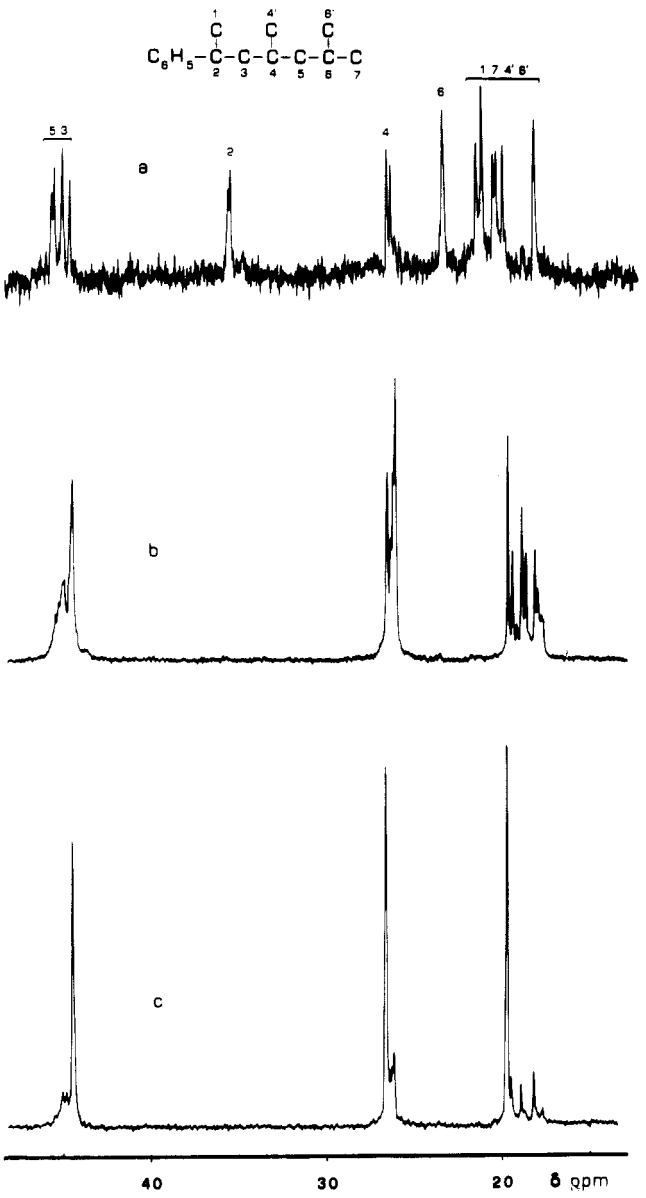

Figure 1. Aliphatic region of ^{13}C NMR spectra of (a) 2-phenyl-4,6-dimethylheptane (mixture of diastereomers), (b) ether-soluble polymer fraction, (c) hexane-insoluble–heptane-soluble polymer fraction. Chemical shifts are in ppm downfield from HMDS.

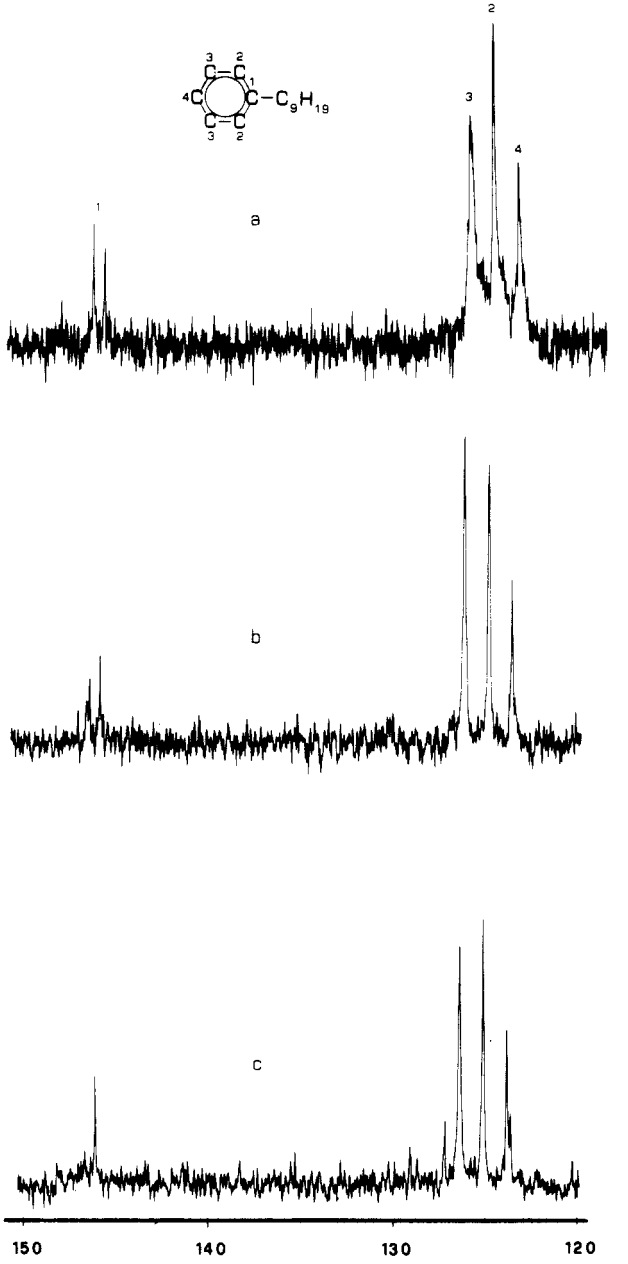

Figure 2. Aromatic region of ^{13}C NMR spectra of (a) 2-phenyl-4,6-dimethylheptane (mixture of diastereomers), (b) ether-soluble polymer fraction, (c) hexane-insoluble–heptane-soluble polymer fraction. Chemical shifts are in ppm downfield from HMDS.

might involve carbene and metallacyclobutane intermediates.

Therefore, we have prepared a sample of polypropylene in the presence of a catalytic system consisting of δ-$TiCl_3$ and $Zn(C_6H_5)_2$. $Zn(C_6H_5)_2$ was used instead of $Al(C_6H_5)_3$ as organometallic cocatalyst in order to increase the chain-transfer processes.[9] The polymer was subjected to sequential exhaustive extraction with boiling solvents (diethyl ether, heptane) and the resulting fractions have been analyzed by ^{13}C NMR. The aliphatic carbon region of the spectra (Figure 1) shows nothing but the usual trend of increasing amount of mm stereochemical triads when going from the ether-soluble fraction (18%) to the hexane-insoluble–heptane-soluble (8%) to the heptane-insoluble one. Three weak resonances of relative intensity 2:2:1 are observed at 126.2_3, 124.8_8, and 123.6_5 ppm downfield from HMDS in Figure 2. Two more resonances of even lower intensity are observed at 145.6 and 146.2 ppm in the spectrum of the ether-soluble fraction (Figure 2b). These resonances can be easily assigned to the quaternary carbon (145.6 and 146.2 ppm) and to the para (123.6_5 ppm), ortho (124.8_8 ppm), and meta (126.2_3 ppm) carbons of the phenyl groups coming from the initiation of the polymerization involving Mt–phenyl bonds. In fact, very close chemical shifts and similar relative intensity are observed for the resonances of the aromatic carbons of a suitable model compound, 2-phenyl-4,6-dimethylheptane (Figure 2a). The resonances of the quaternary aromatic carbons are split both in the spectrum of the end groups and in that of 2-phenyl-4,6-dimethylheptane. As a matter of fact, the 2-phenyl-4,6-dimethylheptane that we have employed is a mixture of diastereoisomers *RR,SS* and *RS,SR* 40% and 60%, respectively. The splitting arises both in the model compounds as well as in the end groups of the ether-soluble fraction of the polymer from the stereochemical effect on the chemical shift of the configuration of the substituted carbon close to that carrying the phenyl group (Figure 3). In the aromatic region of the spectrum of the heptane-soluble fraction (Figure 2c) only one reso-

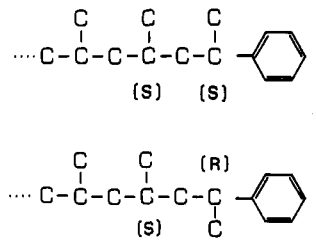

Figure 3. Fischer projection of polymer phenyl end groups deriving respectively from isotactic and syndiotactic insertion of the first monomer unit into the Ti–phenyl bond.

nance at 145.6 ppm is clearly observed for the quaternary carbon. This resonance almost coincides with that of the quaternary carbon of the *RR,SS* diastereoisomer of 2-phenyl-4,6-dimethylheptane.

By considering the structure of (*RR,SS*)-2-phenyl-4,6-dimethylheptane one can easily conclude that the insertion of propene into the titanium–phenyl bonds of the isotactic sites is about as enantioselective as the insertion into metal–isobutyl bonds. As a matter of fact, the arrangement of the two first propylene units subsequently inserted into the considered site is isotactic. No resonance has been detected for the quaternary carbons in the aromatic region of the heptane-insoluble fraction. This fact is easily understood when one considers that the molecular weight of the heptane-insoluble fractions of polypropylene obtained with $TiCl_3$-based catalysts is much higher than that of the heptane- or ether-soluble fractions and that, consequently, the number of end groups is much lower.

In conclusion, the results reported in this paper show that the insertion of the first monomer unit into the Ti–phenyl bond of isotactic catalytic sites is highly enantioselective and that the presence of two carbons in the β position with respect to titanium does not disturb the steric control exerted when there is only one carbon in the β position.

Finally, the very presence of phenyl end groups, detected by ^{13}C NMR and previously by IR analysis,[10] speaks against the mechanism proposed by Ivin[7] and Casey[8] for insertion of propene and supports a simple mechanism of monomer insertion into a metal–carbon bond.

Experimental Section

δ-$TiCl_3$ (HRA Stauffer) was purified by extraction with boiling toluene in a Kumagawa extractor.

Diphenylzinc was prepared by reaction of phenyllithium and sublimed zinc bromide in ether according to the literature.[11]

Polymerization was carried out in an autoclave at 75 °C $p(C_3H_6)$ = 3 atm with the catalytic system δ-$TiCl_3$ (37 mmol)–$Zn(C_6H_5)_2$ (37 mmol) suspended in dry toluene (250 mL). The polymerization was stopped after 48 h: polymer yield, 14.5 g; ethyl ether soluble fraction, 18%; hexane-soluble fraction, 6%; heptane-soluble fraction, 8%; octane-soluble fraction, 32%; boiling-octane-insoluble fraction, 36%.

2-Phenyl-4,6-dimethylheptane has been prepared by reaction at −78 °C in diethyl ether of acetophenone and ((*S*)-2,4-dimethylpentyl)lithium.[12] The resulting (2*RS*,4*S*)-2-phenyl-4,6-dimethyl-2-heptanol was reduced according to the literature[13] and the final product was recovered by GLC (10% yield) and identified from the mass spectrum (Figure 4a).

In order to identify the *RR,SS* and *SR,RS* diastereoisomers of 2-phenyl-4,6-dimethylheptane the mixture was ozonized and the resulting carboxylic acids were esterified. The mass spectrum of the methyl esters is shown in Figure 4b. The identification of the diastereoisomers was performed by comparing their retention times with those of the methyl esters of the pure (*RR,SS*)- and (*RS,SR*)-4,6-dimethylheptanoic acid.[14] Of course, it has been assumed that ozonization did not affect the configuration of the aliphatic substituted carbons.

The assignment of the ^{13}C resonances of 2-phenyl-4,6-dimethylheptane shown in Figures 1 and 2 has been achieved on

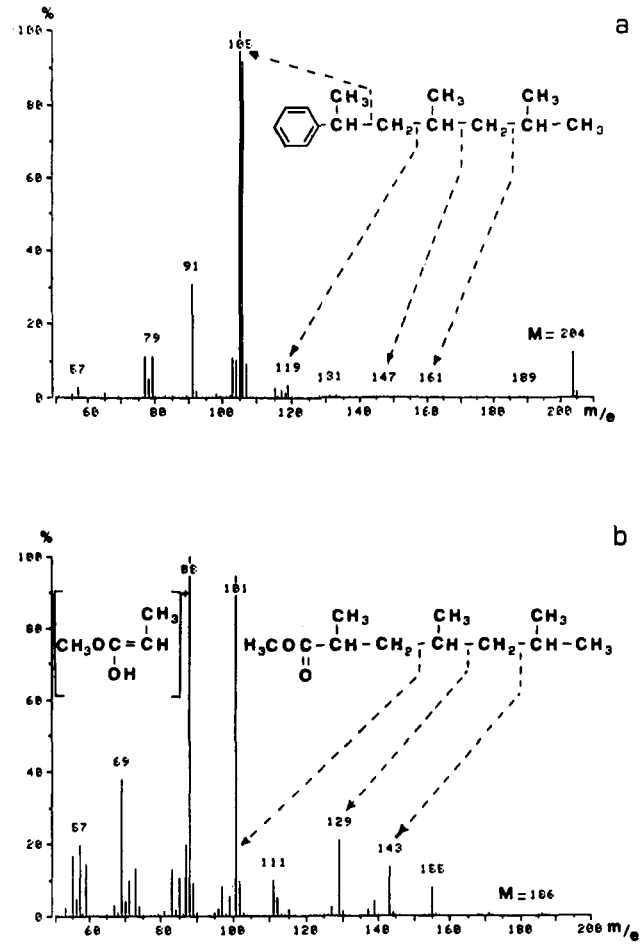

Figure 4. Mass spectra of (a) 2-phenyl-4,6-trimethylheptane and (b) methyl ester of 2,4,6-trimethylheptanoic acid.

the basis of the additivity rules of Lindeman and Adams[15] and by considering the reported ^{13}C chemical shifts of aromatic carbons of monosubstituted benzenes.[16] The identification of the quaternary carbons of the *RR,SS* and *RS,SR* diastereomers of the model compound has been performed by comparing the relative intensities of the resonances detected with the relative amount of the two diastereomers evaluated by GLC.

^{13}C NMR analysis of the polymer and of the model compounds, dissolved in dideuteriotetrachloroethane containing 1% HMDS as an internal standard, was carried out at 110 °C in the PFT mode on a Bruker HX-90 spectrometer operating at 22.63 MHz.

Combined GC/MS analysis of the model compounds was carried out on a Hewlett-Packard 5985 GC-MS system equipped with a SE 54 capillary column: GC temperature from 60 to 180 °C, 4 °C/min.

2-Phenyl-4,6-dimethylheptane was recovered by GLC on an F. and N. Model 770 gas chromatograph equipped with a 2-m 20% SE 52 Chromosorb A supported column: GLC temperature from 100 to 240 °C, 3.8 °C/min.

Acknowledgment. We thank Dr. D. Botta for the purification by GLC of the model compounds and for her helpful advice. Thanks are due to Mr. A. Rossini for technical assistance in performing the GC–MS spectra. Financial support of the Programma Finalizzato di Chimica Fine e Secondaria of the Italian CNR is gratefully acknowledged.

Registry No. $TiCl_3$, 7705-07-9; $Zn(C_6H_5)_2$, 1078-58-6; propylene, 115-07-1; 2-phenyl-4,6-dimethylheptane, 15901-45-8; ((*S*)-2,4-dimethylpentyl)lithium, 95070-29-4; acetophenone, 98-86-2; 2-phenyl-4,6-dimethyl-2-heptanol, 95070-30-7.

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Polydepsipeptides. 11. Conformational Analysis of Polydepsipeptides Containing Methyl, Isopropyl, and Isobutyl Side Chains

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ABSTRACT: The comparative study of the thermal denaturation of polydepsipeptides containing alanine, valine, or leucine residues permits the determination of the relative stability imparted to ordered, helical structures of these different alkyl groups. Thermal melting of four sequence-specific polymers in organic solvents at low temperature was observed by means of circular dichroism. Poly[L-Ala-(*S*)-Lac] and poly[L-Val-(*S*)-Lac] were both observed to undergo order–disorder transitions, while poly[L-Ala-(*S*)-hydroxyisovaleric acid] remained disordered in all solvents studied. The effect of the isopropyl side chain is, therefore, sequence dependent and valine imparts greater or lesser stability than alanine, depending on the specific polymer. The polydepsipeptide poly[L-Leu-L-Leu-(*S*)-Lac] also undergoes an incomplete helix-to-coil transition in trifluoroethanol, while poly[L-Ala-L-Ala-(*S*)-Lac] does not. Thus, leucine imparts greater stability to these polymers than alanine in organic solvents.

Introduction

Previous studies of polydepsipeptides containing alanine and lactic acid have indicated that these polymers can be used to measure the effect of sequence, chirality, and number of hydrogen bonds on polypeptide helical structure and stability.[2-4] Polymers have been prepared which contain L-alanine and (*S*)-lactic acid in ratios of either two amino acids to one hydroxy acid or with equal numbers of amino and hydroxy acids. Polydepsipeptides of this type offer several advantages as compared to randomly polymerized polypeptides in the study of helical structure and stability since they are soluble in a wide range of organic solvents, undergo conformational transitions in single solvents, and are of known sequence.

We have also recently reported the helix-to-coil transitions of polydepsipeptides containing protected polar side chains such as γ-methylglutamic acid in polymers such as poly[$(Glu\text{-}OMe)_2$-(*S*)-Lac].[5] These materials were found to exhibit essentially the same stability to thermal denaturation in tetrahydrofuran as poly[L-alanyl-L-alanyl-(*S*)-lactic acid] {poly[$(Ala)_2$-Lac]}. In trifluoroethanol, however, polydepsipeptides which contain the protected polar side chains are significantly more stable than polymers containing alanine and lactic acid.

Such functional group dependence of helical structure and stability on amino acid type remains an important question in polypeptide chemistry. The characteristics of the bulk of the side chain, whether it is hydrophobic, hydrophilic, ionic, or neutral, have all been invoked in explaining observed conformational tendencies in natural and synthetic polypeptides. Introduction of different side chains into depsipeptides may allow the separation of the effects of hydrogen-bonding and side-chain contributions. Changing the bulk of alkyl side chains in polydepsipeptides probes a different set of factors contributing to helical stability than does introduction of polar side chains. This comparison may be carried out by preparing polymers in which alanine has been replaced by valine (methyl to isopropyl) or leucine (methyl to isobutyl). Poly(valine) itself has proven difficult to study in the past because of its insolubility and tendency to aggregate. Random copolymers of methionine and valine also show aggregation.[6] At low mole fractions of valine the methionine α helix is partially disrupted. Aggregation is a problem in block copolymers of valine and D,L-lysine.[7] The block copolymers poly(Val,Lys) and poly(Lys,Val,Lys) were observed by Scheraga and co-workers to assume self-aggregating β structures in water but to be partially helical in methanol. Qualitative studies in aqueous solutions were carried out for random copolymers of valine and (hydroxypropyl)-glutamine.[8] This work indicated that valine residues in a random copolymer do not support helix formation at room temperature but support partial helicity at elevated temperatures. Valine is therefore regarded as a helix breaker. The conformational tendencies of this amino acid residue are also of interest because of its occurrence in ionophore antibiotics,[9] in which the hydrophobic side chains may participate in the ion transport properties of these compounds.[10]

Polydepsipeptides containing leucine further increase the size of the alkyl side chain by adding an additional methylene to form the isobutyl moiety. There is some question, however, as to how this affects the structure of the alanine α-helix or the relative stabilities of helices formed by alanine and leucine. In aqueous solutions it has been observed that leucine imparts greater helical stability than alanine.[11,12] This arises primarily from the entropic contributions of the hydrophobic side chain since the

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