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Syndiotactic−Atactic Stereoblock Polystyrene Obtained with a Hapto-Flexible Catalyst

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ABSTRACT: Half-titanocene $(CpCH_2CH_2OCH_3)TiCl_3$ (**1**), (Cp = cyclopentadienyl), activated by methylaluminoxane (MAO), has been tested in the polymerization of styrene in a suitable range of temperatures, obtaining a new material consisting of syndiotactic−atactic stereoblocks of polystyrene. The monoanionic bidentate ancillary ligand of the titanium based catalyst, consisting of a cyclopentadienyl bearing an alkyl ether, is a hapto-flexible ligand because the ether group can either be coordinated or not to the metal, depending on reaction temperature. Thus, the ether group can give rise to two possible catalytic sites: (i) syndiospecific, when the ether group is not coordinated to the metal center, and (ii) aspecific, when it is coordinated to titanium. Consequently, it produces polymer chains having syndiotactic and atactic stereoblocks. In fact, in the range of temperature considered (0−19 °C), syndiotactic polystyrene was produced at 19 °C, atactic polystyrene at 0 and 5 °C, and syndiotactic−atactic stereoblock polystyrene at 10 and 15 °C.
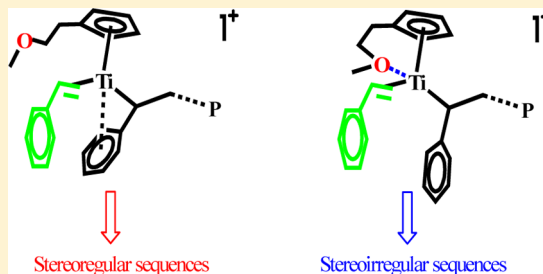
INTRODUCTION

Syndiotactic polystyrene is a highly stereoregular polymer having excellent chemical and physical properties. In fact, it is a semicrystalline polymer, with high glass transition temperature ($T_g \approx 100$ °C) and high melting temperature ($T_m \approx 270$ °C). It is highly resistant to heat and to chemicals such as strong oxidants, acids and bases, has a low dielectric constant that makes it a good electrical insulator, and possesses a high modulus of elasticity, low density, good dimensional stability, low gas permeability and low moisture absorption.[1,2]

Its characteristics have made it of interest industrially as an engineering plastic and have stimulated considerable research into its mechanism of polymerization, in the development of new catalysts and in assessing possible new applications.

After its discovery by Ishihara in 1986,[3] the polymerization mechanism was analyzed both by elegant experimentation[4−6] and by means of computational modeling.[7]

A variety of homogeneous catalysts based on group 4 metal (Ti, Zr)[6] compounds and methylaluminoxane (MAO) are active in the syndiospecific polymerization of styrene. Among the most studied catalytic systems is certainly the one based on CpTiCl_3.

With this catalyst the main features of the reaction mechanism of the syndiotactic specific polymerization of styrene are:

(i) The reaction is a polyinsertion into the metal−carbon bond.[4a,c,5b,c]

(ii) The addition to the double bond is *cis*.[4b]

(iii) The insertion of the monomer takes place by secondary regiochemistry, being the growing chain is bonded to the metal atom of the catalytic complex through a methine carbon.[4a,c,5b]

(iv) The statistical model of the stereospecific insertion is first-order Markovian.[8]

(v) The nature of the active species is Ti(III).[4a,5]

(vi) The stereoselectivity of the insertion step is controlled by the chirality of the growing chain end.[8]

In particular, the syndiotactic specific polymerization mechanism of styrene was reported as the outcome of the following events:[8,9]

(i) η^2-coordination of a monomeric unit to the metal bearing the ancillary ligand (cyclopentadienyl) and the growing chain. The latter is bonded to the metal by a methine carbon and by coordination of the aromatic ring of the last enchained unit.

(ii) Nucleophilic substitution of the coordinated phenyl.

(iii) Insertion of incoming monomer.

Thus, the formation of a syndiotactic diad deriving from a chain-end stereocontrol always requires an η^n interaction ($n \geq 2$) of the aromatic group of the last enchained unit with the metal. In this framework, the insertion of the incoming monomer and the subsequent nucleophilic substitution of arene coordinate, producing an inversion in the absolute configuration of the metal atom; therefore, the coordination of a new monomeric unit will take place on the opposite face with respect to the last inserted unit (see Scheme 1).[8,9] Occasional inversions of configuration to the metal atom can derive from lacking coordinated aromatic ring of the last inserted monomer unit in the growing- chain.[8,9]

Hence, aryl coordination to the catalytic center is essential for the syndiospecific propagation. In fact, substituted styrenes

Scheme 1. Diastereoselective Coordination of Incoming Monomer, Followed by Insertion into the Chain, Subsequent Nucleophilic Substitution of the Previously Coordinated Phenyl and Consequent Inversion of the Absolute Configuration of the Metal
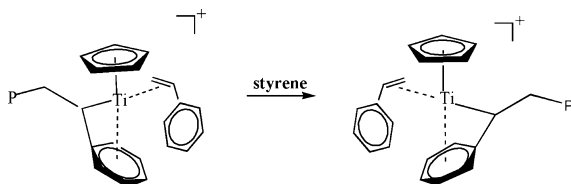
with withdrawing groups on the phenyl that make it less nucleophilic produce polymers with lower stereoregularity.[8c,9]

From the above it can be deduced that in the presence of an ancillary ligand having a suitable group (e.g.: a heterogroup) capable of competing with the aryl in coordinating to titanium, it would be possible to obtain a polymer with different stereoregularity, i.e.: (i) when the phenyl is able to coordinate better than heterogroup a syndiotactic polymer should be obtained, (ii) when the heterogroup has greater coordinating capacity than the aryl, an atactic polymer would be produced, and (iii) in a situation where, with hapto-flexibilty of the heterogroup, a stereoblock polystyrene could be achieved.

The hypothesis that the presence of a hapto-flexible ligand at the catalytic center can significantly influence the stereo-chemistry of polymerization was previously suggested for analogous complexes having a benzyl group as a substituent of the cyclopentadiene ring.[10] This catalyst was able to drive the polymerization of propylene- and styrene-producing polymers whose microstructures were strongly influenced by the possible co-ordination of the nucleophilic aryl substituent of cyclo-pentadiene to the metal center.[10] Moreover, stereoblock polypropylenes have been obtained by performing the polymer-ization of propene at different temperatures in the presence of [1-methyl-1-naphthylethyl-2-inden-1-yl]-zirconium(IV) trichloride and methylaluminoxane.[11]

In a previous paper, some of us reported on the poly-merization of styrene in the presence of 1-(cyclopentadienyl)-ethenyl-2-methoxytitanium trichloride (**1**) and MAO.[9] At reaction temperatures ≥25 °C, this catalytic system produced highly syndiotactic polystyrene ($[r] > 99\%$), whereas at −20 °C it was practically inactive. Probably at high temperature the catalytic species can be reduced to Ti(III), alkylated and cationized by MAO, and the CpCH$_2$CH$_2$OCH$_3$ acts as a monodentate ligand through the cyclopentadienyl ring, being the methoxyl group does not coordinate to the titanium, therefore, the behavior of the titanium species is very close to that of monosubstituted-cyclopentadienyl titanium−trichloride activated by MAO: namely a highly syndiospecific catalyst.[6a] Preparation of the reaction mixture at low temperature prevents the reduction of titanium and possibly its alkylation and cationization, giving rise to an inactive species.[8c,9] It is worth noting that with polymerization via the latter catalytic system using styrenes with aromatic rings possessing electron withdrawing substituents (e.g.: p-chlorostyrene (PCS)), the stereocontrol mechanism is perturbed by the competition between the oxygen of the CpCH$_2$CH$_2$OCH$_3$ ligand and the phenyl group of the last inserted unit of the growing chain. This competition hampers the expected stereochemical outcome of the polymerization reaction, making the nucleophilic substitution of the coordinate aromatic ring that controls the absolute configuration of the metal ineffective. As a consequence, the polyPCS obtained with this catalytic system is essentially stereoirregular.[9]

In this paper, we report on the polymerization results with styrene in the presence of catalytic system **1**/MAO over a narrow temperature range in order to identify conditions that could allow hapto-flexibility of the methoxyl group and so obtain a syndiotactic−atactic stereoblock polystyrene.

This polymer represents a new type of material, which would complement the characteristics of syndiotactic polystyrene. The latter, in fact, in spite of its exceptional properties, is a brittle material. So much so that often, in order to reduce its fragility, it is mixed in polymer blends with various thermoplastic polymers, including the same atactic polystyrene.

Recently a synthetic procedure able to produce a diblock-syndiotactic-atactic polystyrene was reported in the literature.[12] The process consists of two distinct stages: in the first, synthesis of syndiotactic polystyrene takes place by "pseudoliving" polymerization with Ziegler−Natta catalysts; followed, in a second step, by synthesis of atactic polystyrene by means of radical polymerization via ATRP, which is conducted on the previously synthesized chains of syndiotactic polystyrene.[12]

Instead, the stereoblock polystyrene that is the object of this work was obtained in a single step by the action of a single catalytic complex which, by virtue of the hapto-flexibility of the ancillary ligand, occurs in two forms possessing different sterespecificities between which it rapidly interconverts. The great novelty in this synthesis lies in the fact that the synthesis of each block with a different stereochemistry need not be programmed a priori and does not require other reagents in addition to the styrene, the catalyst, and the cocatalyst.

■ RESULTS AND DISCUSSION

The effect of temperature, ranging from 0 to 19 °C, on the catalytic activity of complex **1** after activation by methyl-aluminoxane (MAO) in polymerizing styrene was investigated and the results are reported in Table 1. This temperature range is rather narrow, and was chosen considering that, as reported in ref 9, this system produces highly syndiotactic polystyrene at 25 °C, while below 0 °C (i.e.: −20 °C) it is completely inactive.

Table 1. Polymerization of Styrene in the Presence of 1/MAO Catalytic System

run[a]	T (°C)	time (h)	yield (mg)	RAC[b] (%)	$[r]^c$ (%)	$M_n{}^d$	$M_w/M_n{}^d$	$T_m{}^d$ (°C)	ΔH^d (J/g)
1	19	43.3	115	53	>98	7.1×10^4	1.9	270	24.5
2	15	46.7	197	23	71	$1,0 \times 10^5$	1.3	251	9
3	10	46.4	169	12	86	$1,4 \times 10^5$	1.4	262	18
4	5	46.1	160	0	−	−	−	−	−
5	0	46.4	136	0	−	−	−	−	−

[a]Polymerization conditions: solvent = toluene; titanium complex (1) = 1.36×10^{-5} mol; MAO (based on Al) = 6.8×10^{-3} mol (based on Al); [styrene] in the feed =2.9 mol/L; total volume =20 mL. [b]Acetone insoluble fractions. [c]Percent content of syndiotactic diads in acetone insoluble fractions. [d]Data relative to acetone insoluble fraction.

In the course of the polymerizations the temperatures were held constant as reported in the experimental section.

The tests were carried out at a monomer concentration of 2.9 mol/L, much higher than the 0.83 mol/L used in the previous work. This was done to operate the catalytic system under conditions most favorable to the synthesis of a syndiotactic polystyrene because, as reported in ref 9, the stereoregularity of the polymer increases with a higher monomer concentration if the other experimental conditions are kept constant.

The polymeric samples obtained were subjected to exhaustive extraction in boiling acetone to separate the more stereoirregular from the more stereoregular fraction. In fact, atactic polystyrene is completely soluble in this solvent, unlike the syndiotactic form, which is insoluble. The percentage of insoluble fractions (RAC) is reported in the Table 1. In particular, at 19 °C the insoluble fraction represented about 50% of the total polymer, while at 0 °C, as well as at 5 °C, we found that the polymer synthesized was completely soluble. Thus, the tests conducted at 19, 15 and 10 °C, respectively, showed that in all three cases an insoluble fraction was produced, which gradually diminished going from 19 to 10 °C.

All the fractions were analyzed by ^{13}C NMR, and the spectra showed that all the soluble fractions were constituted of atactic polystyrene; otherwise, the spectra of the RAC fractions from samples 1−3 were quite different from each other. In fact, the ^{13}C NMR analysis of the RAC-fraction of sample 1 proves that it is a relatively highly syndiotactic polystyrene (see Figure 1A),[3,4]
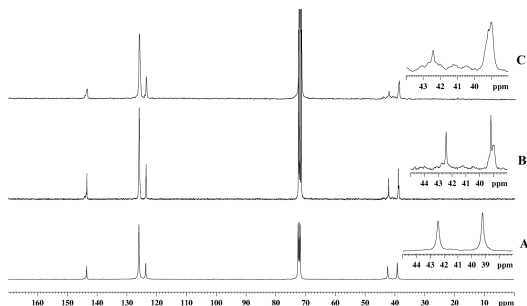

Figure 1. ^{13}C NMR spectra of acetone insoluble fractions of polystyrene samples 1 (A), 2 (B), and 3 (C). In the inset, the aliphatic region of the corresponding spectra are reported.

whereas the ^{13}C NMR spectra of the RAC-fractions from sample 2 and 3 showed a more intriguing microstructural configuration of the polymers (see Figure 1, parts B and C, respectively).

As a matter of fact, the ^{13}C NMR spectrum of the RAC-fraction of sample 1 displayed two sharp signals at 143.5 and

42.6 ppm attributable to carbon *ipso* and methylene carbon, respectively. These two resonances are characteristic of the syndiotactic microstructure of polystyrene.[3,4,13] In contrast, the RAC-fractions of samples 2 and 3 show either in the region of carbon *ipso* than in the region of methylene carbon, in addition to signals of syndiotactic sequences as well as resonances due to more stereoirregular configurations.[3,4,13] Accordingly, the concentration of syndiotactic diads ([r]) in the RAC fraction of samples 1 was higher than 99.8%, whereas those of RAC fraction of samples 2 and 3 were 86 and 71%, respectively. These values were calculated by the following equation:

$$[r] = \{[rrr] + [mrm] + [rrm]/[rrr] + [mrm] + [rrm] \\ + [mmm] + [mmr] + [rmr]\}$$

The tetrad concentrations were achieved by ^{13}C NMR analysis and the attributions were obtained according to refs 9 and 13.

This result could be justified in two different ways: (i) the **1**/MAO catalytic system, under our experimental conditions, produces a polystyrene having both syndiotactic and atactic sequences, or (ii) the two RAC-fractions are made from a blend of syndiotactic polystyrene and less stereoregular polymer.

The first hypothesis is obviously the most likely, because it is well-known that the stereoregularity of produced polymers is increased by performing polymerization at lower temperature, whereas in this case the opposite occurs.[8c]

However, in order to settle the question, the two samples were subjected to gel permeation chromatography (GPC) analysis: the traces of the chromatograms were both monomodal with moderately narrow molecular weight distributions, indicative of single-site catalysts. In Figure 2, the traces of the RAC-fractions of samples 2 and 3 are shown.

Thus, we obtained two samples of polystyrene having a syndiotactic-atactic microstructure.

This result was further confirmed by differential scanning calorimetric (DSC) analysis. In fact, the thermograms of the RAC-fractions of samples 2 and 3 show endothermic events at 251 and 262 °C, respectively, attributable to melting of the crystallites present in our products. It is worth noting that the highly syndiotactic sample obtained in run 1 (RAC-1) has a melting temperature of 270 °C, so if the two fractions RAC-2 and RAC-3 had formed from a mixture of stereoregular and stereoirregular polymer, its enthalpy of fusion would be lower but not its melting temperature, while in a polymer that also contains stereoirregular and stereoregular traits it is to be expected that the melting point is reduced. These data confirm the stereoblock structure. On the RAC-3 sample, X-ray diffraction analysis was also performed after crystallization of
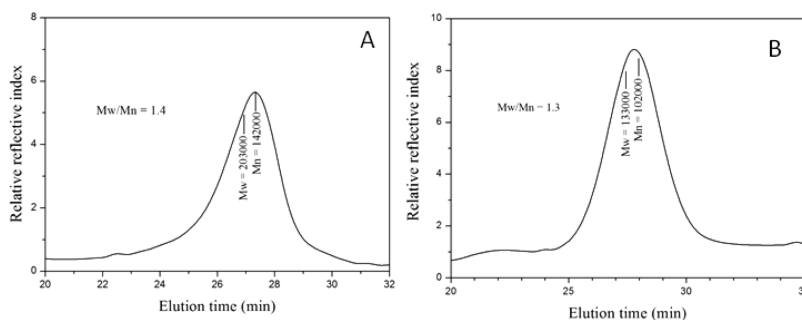

Figure 2. GPC traces of acetone insoluble fractions of samples 2 (A) and 3 (B).

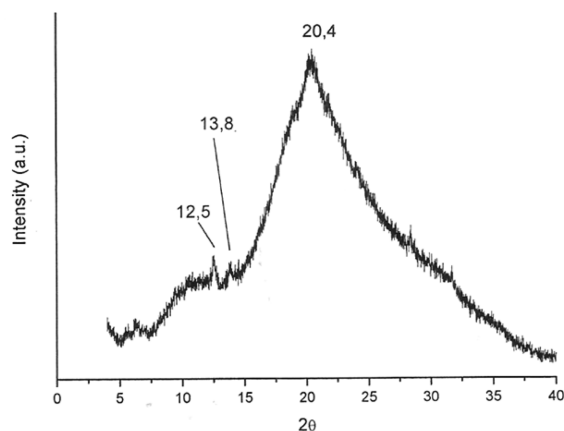the melt and, as can easily be observed from the spectrum shown in Figure 3, it turned out to have a low crystallinity.[14]

Figure 3. X-ray powder diffraction profile of acetone insoluble fraction of sample 2.

Even IRRAS spectroscopic analysis (infrared reflection absorption spectroscopy), which allows IR spectra to be obtained from samples with a very small thickness, further confirmed this conclusion. In fact, observing the IR spectra in Figure 4 of films with a thickness of about 100 nm, prepared by
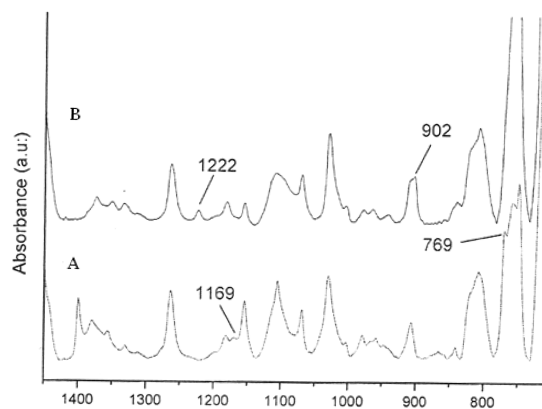

Figure 4. IRRAS spectra of the acetone insoluble fraction of sample 2 obtained by casting in CHCl₃, before (A) and after (B) annealing at 220 °C.

casting in chloroform, it is possible to note the presence of bands at 1169 and 769 cm^{-1} that are typical of the helical conformation s(2/1)2 of syndiotactic polystyrene (Figure 4a). After annealing at 220 °C, these two bands disappear while two new bands at 1222 and 902 cm^{-1}, indicative of the presence of a zigzag conformation and the shape of the α s-PS, respectively, are visible.

Thus, under our experimental conditions, compound **1**, having a monoanionic bidentate ancillary ligand, gives rise by reaction with MAO to reduction of the metal together with alkylation and cationization. The different behaviors seen in polymerization of the titanium(III) species are strictly dependent on the possible coordination of the pendant oxygen of the cyclopentadienyl-ethene-methoxy ligand; the temperature affects the possibility of the methoxy-group coordinating to titanium and this coordination can take place in a reversible manner.[15] At a high temperature (19 °C) the ligand (CpCH₂CH₂OCH₃) is coordinated only by cyclopentadienyl and its behavior should be not very dissimilar from that of the active

species deriving from (monosubstituted-cyclopentadienyl)TiCl₃. At low temperatures (0 and 5 °C) CpCH₂CH₂OCH₃ acts as a bidentate ligand through the cyclopentadienyl ring and the methoxy-group, whereas at intermediate temperatures (10 and 15 °C) the ether group can operate as a fluxional ligand (see Scheme 2).

Scheme 2. Representation of the Competition between the Phenyl of the Last Inserted Monomer Unit in the Chain and the Oxygen of the Ether Group for Coordination to the Metal, Which Involves the Formation of a Polystyrene with both Syndiotactic Styrene Sequences (a) and Atactic Styrene Sequences (b)
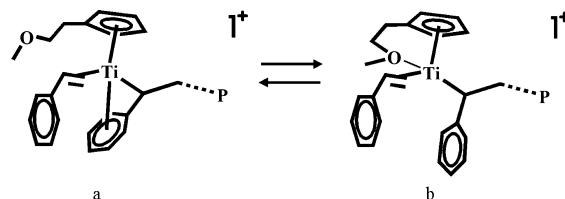
Consequently, at high temperature the catalytic species can coordinate the phenyl group of the last inserted monomer in the polymer chain, activating the stereo control mechanism. At low temperature the coordination of the ether group to the titanium species prevents the coordination of the aryl group, giving rise to a catalyst able to produce only stereoirregular polystyrene. At an intermediate temperature the oxygen of the CpCH₂CH₂OCH₃ ligand can compete with the phenyl group of the last inserted monomeric unit for coordination to titanium. When the aromatic group in the last unit of the growing chain end is coordinated, syndiotactic sequences are obtained. When, instead, the oxygen of the CpCH₂CH₂OCH₃ ligand is coordinated to titanium, atactic sequences are achieved. These possible situations are represented in Scheme 2. It is worth noting that the fluxional coordination in solution to titanium of ether-moiety of bidentate ligand C₅H₄CH₂CH₂OR, has been demonstrated by van der Zeijden and co-workers through an elegant ¹H NMR experiment.[15]

■ CONCLUSIONS

In this paper, we have reported the synthesis and characterization of a new material consisting of syndiotactic−atactic stereoblocks of polystyrene, which should complement the features and possible applications of syndiotactic polystyrene. The synthesis of this new material was performed using a titanium-based catalyst having a monoanionic bidentate ancillary ligand, consisting of a cyclopentadienyl group bearing an alkyl ether. The ether group is hapto-flexible and can give rise to two possible catalytic sites: (i) syndiospecific, when the ether group is not coordinated to the metal center and (ii) aspecific when it is coordinated to titanium. Thus, it will produce a polymer chain having both syndiotactic and atactic stereoblocks. The length of the stereoblock is strongly influenced by temperature, because it may induce the ether part of the ligand to either be coordinated or not to titanium. In the temperature range considered (0−19 °C), it was found that this group (19 °C) is not coordinated to the metal at high temperature, while at low temperature (0−5 °C) it is coordinated, and at intermediate temperatures (10−15 °C) it is hapto-flexible .

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Notes

The authors declare no competing financial interest.

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