NOTE

One-pot synthesis of isotactic-capped syndiotactic polystyrene with a bimetallic homogeneous catalytic system

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INTRODUCTION

Polystyrene can be obtained in atactic (aPS), isotactic (iPS) or syndiotactic (sPS) form by a variety of catalytic systems[1,2] and initiators. For instance, it is known that (pentamethylcyclopentadienyl)titanium derivatives activated by methylaluminoxane (MAO) afford a highly sPS, with %m (defined as *meso* diads content, calculated by ^{13}C-nuclear magnetic resonance (NMR)) below the instrumental detection levels, and T_m=271 °C, contaminated by small amounts of aPS by-product.[3] On the other hand, nickel derivatives/MAO systems afford an isotactic-rich polystyrene (%m=70–80), lacking any melting temperature;[4] also in this case aPS is formed as a by-product. On the other hand, block copolymers of styrene with diolefins or acrylates are also well known.[5,6] To our knowledge and according to the recent literature on the subject,[1] the preparation and characterization of polystyrene with blocks of different tacticities have not been reported before; the only published paper on a polystyrene copolymer containing both syndiotactic and atactic sequences is that describing the two-step synthesis of an sPS–graft–aPS, prepared by syndiospecific polymerization (catalyst: CpTiCl$_3$/MAO) of styrene with atactic vinyl-terminated styrene macromonomers obtained by anionic polymerization.[7] As dual catalytic systems have been found to be able to produce other stereoblock polymers (for example, polypropylene, polymethyl methacrylate, etc.),[8–12] we decided to test a homogeneous bimetallic nickel-titanium catalytic system in the polymerization of styrene.

Here we report the synthesis of polystyrene using the $[\eta^5$-(CH$_3$)$_5$C$_5]$TiCl$_3$/Ni(η^2-CH$_3$COCHCOCH$_3$)$_2$/MAO (Cp*TiCl$_3$/Ni(acac)$_2$/MAO) system (Figure 1), either using or not using triisobutylaluminum as an additional component.

Figure 1 Chemical structure of catalyst precursors.

EXPERIMENTAL PROCEDURE

Materials

Styrene was purified by overnight treatment with calcium hydride followed by percolation trough activated basic alumina. Toluene was refluxed and distilled in the presence of sodium/benzophenone and stored over activated molecular sieves. Nickel *bis*(acetylacetonate) and pentamethylcyclopentadienyl(titanium) trichloride were used as received. MAO (10% solution in toluene) was treated at 60 °C under vacuum for 2 h to drive off most of the free trimethylaluminum, and re-dissolved in anhydrous toluene before use. Triisobutyl aluminum (1 M solution in toluene) was used as received.

Polymerization reactions

A polymerization run is described in detail as a typical example. All operations were carried out under nitrogen atmosphere. To a Schlenk tube (Tecnovetro srl, Monza, Italy) containing 8.0 ml of styrene (70 mmol) and 10.8 ml of toluene, 2.27 ml of MAO 1.54 M in toluene (3.49 mmol) were added. Finally, 1.78 ml of Cp*TiCl$_3$ 1.04×10^{-2} M in toluene (8.75 μmol) and 3.70 ml of Ni(acac)$_2$ 1.0×10^{-2} M in toluene (17.50 μmol) were premixed and added to the reaction mixture. The tube was immersed under stirring in an oil bath at 60 °C and after 2 h the reaction was stopped with acidified ethanol. After filtration, the polymer was dried overnight at 70 °C in a vacuum oven.

Characterization

Polymer samples have been exhaustively extracted (24 h) with boiling methylethylketone (MEK) to dissolve the atactic fraction, according to the common

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Table 1 Polymerization of styrene with the Cp*TiCl₃/Ni(acac)₂/MAO/TIBA catalytic system and crude polymer properties

Entry	$T_r{}^a$ (°C)	[Sty] : [MAO] : [TIBA] : [Ni] : [Ti][b]	Yield (%)	$10^3 M_w$	M_w/M_n	MEK-insoluble fraction	T_m (°C)
C1[c]	90	10 000 : 100 : 0 : 2 : 0	90	45	6.1	0	Amorphous
C2[d]	90	28 000 : 300 : 0 : 0 : 1	68	380	3.0	0.94	270
1	60	8000 : 400 : 0 : 2 : 2	82	24	1.7	ND	272
2	60	8000 : 400 : 0 : 2 : 1	94	23	1.8	0.03	270
3	60	8000 : 400 : 40 : 2 : 1	70	64	2.4	0.86	270
4	60	8000 : 400 : 400 : 2 : 1	63	∼3	ND	0.58	247
5	90	8000 : 400 : 0 : 2 : 2	57	17	1.8	0.03	260
6	90	8000 : 400 : 0 : 2 : 1	70	16	1.8	0.11	262
7	90	8000 : 400 : 40 : 2 : 1	92	17	4.7	0.45	254
8	90	8000 : 400 : 400 : 2 : 1	62	∼3	ND	0.49	238

Abbreviations: MAO, methylaluminoxane; ND, not determined; TIBA, triisobutylaluminum; T_m, melting temperature; T_r=reaction temperature.
[a]Reaction time: 2 h.
[b]Relative molar ratios.
[c]Comparative run without Ti.
[d]Comparative run without Ni.

practice reported in the literature. Characterization has been carried out on both crude and extracted samples.

Molecular weight determinations were made using a Waters 150C chromatograph (Waters Corp., Milford, MA, USA) equipped with an RI detector on 1,2,4-trichlorobenzene solutions at 135 °C. Molecular weight calibration was performed using monodisperse aPS standards.

^{13}C-NMR spectra were run on an AM-300 Bruker instrument (Bruker Corp., Madison, WI, USA) at 110 °C. The samples were prepared by dissolving 150 mg of polymer in 2.5 ml of o-dichlorobenzene. Chemical shifts were referred to tetramethylsilane=0.00 p.p.m. The degree of stereoregularity of the polymers was evaluated from the intensities of the aromatic quaternary carbon peak according to reported methods.[13]

Differential scanning calorimetry spectra were recorded with a Perkin-Elmer DSC-Series 7 system (Perkin Elmer Inc., Waltham, MA, USA), using 5–10 mg of polymer for each run. Samples were heated (20 °C min⁻¹) up to 300 °C. For all samples the T_m values reported are those corresponding to the first heating scan, although in a more rigorous treatment (namely, measuring the T_m in the second heating scan), a slow cooling and re-melting should be applied.[13]

RESULTS AND DISCUSSION

Polymerization reactions were carried out in bulk, at different temperatures and with different reagent concentrations (Table 1). As expected, comparative runs with either Cp*TiCl₃ or Ni(acac)₂ produced syndiotactic (T_m=271 °C) and isotactic-rich (amorphous) polystyrene, respectively. When they are combined, in principle, if the catalytic centers were independent the final products would be complex mixtures of polymers having different tacticities: sPS (afforded by titanium sites); iPS (afforded by nickel sites); and aPS (afforded by MAO and other non-stereospecific sites). As hot methyl ethyl ketone (MEK) dissolves aPS and iPS (up to %m=90),[4] as well as the low-molecular-weight fraction of sPS,[14] extraction with MEK was applied to isolate the syndiotactic fraction for a better elucidation of the products structure. The results are reported in Table 2.

Surprisingly, some MEK-insoluble fractions (**6i, 5i**) are high melting, with single, narrow differential scanning calorimetry peaks, but not totally syndiotactic, as would be expected on the basis of the very high syndiospecificity of Cp*TiCl₃. Therefore, the formation of steric defects must be attributed to the presence of nickel sites in the catalytic system. As iPS has been removed from the crude products by extraction with MEK, these defects must be incorporated in the syndiotactic chains. The possibility that the polymers are mixtures of perfectly syndiotactic and highly isotactic (MEK-insoluble) polystyrenes is ruled out because no long meso sequences (tetrads or

Table 2 Properties of MEK-insoluble fractions of polystyrenes

Entry[a]	Yield[b] (%)	$10^3 M_w$	M_w/M_n	%m diads (%)	T_m (°C)	ΔH_m (J g⁻¹)
C2i	64	425	2.0	≪0.1	271	41.0
3i	60	74	2.3	0.1	272	33.3
4i	36	11	1.8	2.1	255	34.2
5i	1.7	111	1.7	2.9	269	29.3
6i	8	181	1.8	3.1	271	30.5
8i	31	6	1.4	2.8	252	39.9

Abbreviation: MEK, methyl ethyl ketone; T_m, melting temperature.
[a]The samples have the same notation as the corresponding polymers in Table 1, with the addition of a suffix 'i'.
[b]Calculated as (crude polymer yield)×(MEK-insoluble fraction).
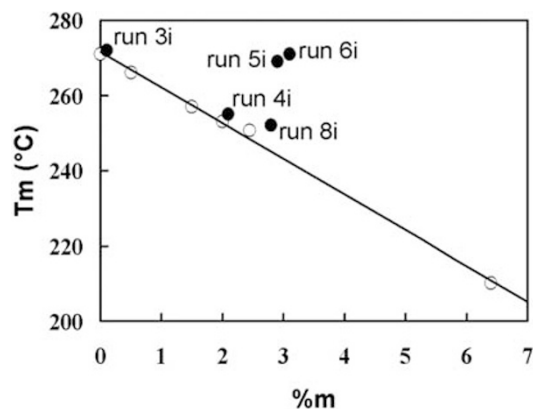
Figure 2 Melting temperature–meso diad relationship for sPS samples (○) and the MEK-insoluble fraction of PS obtained from Ti–Ni systems (●).

higher) are found in NMR spectra. Moreover, from what is known about the behavior of phenoxy-imine catalysts that produce iPS/sPS mixtures, two well-separated T_m values would be expected.[15]

To explain these findings, it is useful to consider the correlation between %m and T_m. It is known that the higher the steric defect content in sPS, the lower the crystalline lamellae thickness and the melting temperature, and these parameters have been quantitatively correlated.[13,16] Figure 2 shows the %m–T_m relationship for several high–M_w sPS samples obtained by using different catalysts (Cp*TiCl₃,
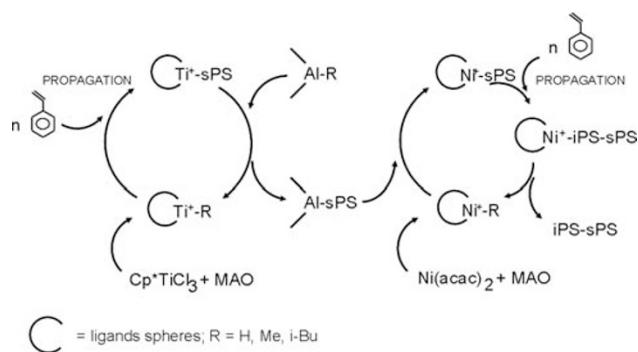
Figure 3 Proposed mechanism of formation of isotactic-capped syndiotactic polystyrene.

CpTiCl$_3$, IndTiCl$_3$, Ti(OEt)$_4$) or conditions (empty circles).[14] The lowest melting polymer (210 °C) corresponds to an sPS obtained with a zirconium catalyst.[17] It must be remarked that the %m–T_m relationship is linear: this behavior is a consequence of the random distribution of the steric defects.

By placing **5i** and **6i** in the %m–T_m correlation plot, it is evident that the points are well above the line representing the polymers having randomly distributed steric defects. This implies that the steric defects are not randomly located along the whole chain, but are cumulated, that is, the polymer structure is stereoblock. The possibility that a multiblock structure, deriving from a 'chain-shuttling' mechanism,[18] is formed is believed to be very unlikely. Indeed, the ^{13}C-NMR spectra show the presence of a peak at about 137 p.p.m., diagnostic of vinylene –CH=CHPh end groups, arising from β-hydride elimination.[19] As the chain-termination mechanism for Ti/MAO/triisobutylaluminum catalytic systems is the transfer to aluminum (no unsaturated tail end groups are detectable in those cases),[14] whereas β-hydride elimination takes place easily at C–Ni centers, the NMR data strongly suggest that the isotactic block is at the chain end, thus leading to an isotactic-capped sPS (isPS). Furthermore, the lamellae formation is not disturbed and the melting temperature is not altered by a capping block, which is a further clue that the isotactic blocks are not spread along the chain in a multiblock structure. Polymer **8i** is near the correlation line. However, it is implausible that its defects are randomly distributed because Cp*TiCl$_3$ is a highly syndiospecific catalyst (see run **C2i** and the literature[1–3]). Thus, the reason for the low T_m value (252 °C) can be attributed solely to the low average molecular weight[16] (M_w=6000 Da), and the relatively high amount of defects should be ascribed again to a diblock structure in which the syndiotactic chain is capped with a short isotactic block. Similar considerations may apply to polymer **4i** (M_w=11000 Da).

In all cases, isPS is possibly accompanied by a fraction of sPS, which is MEK-insoluble and therefore difficult to quantify, causing an underestimation of the iPS block length (*vide infra*). Very likely, in sample **3i** the sPS fraction is largely prevailing, and accordingly the %m value is very low.

The proposed mechanism for isPS formation could be sketched as follows (Figure 3): a syndiotactic chain grows on titanium centers, after some time is transferred to aluminum (worth to be mentioned, transfer to aluminum is also the origin of formation of stereoblock polypropylene with a dual zirconium system),[8] and eventually to nickel centers, where other monomers are added before the chain terminates. Based on what it is known about the behavior of Ni(acac)$_2$/MAO,[4] this last segment is likely to be isotactic (%m∼70)

and much shorter than the syndiotactic block: the lengths, estimated from the here-reported experimental *meso* diads content and typical *meso* diads content values found for iPS and sPS produced by Cp* catalysts, are about 5% of the syndiotactic block.

CONCLUSION

In conclusion, the possibility to prepare a syndiotactic polystyrene capped with a short isotactic block using a binary Cp*TiCl$_3$/Ni(acac)$_2$ catalytic system activated by MAO has been shown. The formation of the stereoblock structure, in the mixture containing also syndiotactic, atactic and isotactic-rich polystyrene was evidenced by exhaustive solvent extraction, ^{13}C-NMR spectroscopy, differential scanning calorimetry and size exclusion chromatography measurements. The conditions to obtain isPS are critical in terms of catalyst component concentration and reaction temperature; high portions of atactic, isotactic-rich and syndiotactic polystyrene always accompany isPS as by-products. This finding suggests that the polymer chains do not grow independently on the two metal centers, but undergo, at least in part, an exchange process. It is believed that a careful optimization of the ligands around the transition metals might improve the activity toward the stereoblock polymer formation, as well as the length and tacticity of the isotactic block.

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