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Effect of aluminium alkyls on the synthesis of syndiotactic polystyrene with titanium complexes/methylaluminoxane catalytic systems

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Syndiotactic polystyrene (sPS) was synthesised using homogeneous catalytic systems based on titanium derivatives (tetraethyl orthotitanate, (cyclopentadienyl)titanium trichloride), methylaluminoxane (MAO) and aluminium alkyls (trimethylaluminium, triisobutylaluminium). The polymers were characterised by gel permeation chromatography (GPC) and nuclear magnetic resonance (n.m.r.) spectroscopy.

Trimethylaluminium was found to decrease both the catalytic activity and the polymer molecular weight. Triisobutylaluminium causes a reduction in activity only for low (< 600) methylaluminoxane/titanium molar ratios. While the molecular weight decrease is almost linear with the increase of the amount of aluminium in the catalytic system in the case of trimethylaluminium, a very sharp decrease of molecular weight is observed by addition of triisobutylaluminium even in moderate amounts. The results were interpreted on the basis of the different ability of the two aluminium alkyls to behave as chain transfer agents. Moreover, the reactions of termination and re-initiation of the polymer chains were examined taking into account the end-group structures, and a polymerisation mechanism to explain the experimental results was put forward. © 1997 Elsevier Science Ltd.

(Keywords: syndiotactic polystyrene; coordination polymerisation; methylaluminoxane; aluminium alkyls)

INTRODUCTION

Syndiotactic polystyrene (sPS) was originally synthesised in 1985 by using homogeneous catalysts based on titanium complexes and methylaluminoxane (MAO)[1].

MAO is generally considered as a mixture of linear, cyclic and/or 'cage' oligomers having the repeating unit $-(OAlCH_3)-$. However, its real structure has not yet been fully elucidated, and certain aspects about its role in α-olefin and styrene polymerisation are still debated[2,3].

MAO also contains trimethylaluminium (TMA) in both 'free' and 'associated' forms, and its presence is considered relevant for catalytic behaviour[4,5]. Commercial MAO generally contains about 30% TMA; Campbell *et al.*[6] found that TMA content can be lowered to less than 10% by treatment of the commercial solution at 70°C/0.1 Torr. Correspondingly, a dramatic increase of both activity and polymer molecular weight is observed by carrying out the syndiospecific polymerisation of styrene in the presence of this modified MAO. On the other hand, aluminium alkyls are added to Kaminsky–Sinn catalytic system formulations to obtain certain performances, such as the polymer molecular weight control in styrene polymerisation[7] or the partial substitution of the much more expensive MAO[8].

In view of these considerations, a better understanding of the participation of the aluminium alkyls in the several steps of the syndiospecific polymerisation of styrene would be highly desirable.

The aim of this work is to report on the effect of TMA and triisobutylaluminium (TIBA) on the activity and polymer properties in the syndiospecific polymerisation of styrene, using the $CpTiCl_3$/MAO and the $Ti(OEt)_4$/MAO catalysts.

EXPERIMENTAL

Reagents

Styrene (EniChem) was used after 10 h storage on CaH_2 followed by passage on basic alumina. Toluene (Carlo Erba) was refluxed on $LiAlH_4$ and distilled under nitrogen atmosphere. Trimethylaluminium 2 M in toluene (Aldrich) and triisobutylaluminium 1 M in toluene (Aldrich) were used as received. 10% solution of methylaluminoxane in toluene was purchased from Witco GmbH; 35% of the aluminium is present as trimethylaluminium, according to the analytical sheet. (Cyclopentadienyl)titanium trichloride (Strem) and tetraethyl orthotitanate (Fluka) were dissolved in toluene to prepare solutions of about 0.01 M.

Polymerisation runs

Polymerisations were carried out at 60°C in bulk. Styrene, MAO, the aluminium alkyl and the titanium complex were added to a Schlenk tube in nitrogen atmosphere in that order. After 2 h reaction, the mixture was cooled and added to 200 ml ethanol and 1 ml conc. HCl to deactivate the catalyst. The solid was filtered and dried at 80°C in a vacuum oven. The polymer was further extracted with methylethylketone (MEK) in a Kumagawa extractor to eliminate the atactic polymer fraction, and finally dried at 80°C in a vacuum oven.

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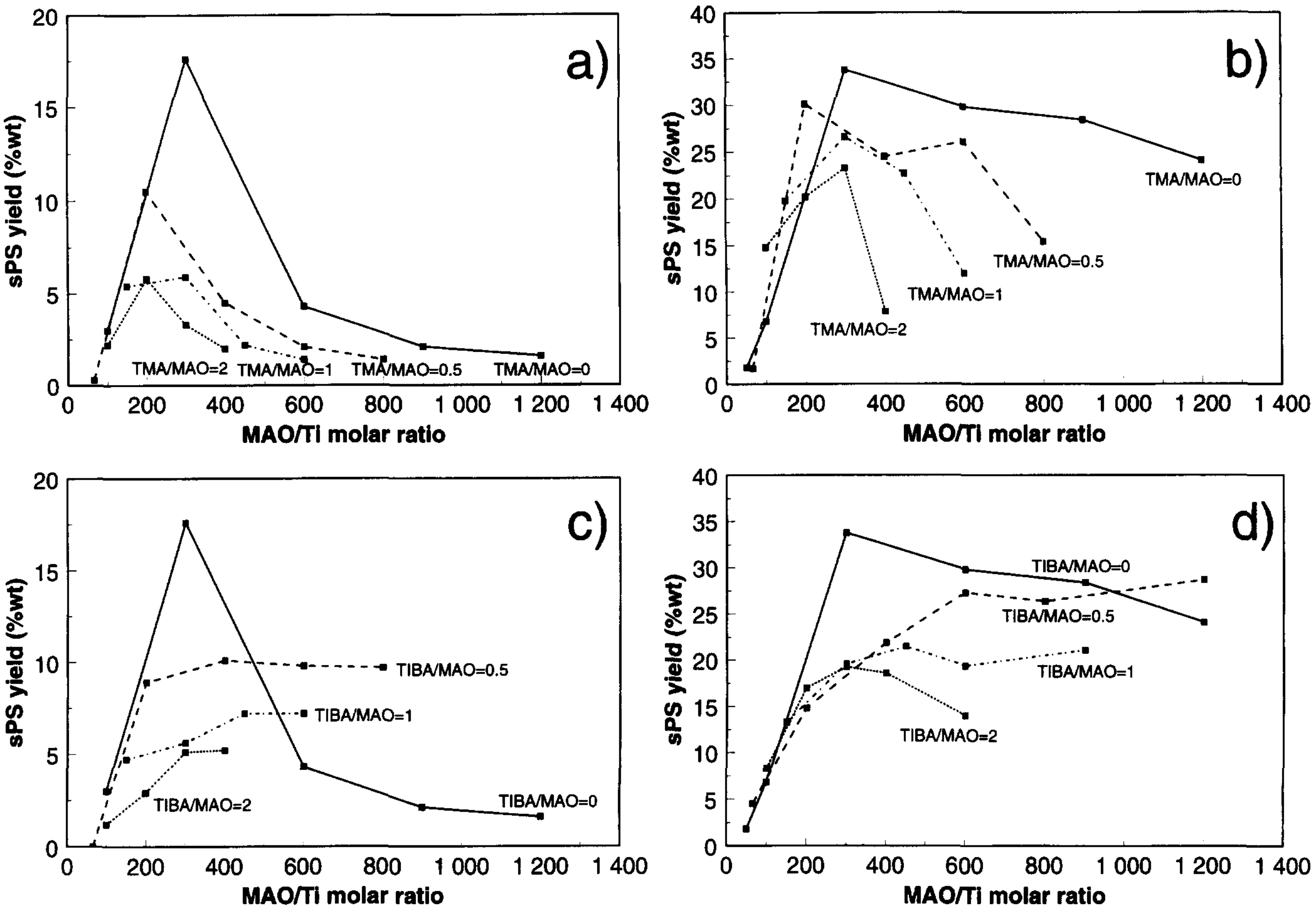

Figure 1 Yield of syndiotactic polystyrene as a function of MAO/Ti molar ratio with different catalytic systems: (a) $Ti(OEt)_4$/TMA/MAO; (b) $CpTiCl_3$/TMA/MAO; (c) $Ti(OEt)_4$/TIBA/MAO; (d) $CpTiCl_3$/TIBA/MAO

Characterisation

Molecular weight determinations were made using a Waters 150C chromatograph at 135°C in trichlorobenzene. Molecular weight calibration was performed using atactic polystyrene standards. ^{13}C n.m.r. spectra were run at 110°C on a Bruker AM 300 spectrometer operating at 75.4 MHz on ^{13}C nucleus. Samples were prepared by dissolving 200 mg of polymer in 3 ml of a mixture 1:1 of $C_2H_2Cl_4/C_2D_2Cl_4$. Chemical shifts were referred to tetramethylsilane = 0 ppm.

RESULTS AND DISCUSSION

Four different catalytic systems were tested in this study: $Ti(OEt)_4$/TMA/MAO, $CpTiCl_3$/TMA/MAO, $Ti(OEt)_4$/TIBA/MAO and $CpTiCl_3$/TIBA/MAO. Since the commercial solution of MAO received from the supplier contains about 35% of TMA, the two last catalytic systems actually comprise a certain amount of TMA along with TIBA as a aluminium alkyl component. However, in the following discussion such TMA (TMA_f) is considered an integral part of MAO concerning molar ratios definitions, because is not possible to distiguish between really 'free' and associated TMA. Nevertheless, the reader must be aware that a TMA/MAO molar ratio equal to zero does not actually mean that TMA is absent from the polymerisation mixture.

The polymerisation temperature was fixed at 60°C and the chosen monomer/titanium molar ratio was 28 000, while both the MAO/titanium and the aluminium alkyl/titanium molar ratios were varied in the 33–1200 range; the aluminium alkyl/MAO molar ratio varied from 0 to 2.

In syndiospecific styrene polymerisation, the yield of sPS and its molecular weight depend mainly on the particular catalyst used and on the polymerisation temperature[3]. The polymerisation reaction actually affords a mixture of sPS and atactic PS (aPS), formed as a by-product of ionic and radical aspecific polymerisations. Such atactic fraction is usually separated by extraction with boiling methylethylketone (MEK).

aPS obtained in this study, which usually corresponds to 4–8% of the polymerised styrene in the absence of aluminium alkyls, has a Bernoullian random distribution of steric sequences, as revealed by ^{13}C n.m.r. analysis. The syndiotactic fraction was also analysed by ^{13}C n.m.r. to measure polymer stereoregularity. The samples reported here have a high degree of stereoregularity. Therefore, the number of signals other than syndiotactic sequences, arising from the insertion of *m* diads into the *r* diads is small. Either the aromatic quaternary carbon or the aliphatic CH_2 appear to be sensitive to pentad and hexad sequences, respectively; however, only the latter show well separated signals and were considered for the calculations. In particular, in the region ranging from 43.0 to 47.0 ppm the presence of an intense peak at 44.47 ppm and three other small peaks at 43.34, 45.12 and 46.00 ppm in the ratio 2:2:1 was observed. Comparing these shifts with those reported in the literature[9,10], they have been assigned to *rrrrr, rrrmr, rrrrm* and *rrmrr* hexads, respectively. Steric meso defects (m%) were counted by dividing half area of the *rrrmr* units by the sum of the whole hexads. The percentage of steric defects was about 2% and 0.5% for $CpTiCl_3$ and $Ti(OEt)_4$, respectively.

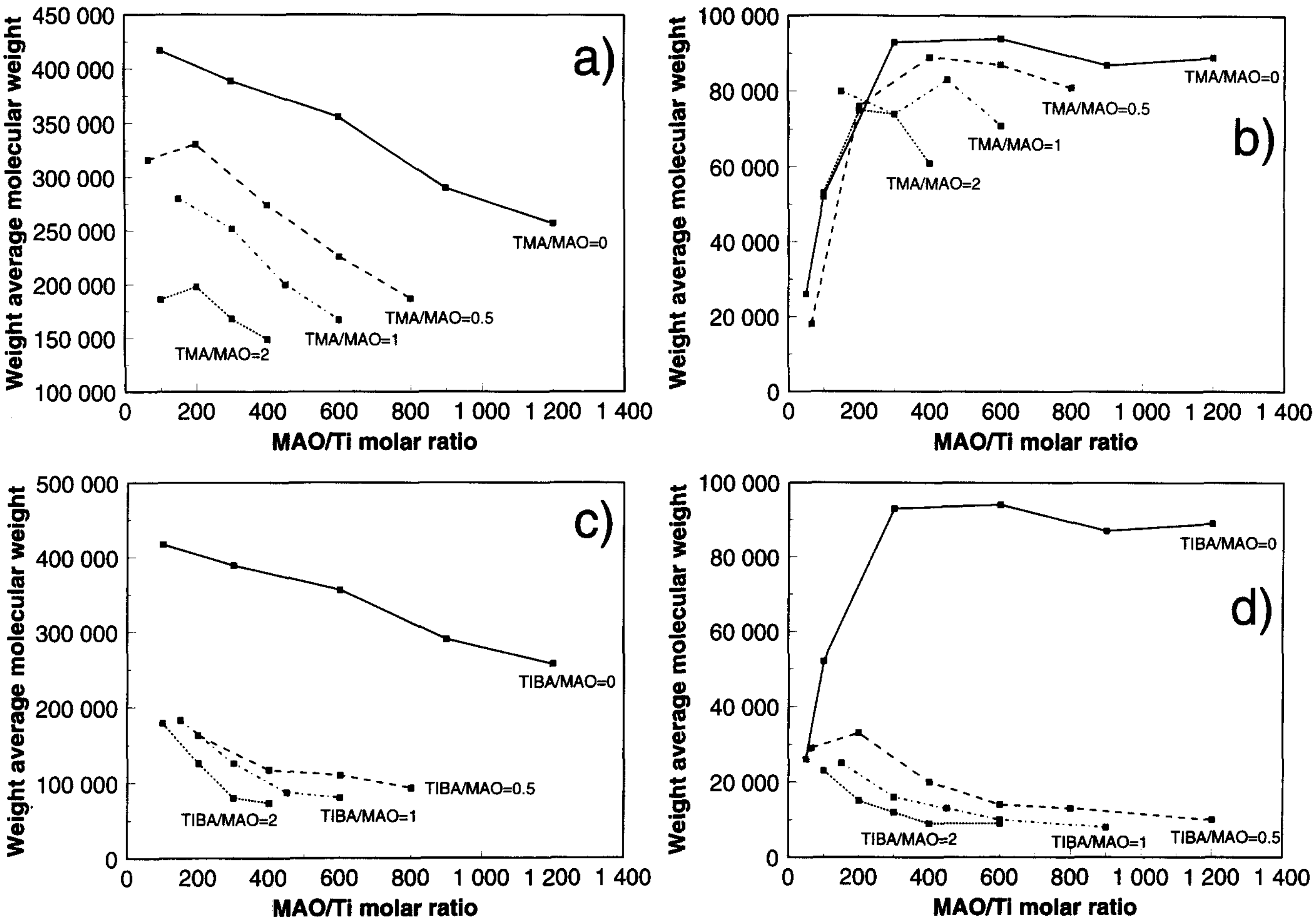

Figure 2 Weight average molecular weight of syndiotactic polystyrene as a function of MAO/Ti molar ratio with different catalytic systems: (a) $Ti(OEt)_4$/TMA/MAO; (b) $CpTiCl_3$/TMA/MAO; (c) $Ti(OEt)_4$/TIBA/MAO; (d) $CpTiCl_3$/TIBA/MAO

No effect caused by the presence of aluminium alkyls was observed.

The effect of the aluminium alkyls on catalyst activity is shown in *Figure 1a–d*, while the effect on the molecular weight (M_w) is reported in *Figure 2a–d*. $CpTiCl_3$ is at least twice as active as $Ti(OEt)_4$, and best yields were generally obtained in the absence of added aluminium alkyls. The yield is low below MAO/Ti $\approx$ 200 with both titanium complexes. For both catalytic systems, MAO/Ti = 300 appears to be the best ratio, at least under the adopted reaction conditions, in agreement with other previously reported data[11]. Finally, a slow decrease is observed above MAO/Ti $\approx$ 400 for $CpTiCl_3$, while the decrease is sharp for $Ti(OEt)_4$.

The two titanium complexes behave quite differently also from the point of view of the produced molecular weights. $Ti(OEt)_4$ affords sPS having an M_w which almost linearly decreases from about 400000 to 250000 by increasing the MAO/Ti molar ratio. $CpTiCl_3$ gives sPS with a much lower M_w (90000); the M_w increases rapidly by increasing the MAO/Ti molar ratio up to 300, and remains constant above this value. The different behaviour of the two titanium complexes can very likely be attributed to their abilities to prevent the β-hydride elimination, one of the reactions responsible for the molecular weight control. Another very important reaction is the chain transfer to aluminium (either to the MAO or to the TMA_f)[11,12]. With $CpTiCl_3$, the β-elimination reaction is probably so overwhelming that no noticeable effect is produced by the increase of MAO and TMA_f amounts in the polymerisation mixture. With $Ti(OEt)_4$ the β-elimination reaction is much less important and the transfer to aluminium accounts for the steady Mw decrease with increasing the MAO/Ti ratio.

The addition of TMA to the polymerisation mixture causes a clear decrease in the sPS yield. Such a decrease is very sensitive for the $Ti(OEt)_4$ based system. The addition of an amount of TMA corresponding to the half of the MAO, leads to a reduction of more than 60% in activity. Further addition of TMA have a less dramatic effect. For the $CpTiCl_3$ based system the activity loss is more limited, but becomes increasingly evident at high MAO/Ti ratios. The reason of this behaviour is not clear, and may arise from either the deactivation of the metallocene complexes through bimolecular reactions[13] or the progressive depolymerisation of MAO, with modification of its structure[14].

The situation is more complex with TIBA (it should be reminded that also some TMA arising from MAO is present in this system). When the catalyst is $Ti(OEt)_4$, the deactivation of the catalytic systems is observed only for MAO/Ti ratio < 600, while the yields of sPS are improved above this ratio. In this case, alkyl exchange reactions between TIBA and MAO can produce an aluminoxane bearing both methyl and isobutyl groups, and it is worth to be mentioned that isobutylaluminoxanes have a different cocatalytic activity and were found, in some cases, to be even more active than MAO in olefin polymerisation[15].

With $CpTiCl_3$, the behaviour is probably very similar, but the graphic in *Figure 1d* is misleading. Indeed, it should be reminded that the yields reported in *Figure 1a–d* are those obtained *after* extraction of the atactic fraction; experimental

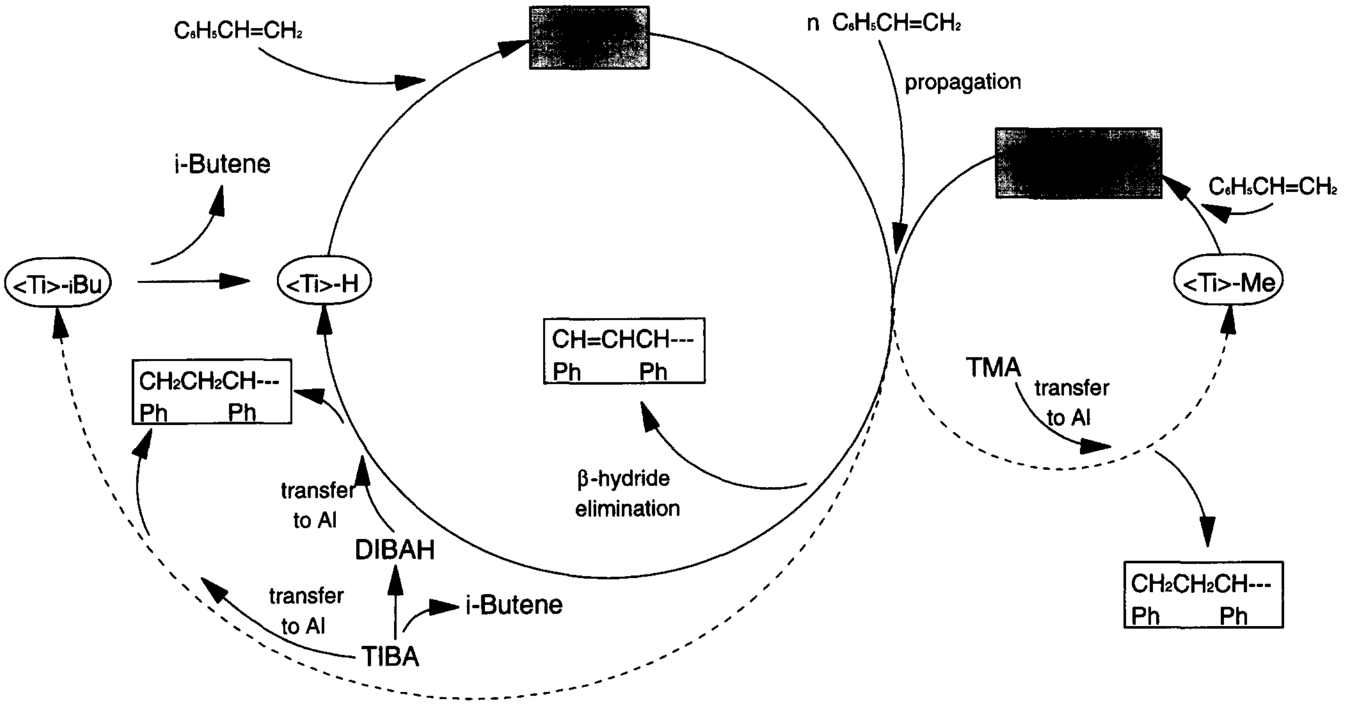

Figure 3 Proposed mechanism for syndiospecific polymerisation of styrene in the presence of aluminium alkyls. TMA, trimethylaluminium; TIBA, triisobutylaluminium; DIBAH, diisobutylaluminium hydride. White rectangles, tail end-groups; grey rectangles, head end-groups; ovals, initiating species

data show that the amount of MEK soluble fraction is comparable in amount to the insoluble one. From n.m.r. analysis of the soluble fractions, a degree of stereoregularity of 90% and a non-Bernoullian steric sequences distribution were found. Very likely, the extraction step causes also the extraction of the syndiotactic low molecular weight fractions from the product. This fact is particularly relevant with this catalytic system, producing polymers having average molecular weights under 30 000, and often as low as 10 000 (*Figure 2d*). As a further evidence that the soluble fractions are mixtures of aPS and syndiotactic low molecular weight PS, the molecular weight distributions of the corresponding insoluble fractions are 1.4–1.5, against 1.9–2.4 found with the other systems, suggesting that the treatment with boiling MEK causes also an effective molecular weight fractionation.

The addition of both TMA and TIBA causes a decrease in the molecular weight (*Figure 2a–d*). The decrease is regular in the first case, as emphasised by the evenly ranged curves of *Figure 2a* and *b*. On the other hand, a dramatic lowering of the molecular weight is already observed for TIBA/MAO = 0.5, while the reduction with the further increase of TIBA is only marginal.

As previously pointed out, aluminium alkyls are good chain transfer agents in the homogeneous coordination polymerisation of olefins and styrene[7,12,16]. These results are a strong indication that TIBA is much more effective than TMA in this respect.

To characterise the polymers end-group structure and to enlighten the reaction mechanism, a detailed n.m.r. study was performed. Only polymers having M_w lower than about 60 000 (average polymerisation degrees under 250) were considered, because the instrumental sensitivity does not allow the detection of the end-groups in higher polymers. Thus, three samples were examined in detail: polymer **A**, prepared using $CpTiCl_3$/TIBA/MAO in the ratio 1:400:800, polymer **B** ($CpTiCl_3$/TIBA/MAO 1:900:900) and polymer **C** ($CpTiCl_3$/TMA/MAO ratio 1:800:400).

Several peaks with small intensities appear in the aromatic and aliphatic regions of the ^{13}C n.m.r. spectra. Their attribution is not straightforward owing to different mechanisms which can be foreseen for monomer insertion and polymer chain elimination. In principle three types of head end-groups (H) and two types of tail end-groups (T) are possible (*Table 1*): indeed the polymer chain may either initiate through the styrene insertion on a Ti–H, a $Ti-CH_3$ or a $Ti-CH_2CH(CH_3)_2$ bond (the latter is possible only when TIBA is used), and terminate with either a $CH_2Ph-CH_2-CHPh-$ or a $CHPh=CH-CHPh-$ group. For each kind of expected end-group, chemical shifts have been calculated by using the on-line Specinfo-STN data-bank and compared with the experimental ones for the assignment (*Table 1*). Attributions were further supported by Distortionless Enhanced Polarisation Transfer (DEPT) experiments.

Inspection of *Table 1* leads to the following results. For all the polymers, the calculated resonances at 28.12 and 12.12 ppm are absent from the spectra, ruling out the formation of significant amounts of $-CHPh-CH_2-CH_3$ and $-CHPh-CH_2-CH_2-CH(CH_3)_3$ end-groups. For polymer **C** two peaks at 37.81 and 22.98 ppm which arise from $-CHPh-CH_3$ end-group are observed in the aliphatic region; furthermore in the aromatic region a resonance at 134.9 ppm occurs, assigned to the $CHPh=CH-CHPh-$ termination. In the aliphatic region of the spectra of polymers **A** and **B**, the aforementioned resonances due to $-CHPh-CH_3$ end-group were found; in addition, there are two other resonances at 33.84 and 38.99 ppm having the same intensity, which are consistent with the presence of a $CH_2Ph-CH_2-CHPh-$ termination. The molar ratio between the H and T end-groups is 1.4 in sample **B** and 2.7 in sample **A**. Close to the carbons of $-CHPh-CH_3$ group, other two small peaks at 37.23 and 21.43 ppm occur, assigned to methyne and methyl groups, respectively: very likely, they arise from the same end-group which can assume the erythro and the threo configuration.

As far as concerns the aromatic region, a peak is present

Table 1 ^{13}C n.m.r. chemical shifts of calculated (in parentheses) and experimental end-groups

End-group	Type[a]	C^1	C^2	C^3	C^4	C^5
$-C^1HPh-C^2H_3$	H	(37.23) 37.81 37.23	(22.43) 22.98 21.43			
$PhC^1H{=}C^2H-CHPh-CH_2-$	T	(128.23)	(133.49) 134.90	(38.7)		
$PhC^1H_2-C^2H_2-C^3HPh-CH_2-$	T	(33.57) 33.84	(36.56) 38.99	(42.45)		
$-C^1HPh-C^2H_2-C^3H_3$	H	(47.61)	(29.78)	(12.12)		
$-C^1HPh-C^2H_2-C^3H_2-C^4H(C^5H_3)_2$	H	(42.45)	(34.32)	(30.23)	(28.12)	(22.62)

[a] H, head end-group; T, tail end-group

at 134.9 ppm, arising from CHPh=CH–CHPh– end-group; sample **B** shows a very small peak which becomes more intense in sample **A**; the ratio between the areas of CHPh=CH–CHPh– and $-CHPh-CH_3$ is 0.05 in sample **B** and 0.4 in sample **A**.

A reaction scheme taking into account the above experimental findings is reported in *Figure 3*. When MAO or MAO/TMA mixtures are used as cocatalyst the first polymer chains initiate on a $Ti-CH_3$ bond ($-CHPh-CH_2-CH_3$ head end-group). β-hydride elimination causes the chain termination (CHPh=CH–CHPh– tail end-groups), and the following polymer chains produced by the same titanium atom begins with the insertion on a Ti–H bond ($-CHPh-CH_3$ head end-group). The n.m.r. end-groups analysis demonstrate that the β-hydride elimination is greatly favoured compared with the transfer to aluminium (either TMA or MAO); therefore the $-CHPh-CH_3$ end-groups prevail over $-CHPh-CH_2-CH_3$ ones. At any rate, transfer to aluminium acquires increasing importance by increasing the TMA amount in the polymerisation mixtures, as revealed by GPC data.

Transfer to aluminium becomes by far the most important chain termination mechanism when TIBA is added to the polymerisation mixture. In this case no unsaturated tail end-groups are present in the polymer, the only one found being the $CH_2Ph-CH_2-CHPh-$ ones. Head end-groups $-CHPh-CH_3$ are formed through styrene insertion on a Ti–H bond. However, it is not still clear how the hydridotitanium species is formed.

A first hypothesis is that the Ti–polymer complex exchanges with one alkyl group belonging to TIBA, forming the 'dead' Al–polymer chain (which gives the $CH_2Ph-CH_2-CHPh-$ after killing) and a species containing a $Ti-CH_2CH(CH_3)_2$ bond. The latter does not give styrene insertion ($-CHPh-CH_2-CH_2-CH(CH_3)_3$ end-groups are absent), but eliminates isobutene giving a Ti–H species, which is able to insert a monomer molecule and re-initiate the chain growth.

According to the literature[17–21], the thermal stability of bis(cyclopentadienil)titanium alkyls decreases with increasing the length of the alkyl groups. So, for instance, while $Cp_2Ti(CH_3)_2$ is moderately stable[17–19], $Cp_2Ti(C_2H_5)_2$ decomposes at room temperature and $Cp_2Ti(C_4H_9)_2$ at −50°C[20,21]. Although the catalytic species has different substituent groups compared with the above mentioned compounds and is a cationic complex, and not a neutral molecule, a similar relative stability can be expected, and the tendency to decompose of $Ti-CH_2CH(CH_3)_2$ species could be explained.

The second hypothesis is that the Ti–polymer complex gives an exchange reaction similar to that reported above, but with the hydride group of a molecule of TIBA. Indeed a small amount of diisobutylaluminium hydride (DIBAH) is present in the commercial TIBA; anyway, TIBA decomposes spontaneously in part at 60°C giving DIBAH and isobutene, as found by gas chromatographic analysis. Therefore, in this case the transfer reaction would directly lead to the hydridotitanium species.

CONCLUSIONS

Catalytic systems based on $Ti(OEt)_4$ or $CpTiCl_3$ and MAO afford syndiotactic polystyrene. Addition of trimethyl aluminium to the polymerisation mixture causes a decrease in activity, while triisobutyl aluminium depresses the activity below a MAO/Ti ratio of 600, and promotes the activity above this value. The different behaviour can be attributed to the alkyl exchange reactions occurring between the organo aluminium compounds.

Aluminium alkyls are good chain transfer agents in the syndiospecific polymerisation of styrene; β-hydride elimination is the prevailing reaction responsible for chain termination when TMA is present in the polymerisation mixture, but tends to become less and less important by increasing the amount of aluminium alkyl. TIBA is a much powerful chain transfer agent than TMA; in this case the β-hydride elimination reaction is virtually absent.

The analysis of the polymer end-groups shows that the first styrene insertion takes place on a Ti–H bond. With TMA, this species is formed through the β-hydride elimination. With TIBA, Ti–H species could be formed trough two different mechanisms, corresponding to the two following reaction pathways:

(1) polymer chain transfer to aluminium alkyl (which would be mostly favoured by an isobutyl group in comparison with a methyl group), followed by β-elimination of isobutene from the so formed isobutyltitanium species;
(2) formation of diisobutylaluminium hydride by thermal decomposition of TIBA, followed by polymer chain transfer to the aluminium hydride and formation of a titanium hydride species.

In both cases the insertion of a styrene molecule on the Ti–H bond occurs and the chain growth starts again.

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