Copolymerization of styrene with methyl-substituted styrenes in the presence of titanium monometallocenes

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Abstract: This paper investigates the homo- and copolymerization of styrene with *p*-methylstyrene, *m*-methylstyrene, 2,4-dimethylstyrene, 2,5-dimethylstyrene and 2,4,6-trimethylstyrene using a Cp*TiCl$_3$ (Cp: cyclopentadienyl) semimetallocene catalyst activated with methylaluminoxane. Syndiotactic homo- and copolymers were obtained only for the monosubstituted monomers. For the di- or trisubstituted monomers, reduced reactivities, stereoregularities, and degrees of polymerization were obtained with respect to the monosubstituted monomers. More specifically, the homopolymerization of 2,5-dimethylstyrene and 2,4,6-trimethylstyrene and their copolymerization with styrene was inhibited. The reason for this are combined steric and inductive effects. The presence of methyl groups in *para* position seems to inhibit crystallization of the syndiotactic polymers. In contrast, crystallinity was evidenced in the materials produced in the presence of *m*-methyl substituted monomers.

Introduction

Due to its high melting point (265°C), high crystallinity, and excellent solvent resistance, syndiotactic polystyrene (sPS) exhibits a wide range of applications. In the last ten years, several works have been published [1-6] that deal with the synthesis of sPS through highly active and stereospecific catalytic systems. The nature of the active species and of the mechanism controlling the stereoregularity has been also investigated [7-11]. Zambelli *et al*. [11] proposed an explanation for the syndiospecific polymerization of styrene based on Zirconium cationic complexes, and on the regiochemistry of the insertion. Their model proposed the η^n coordination of the growing chain end and diasteroselective monomer coordination imposed by the direct interactions with the secondary ligands of the metal complex. This complex (a pseudotetrahedral chiral Ti(III) cation), inverts its configuration after every syndyospecific insertion step.

The polymorphic behavior of sPS has been recently described [12-21]. The α and β crystalline forms contain zig-zag planar chains, and the γ and δ forms contain s(2/1)2 helical chains. De Rosa *et al*. [22] observed two melting peaks corresponding to a β' modification, and that the relative intensities of such peaks change with the heating

rate. By performing differential scanning calorimetry at different heating rates, it was assumed that the double peak corresponds to a recristallization phenomenon toward a more perfect β form. Zun *et al.* [23] explained the second endothermic peak as a melting of small lamellas in β form, followed by a fast recristallization into larger lamellas. Similarly, syndiotactic poly(*p*-methylstyrene) (*p*-MeS) crystallizes relatively slowly when either cooling the melt or when annealing the amorphous samples, and more quickly when either casting or precipitating the *p*-MeS from a solution or by induced crystallization from the amorphous state [24]. X-ray diffraction patterns of non oriented samples of *p*-MeS have allowed to identify three crystalline forms, one mesomorphic form and several chlatrate forms containing solvent molecules [25].

Some catalysts that are active in the sPS polymerization can be also used for polymerizing styrene monomers with substituents in the aromatic ring. Electron donor aliphatic groups increase the reactivity with respect to styrene, while the opposite occurs for electron acceptor substituents such as the halogens [26]. Zambelli [26] and Soga [27] investigated the active species involved in the homo- and copolymerization of styrene and monosubstituted styrenes for the production of syndiotactic polymers. The stabilization of the catalyst active center by the monomer electron donor could be perturbed by possible steric interactions between the last inserted monomeric unit and the incoming monomeric unit.

Ishihara *et al.* [28] homopolymerized monosubstituted styrene monomers in the presence of $CpTiCl_3$/methylaluminoxane (MAO). It was found that the reaction rate increases in the following order: styrene < *p*-methylstyrene (*p*-MeS) < *m*-methyl-styrene (*m*-MeS). The increased reaction rates observed in the presence of bulkier substituents were explained by the strong polar effect of these on the addition rate.

The polymorphic behavior of a homopolymer can be altered by mixture with other homo- or copolymers, or by introducing different comonomer units into the original chain. Particular crystalline forms can be favored by specific combinations of thermo-dynamic and kinetic effects. Furthermore, the energy of a crystal tends to increase in the presence of comonomeric units, even if excluded from the crystallites. Also, the comonomer can modify the polymorphic behavior by changing the crystallization rate of the different crystalline forms.

Manfredi *et al*. [29] compared the melting point of a syndiotactic styrene homopolymer with styrene/*p*-MeS copolymers with different compositions. T_m decreased from 265°C for the sPS homopolymer to 210°C for the styrene/*p*-MeS (80%/20%) copolymer obtained under identical reaction conditions. Apparently, the *p*-MeS monomeric units destabilize more the β form than the α form; and for this reason β forms are not obtained with *p*-MeS content higher than 20%. The partial inclusion of the *p*-MeS units in the crystalline phase was verified by comparing the X-ray diffraction patterns of sPS with those of a styrene/*p*-MeS copolymer with 20% of *p*-MeS units.

In this work, homo- and copolymers of different methyl substituted styrenes were synthesized and characterized. The well known Cp^*TiCl_3 with MAO catalytic system was used. The investigated monomers were styrene, *p*-methylstyrene (*p*-MeS), *m*-methylstyrene (*m*-MeS), 2,4-dimethylstyrene (2,4-diMeS), 2,5-dimethylstyrene (2,5-diMeS) and 2,4,6-trimethylstyrene (2,4,6-triMeS). The obtention of styrene substituted polymers with more than one methyl group via semimetallocene catalysts has not been previously reported.

Results and discussion

The reaction conditions and the results of the homo- and copolymerizations are presented in Tab. 1. The upper half of Tab. 1 corresponds to the homopolymerization of styrene and substituted styrenes. The lower half of Tab. 1 corresponds to the copolymerizations of styrene with the substituted styrenes. In most of the reactions, $Cp*TiCl_3$ was the applied catalyst, with the exception of styrene homopolymerizations S2 - S4, where other catalysts were used.

The global results obtained for the homo- and copolymerizations are presented in Tab. 1. ^{13}C NMR spectra were determined for all of the synthesized homo- and co-polymers. In Fig. 1 and 2, two typical spectra are presented.

Reactivity, microstructure, and composition

Consider first the homopolymerization results summarized in the upper part of Tab. 1. The methyl groups contained in the cyclopentadienyl ring of the catalyst and of the monomers stabilize the cationic catalytic species. This is particularly true for methyl groups in positions 2, 4, 6 of the monomer aromatic ring.

As observed in Tab. 1, the order of reactivities resulted: styrene $\cong$ p-MeS > m-MeS > 2,4-diMeS > 2,5-diMeS $\cong$ 2,4,6-triMeS. The steric effect seems to prevail over the inductive effect in the homopolymerization of substituted styrene monomers with methyl groups in positions 2 and/or 6. Also, for a given substituent, its steric hindrance increases when the subtituent changes from *para* to *meta* position. In general, the monomer reactivity decreases when increasing the number of the substituents. According to the model in ref. [11], the steric interaction disturbs the coordination between the substituent in *ortho* position, the growing chain, and the catalyst. This limitation is not evident when the substituent is in *meta* or *para* position. The mentioned reactivity order has been previously observed for the isotactic polymerization of styrenes with $TiCl_4/Al(I-C_4H_9)_3$ [30].

The ^{13}C NMR spectra of the homopolymers all indicate a certain degree of stereo-regularity. For the monosubstituted monomers, only the signals corresponding to the syndiotactic sequences are observed. In contrast, poly-(2,4-diMeS) was only partially stereoregular.

Consider now the copolymerizations. The copolymerization rates were always lower than the homopolymerization rates of styrene, except for the case of styrene/p-MeS reaction, where no specific tendency was observed. The composition of the copolymers was calculated from the signals corresponding to the quaternary carbon atoms in styrene and in the substituted styrene. In the case of m-MeS, the quaternary carbon signal coincides with the chemical shift of the styrene, and the total signal is the sum of its different contributions (Fig. 2). The polymer composition was determined from the integrated signals of the substituted carbon atom in the case of m-MeS and of the quaternary carbon atom in the case of styrene [(C_1 of S + C_1 of m-MeS) – C_3 of m-MeS].

In the copolymerization of styrene and 2,4-diMeS, the reactivity ratios were calculated using the Fineman-Ross equation [28]; that requires to input the composition of the feed, the conversion, and the copolymer composition. The following values were obtained: r_s = 2.01 and $r_{2,4-diMeS}$ = 1.08, thus indicating the tendency to form a block copolymer. Due to the high conversion, it was not possible to obtain the reactivity ratios for the copolymerization of styrene with m- and p-MeS.

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Tab. 1. Global results in the homo- and copolymerizations of styrene and substituted styrenes

Exper. no.	Comonomer	Styrene/comonomer mole ratio in the feed	Styrene/comonomer mole ratio in copolymer	Relative reactivity	Global conversion in wt.-%	$\overline{M}_n \times 10^{-3}$	$\dfrac{\overline{M}_n}{\overline{M}_w}$	$\overline{DP}_n$	T_g in °C	T_{m1} in °C	T_{m2} in °C	T_c in °C
S1	—	100/0	100/0	1	61.0	a)	—	—	100	271	261/271	236
S2 [b)]	—	100/0	100/0	1	27.0	85.0	2.07	817	100	273	264/273	245
S3 [c)]	—	100/0	100/0	1	3.0	9.0	2.17	87	100	263	264/268	228
S4 [d)]	—	100/0	100/0	1	11.2	3.0	1.56	29	100	226	206/225	197
H1	p-MeS	0/100	0/100	0.93	56.7	299.0	2.3	—	108	—	—	—
H2	m-MeS	0/100	0/100	0.71	43.6	a)	—	—	—	217	216	152
H3	2,4-diMeS	0/100	0/100	0.04	2.6	12.0	3.2	—	119	—	—	—
H4	2,5-diMeS	0/100	—	—	―	—	—	—	—	—	—	―-
H5	2,4,6-triMeS	0/100	—	—	―	—	—	—	—	—	—	―-
C1	p-MeS	75/25	68/32	—	38.6	137	2.45	1260	98	206/212	—	—
C2		50/50	56/44	—	91.3	184	2.50	1670	102	—	—	—
C3		25/75	39/61	—	71.5	253	2.26	2245	105	—	—	—
C4	m-MeS	75/25	85/15	—	6.2	49.0	4.89	461	99	several peaks	261/271	219/239
C5		50/50	35/65	—	26.8	146	2.61	1290	—	189	—	—
C6		25/75	20/80	—	32.7	214	2.66	1855	—	202	203	—
C7	2,4-diMeS	75/25	85/15	—	1.7	21.0	2.19	194	94	—	—	—
C8		50/50	52/48	—	1.4	12.0	2.45	102	108	—	—	—
C9		25/75	34/66	—	2.5	8.60	2.73	70	115	—	—	—
C10	2,5-diMeS	75/25	85/15	—	1.1	38.0	1.96	348	—	several peaks	245/263	223
C11		50/50	64/36	—	1.1	36.5	2.35	316	—	several peaks	267	230
C12		25/75	—	—	—	—	—	—	—	—	—	―-
C13	2,4,6-triMeS	75/25	100/1	—	5.4	22.0	4.33	210	100	272	—	―-
C14		50/50	100/1	—	2.2	12.5	2.79	120	—	—	—	―-
C15		25/75	100/1	—	5.3	18.6	2.60	180	—	—	—	―-

Reaction conditions: T = 50°C; Al/B = 1.8; [Al]/[Ti] = 500; [monomer]/[catalyst] = 2000; catalyst: Cp*TiCl₃; toluene: 64 ml.
[a)] Insoluble. [b)] Cp*Ti(OAc)₃; [Al]/[Ti] = 400; polymerization time: 1h. [c)] InTiCl₃; [Al]/[B] = 1.6; [Al]/[Ti] = 800; polymerization time: 6 h. [d)] CpTiCl₃; [Al]/[Ti] = 500; polymerization time: 6 h.
Relative reactivity is the ratio between conversion in each case and styrene homopolymerization conversion, at the same experimental conditions.
T_g: glass transition; T_{m1} and T_{m2}: melting points observed during first and second heating, respectively; T_c: crystallization temperature.
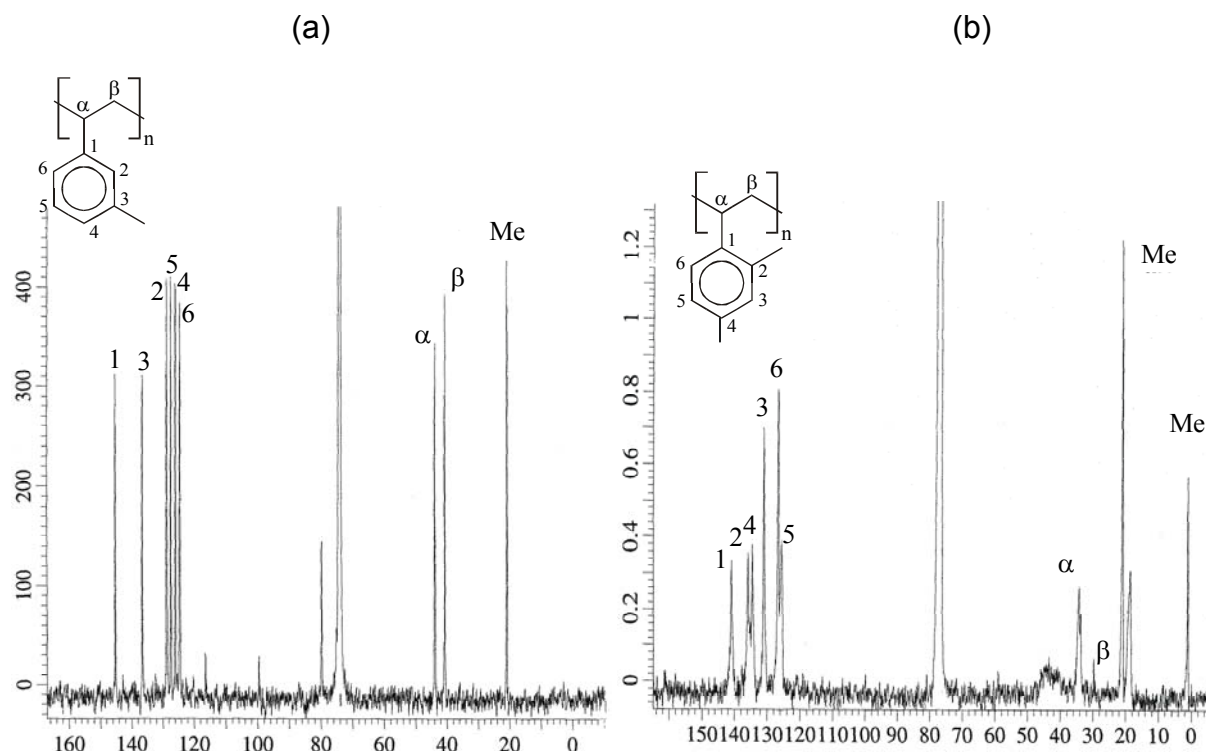
Fig. 1. ^{13}C NMR spectras: (a) poly(m-methylstyrene); (b) poly(2,4-dimethylstyrene). $T_{polymn.}$ = 50°C; [Al]/[B] = 1.8; [Al]/[Ti] = 500; [monomer]/[catalyst] = 2000; catalyst: Cp*TiCl$_3$; toluene: 64 ml

In the case of 2,5-dimethylstyrene, the reactivity ratios could not be obtained because no copolymer was detected for feed ratios higher than 25% in this comonomer.

Consider in what follows some comments on the obtained ^{13}C NMR spectra:

- In the styrene/p-MeS copolymer, the quaternary carbon peak indicates a loss of stereoregularity with respect to the p-MeS homopolymer, when the content of styrene in the copolymer increased.
- In the styrene/m-MeS copolymer, a good signal resolution was observed, that is indicative of stereoregularity.
- In the styrene/2,4-diMeS copolymer, the region of the quaternary carbon atom indicates that the stereoregularity of styrene units is affected by the insertion of 2,4-diMeS units; and (as previously observed in the homopolymerization of the substituted monomers); this is probably due to the steric effect.
- In the styrene/2,5-diMeS copolymer, the steric effect seems again to affect the regularity. In the reaction with the highest amount of 2,5-diMeS, the position of the methyl groups in the ring prevents the homopolymerization of the substituted monomers and also their copolymerization.
- The production of styrene/2,4,6-triMeS copolymer could not be verified; instead only styrene homopolymer was observed. However, the microstructure of this polystyrene exhibits a syndiotacticity that is lower than that of the homo-polymerization. Also, an increasing amount of substituted monomer decreases the stereoregularity of the styrene block. This indicates that an interaction between the substituted monomer and the active center interferes with the coordination of styrene.
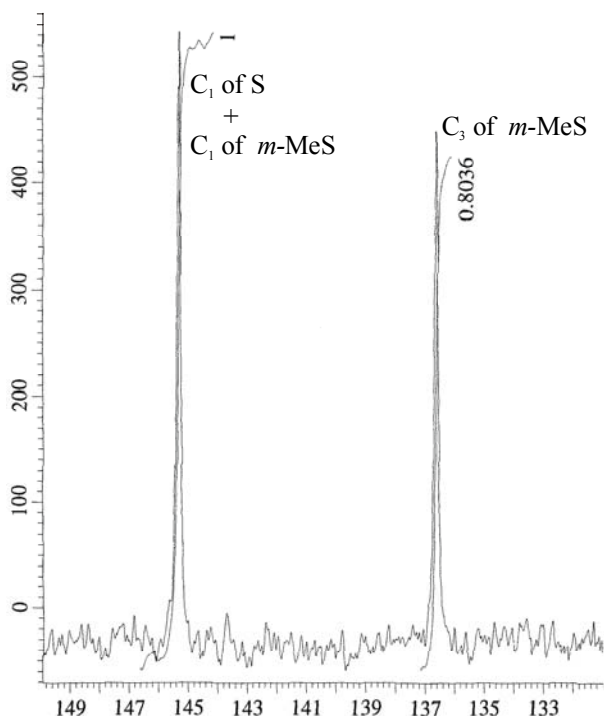
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Fig. 2. ^{13}C NMR spectra of the quaternary carbons region of the styrene/*m*-methyl-styrene copolymer. Monomer contents: styrene 20 mol-%, *m*-methylstyrene 80 mol-%. $T_{polymn.}$ = 50°C; [Al]/[B] = 1.8; [Al]/[Ti] = 500; [monomers]/[catalyst] = 2000; catalyst: Cp*TiCl$_3$; toluene: 64 ml

A general remark: The styrene contents and the low copolymerization reactivity with respect to the homopolymerization of styrene indicates that, apart from the steric effect, the electronic effect prevails in the homo- and copolymerization of substituted monomers with more than one methyl group. The electron donor substituents increase the stability and therefore decrease the activity of the Ti complex by an increased interaction between the metal center and the monomer electrons.

Degree of polymerization

The following comments can be made:

In the copolymerizations, the number average degree of polymerization $\overline{DP}_n$, was calculated from $\overline{M}_n$ and the average chemical composition. In the case of the co-polymers with *para* and *meta* monosubstituted styrenes, $\overline{DP}_n$ increases with the concentration of methylstyrenes in the feed. This suggests a stabilization of active sites by the electrodonating substituent. For these copolymers, polydispersity $\overline{M}_w/\overline{M}_n$ is in the range 2.2 - 2.7, with the single exception of the 75/25 S/*m*-MeS copolymer. This is typical of an olefin polymerization with a predominant monosite character.

In the case of the dimethyl substituted copolymers, the electronic and the steric effects explain the decrease in $\overline{DP}_n$ and the increase in $\overline{M}_w/\overline{M}_n$ with respect to that of the styrene homopolymerization. Moreover, a decrease in the propagation rate was also observed, due to a lower activity of the Ti complex.

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With the trisubstituted monomer, the conversion was similar to disubstituted monomers, but basically polystyrene homopolymer was produced. In a metallocene polymerization, the rate of propagation depends on the last added repetitive unit. When styrene is copolymerized with 2,4,6-triMeS, then the rate of propagation is high only while styrene units are being added. But as soon as a trisubstituted styrene unit is incorporated, then its high steric hindrance considerably inhibits further propagation. This explains the following observations: (a) 2,4,6-triMeS did not homopolymerize; and (b) in the copolymerization of styrene and 2,4,6-triMeS, a low-molecular-weight polystyrene was basically produced, and its polydispersity was higher than that observed in the homopolymerization of styrene under identical reaction conditions.

Thermal behavior

In what follows, the differential scanning calorimetry (DSC) analyses for each of the synthesized homo- and copolymers will be discussed.

Syndiotactic polystyrene

The following was observed: a melting peak during the first DSC heating, a crystallization peak during the cooling down, and at least two melting peaks during the second heating. The first of these latter melting peaks appears between 10 and 15°C before the peak of the first heating, while the second melting peak coincides with that first peak. This result has been previously reported by other authors, and is a consequence of the polymorphism of syndiotactic polystyrenes [14, 22].

Syndiotactic poly(*p*-MeS)

While NMR traces show a highly syndiotactic structure, the thermal behavior does not indicate thermal transitions. This includes the first heating run of the polymer precipitated from a toluene solution. Previous reported values of T_m during the first heating are: 173°C [28] and 176°C [31]. No crystallization or fusion peaks were observed during the cooling and the second heating. This can be tentatively attributed to the high molecular weights produced ($\overline{M}_n$ = 299000 with $\overline{M}_w/\overline{M}_n$ = 2.3). In contrast, the reported values corresponded to $\overline{M}_n$ = 192000 with $\overline{M}_w/\overline{M}_n$ = 2.1 [31]. The observed T_g = 108°C is slightly higher than the published value of 106°C [28].

Syndiotactic poly(*m*-MeS)

A melting point was observed during the first heating at T_m = 217°C. This is 13°C higher than a published value [28]. The polymer did not crystallize on cooling; but during the second heating the exothermic crystallization peak was observed at 152°C (Fig. 3).

Poly(2,4-diMeS)

This polymer does not show a melting point; and this can be justified by its low stereoregularity which hinders crystallization. Compared to the monosubstituted homopolymers, these macromolecules are stiffer, as it is evidenced by their relatively high T_g ($\cong$ 119°C).
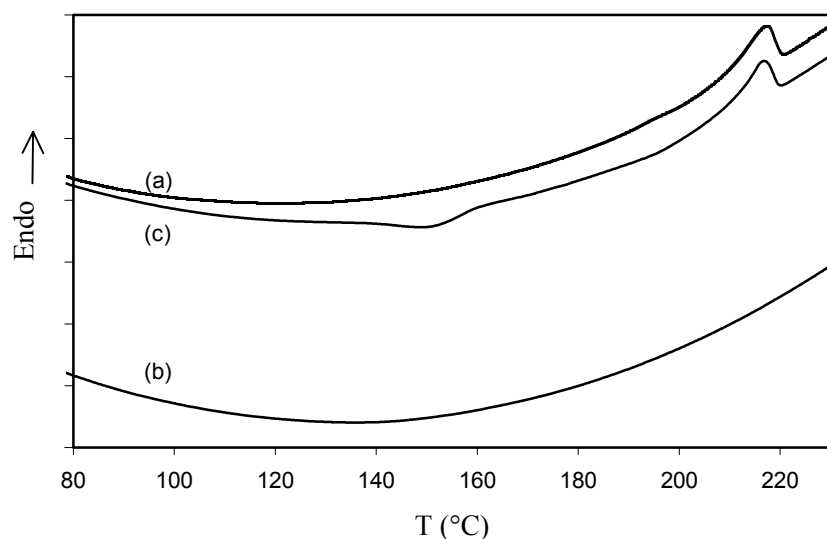
Fig. 3. DSC scans (10°C/min) of poly(*m*-methylstyrene): (a) first heating; (b) cooling scan after 5 min at 300°C; (c) subsequent heating scan after cooling in (b)

Poly(2,4,6-triMeS)

This homopolymer was not detected.

S/*p*-MeS

Only the 75%/25% S/*p*-MeS copolymer shows a crystalline melting point during the second heating. This temperature is below that of the styrene homopolymer, suggesting that the *p*-methylstyrene units are not entirely confined in the amorphous phase. As expected for a random copolymer, T_g increases with the *p*-MeS contents. This tendency is also observed in $\overline{M}_n$, due to a reduced chain transfer to the substituted comonomer.

S/*m*-MeS

All S/*m*-MeS copolymers were crystalline (Fig. 4). During the second heating, the sample richer in styrene shows the typical melting point of a syndiotactic homo-polystyrene, while all other compositions exhibit lower T_m's with respect to *m*-MeS homopolymer, these melting points increasing with the *m*-MeS content in the co-polymer. T_g is not easily detectable, and $\overline{M}_n$ increases with the substituted co-monomer content, as in the case of *p*-MeS. This suggests the formation of a substantially random copolymer. Even though *m*-MeS homopolymerizes more slowly than styrene, the copolymer composition exhibits a similar or a higher styrene content than the feed. This indicates that after the incorporation of a styrene unit, the insertion of a *m*-MeS is favored over a second styrene unit.

2,4-diMeS/S and 2,5-diMeS/S

In both cases, the copolymerization proceeded to low global conversions. Copolymers with 2,4-diMeS were all amorphous and the regular increase in T_g and polydispersity with the amount of 2,4-diMeS in the feed suggests that during the copolymerization, the insertion of the dimethyl substituted unit slows down the homopropagation and the styrene insertion. In general, this comonomer exhibits a significant inhibiting effect on the catalyst. This last effect is more dramatic in the

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case of 2,5-diMeS. The small amount of polymer produced did not allow its systematic characterization. In the obtained copolymers with 2,5-diMeS, a melting peak similar to that of a syndiotactic polystyrene was observed. This suggests that a methyl substituent in *para* position inhibits the crystallization with respect to a methyl substituent in *meta* position.

2,4,6-triMeS/S
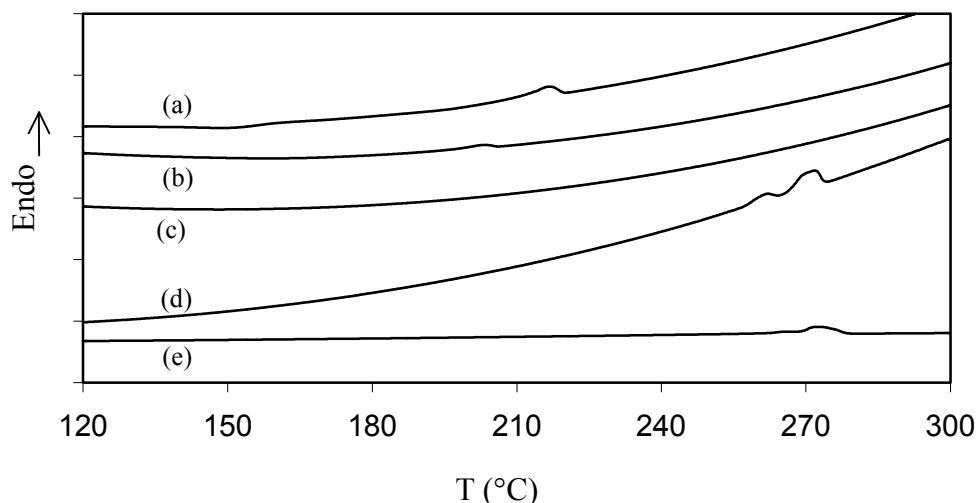
Here again, only homopolystyrene was detected.

Fig. 4. DSC second heating scan at 10°C/min: (a) poly(*m*-methylstyrene); (b) co-polymer with 15 % of *m*-MeS; (c) copolymer with 65 % of *m*-MeS; (d) copolymer with 80 % of *m*-MeS; (e) sPS

Experimental part

Materials

Toluene solvent (E. M. Science) was first purified on Na in the presence of benzo-phenone as indicator, and then distilled and collected under Ar.

Styrene (Chevron), *p*- and *m*-MeS (Aldrich), 2,4- and 2,5-diMeS (Aldrich) and 2,4,6-triMeS (Aldrich) were first refluxed on $LiAlH_4$ at 40 - 80°C for 4 h, and then distilled under reduce pressure.

Phenylboric acid (Aldrich) was dried under vacuum until constant weight. $AlMe_3$ (2.0 M in toluene) was used without purification. To obtain $Cp*TiCl_3$, $Cp*SiMe_3$ was pro-cessed according to the procedure by Yamamoto *et al.* [32]. For comparison pur-poses, syndiotactic polystyrene was also synthesized using $InTiCl_3$ and $Cp*Ti(OAc)_3$. These catalysts were prepared according to Ready *et al.* [33] and Mena *et al.* [34], respectively.

The MAO cocatalyst was prepared following Arribas *et al.* [35] The procedure was as follows: in a 300 ml glass flask, previously dried and purged with Ar, 58 ml of phenyl-boric acid (0,1 M in toluene) and 5 ml of $AlMe_3$ (2 M in toluene) were added, under continuous agitation and at -10°C. MAO obtained was active in styrene poly-merization when [Al]/[B] = 1.8 was used.

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Polymerization procedure

When using Cp*TiCl₃, the same homopolymerization conditions were used with all investigated monomers .The synthesis of sPS is described in what follows. First, the cocatalyst was prepared in a glass reactor. Then, 4.4 ml (41,6 mmol) of styrene were introduced in the same glass reactor at 50°C with mechanical stirring. After 5 min, 2.1 ml (20.8 μmol) of a 10 μM semimetallocene catalyst solution were added. The reaction was stopped after 5 h, by addition of HCl. The polymer was washed with ethanol and dried in vacuum at room temperature.

The copolymerization experiments were identical to that described, except for the addition order of the comonomers. First, the catalyst solution was added to a mixture of styrene/MAO in toluene maintained at 50°C. Immediately after, the second co-monomer was added. The styrene/comonomer ratio in the final polymer depends on the styrene/comonomer ratio in the reaction feed.

^{13}C NMR was used to determine the stereoregularity of the obtained homopolymers and the global composition and microstructure in the case of the copolymers. A JEOL Eclipse 270 spectrometer at 67.94 MHz was used. The sample was dissolved in CDCl₃, tetramethylsilane was the internal standard, and during the analysis the solution was maintained at 60°C.

The molecular weight distribution was determined by gel permeation chromatography using a Waters 991 chromatograph equipped with Zorbax PSM60S and PSM1000S columns, a refractive index detector, and a Waters 717 injector. The molecular weight calibration was carried out with narrow (atactic) polystyrene standards.

Except the poly(*m*-MeS), all samples were soluble in hot chloroform (J. T. Baker, HPLC grade). The sPS sample was soluble in hot chloroform but insoluble at room temperature. Poly(*m*-MeS) was insoluble both in hot chloroform and in tetra-hydrofurane.

Differential scanning calorimetry was carried out using a Perkin Elmer DSC-7. The analyses were performed under a nitrogen flow. Each analysis involved a heating-cooling-heating cycle from 30 to 300°C at 10°C/min.

Final remarks

For the investigated homopolymerizations, the following reactivity order was ob-served: S ≥ *p*-MeS > *m*-MeS >> 2,4-diMeS ≥ 2,5-dimeS > 2,4,6-triMeS. A rather high syndiotacticity was observed in the homopolymers of styrene and monomethyl-substituted styrenes. For the di- or trisubstituted styrene homo- and copolymers, both stereoregularity and conversions are considerably lower due to their strong steric and electronic interaction with the active catalyst sites.

The copolymerization of styrene with monosubstituted styrene derivatives yield random copolymers with a significant crystallinity, as a consequence of the persistence of the stereoregular enchainment. The incorporation of substituted styrene units increase the average molecular weights, thus indicating a stabilization of the active sites towards the transfer reactions.

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