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Styrene/(substituted styrene) copolymerization by Ph_2Zn–metallocene–MAO systems: Synthesis and characterization of poly(styrene-*co*-*p*-hydroxystyrene) copolymers[☆]

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Abstract

Poly(styrene-*co*-*p*-*tert*-butyldimethylsilyloxystyrene) copolymers, P(S/*p*-TBDMSOS), with contents in the substituted comonomer within the 0–50% range were prepared using combined Ph_2Zn–$CpTiCl_3$–MAO initiator systems and some of them were used as precursors of poly-(styrene-*co*-*p*-hydroxystyrene), P(S/*p*-HOS), copolymers. *p*-*tert*-Butyldimethylsilyloxystyrene was synthesized from *p*-hydroxybenzaldehyde by protecting the hydroxyl group with *tert*-butyldimethylchlorosilane and converting the aldehyde group into vinyl through the Wittig reaction. The P(S/*p*-TBDMSOS) copolymers with contents in substituted units equal or higher than 25% were atactic and those with content higher than 5% were amorphous. P(S/*p*-HOS) copolymers containing up to 20% of hydroxylated units were obtained by full hydrolysis in acidic medium of the corresponding P(S/*p*-TBDMSOS). The hydroxylated copolystyrenes displayed crystallinity for the whole range of studied compositions and their crystalline structure was essentially similar to that of s-PS homopolymers. The influence of the substituent on the modified-MAO catalyzed copolymerization and on the thermal properties of the resulting copolymers was comparatively examined.

Keywords: Styrene/(substituted styrene) copolymerization; Metallocene catalysts; Hydroxylated polystyrene

1. Introduction

Since the discovery of syndiotactic polystyrene in the eighties [1–5], several research groups have been working on the stereoregular homo- and copolymerization of styrene with the aim of improving the polymer properties and elucidating the mechanism of the stereospecific styrene polymerization. In general, titanium complex compounds, particularly titanocenes, in combination with methylaluminoxanes (MAO), are well known catalytic systems able to produce efficiently syndiotactic polystyrene (s-PS). Schellenberg and Tomotsu [6] reported a large number of transition metal complexes, which combined with MAO can be used to produce s-PS.

More recently, efforts have been centered on homo- and copolymerization of substituted/functionalized styrene with the aim of obtaining polymers or copolymers useful for compatible blends. Regarding metallocene polymerization, half-metallocene $IndTiCl_3$ and MAO were used to obtain poly (styrene-*co*-*p*-hydroxystyrene) through hydrolysis of the corresponding poly(styrene-*co*-*p*-*tert*-butyldimethylsilyloxystyrene) precursor. The protected *p*-hydroxystyrene was prepared by the "Wittig-type" reaction using *p*-hydroxybenzaldehyde with

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the hydroxyl group protected with *tert*-butyldimethylchlorosilane (the "Tebbe" reagent) [7]. On the other hand, Kim and Do [8], reported the synthesis of syndiotactic poly(*p*-hydroxystyrene) after hydrolysis of poly(*p*-*tert*-butyldimethylsilyloxystyrene), which was obtained by using Cp*Ti(TEA) as catalyst. They claimed that the polymer obtained is unattainable by traditional methods.

The copolymerization of several styrene/substituted styrenes, S/*p*-alkylS, S/*p*-MeOS, S/*p*-halideS, S/di-MeS, S/tri-MeS, and also S/α-MeS and other styrene/(styrene derivative) pairs initiated by Ph_2Zn–metallocene–MAO initiator has been extensively studied by our group for years [9]. In these studies it was firmly established that both the nature of the substituent and its position either on the aromatic ring or on the vinyl group, critically affects both the conversion of the reaction and the nature of the copolymer that is produced. In the present paper we wish to report on the copolymerization of styrene/(*p*-*tert*-butyldimethylsilyloxystyrene) (S/*p*-TBDMSOS) using our Ph_2Zn–$CpTiCl_3$–MAO initiator system and starting from feeds with different comonomer ratios. This research was undertaken with the aim of evaluating the efficiency of this system to produce polystyrenes with bulky attached groups and to see how the copolymer structure and properties become affected by the nature of the comonomer. After hydrolysis by acids the corresponding poly(styrene-*co*-*p*-hydroxystyrene)s were obtained.

2. Experimental

The polymerization reactions, purification and handling of styrene monomer and solvents were done according to a previously reported procedure [9–11]. Homo- and copolymerization experiments were carried out in an argon atmosphere in a 100 mL Schlenk tube equipped with a magnetic stirrer. Solvent toluene (ca. 10–30 mL), MAO solution, Ph_2Zn and metallocene solutions in toluene were charged sequentially by syringe under argon pressure. Polymerization was initiated by injecting either the styrene followed by the comonomer or both of them simultaneously. The reactions were kept at 60 °C under stirring for the required length of time. Polymerization was ended by adding a mixture of hydrochloric acid and methanol. The polymers coagulated in the acidified methanol were recovered by filtration after washing several times with methanol, and the filtrate was dried under vacuum at 60 °C.

Gel permeation chromatograms were acquired at 35 °C with a Waters instrument equipped with two styragel columns of styrene–divinylbenzene. Tetrahydrofuran was used as eluent and calibration was made against polystyrene standards. Differential scanning calorimetric (DSC) analyses were performed using a Rheometric Scientific or a Perkin–Elmer Pyris 1 DSC apparatus with the samples placed under a nitrogen atmosphere; 3–4 mg of samples were heated at a rate of 10 °C min^{-1}, and after cooling to room temperature, reheated at the same rate. T_g and T_m were recorded on the second heating scan. Thermogravimetric analyses (TGA) were carried out under a nitrogen atmosphere on a Perkin–Elmer TGA-6 thermobalance at a heating rate of 10 °C min^{-1}.

NMR spectra were recorded on a Bruker Avance DRX-250 and AMX-300 spectrometers at 70 °C, operating at 250.1, 300.1 and 62.9, 75.5 MHz for ^1H and ^{13}C, respectively. The polymers and copolymers were dissolved in deuterated benzene (1–5% w/v). A total of 64 and 4000 scans with 16K and 32K data points and with a relaxation delay of 1 and 2 s were collected for ^1H and ^{13}C, respectively. Chemical shifts were calibrated with tetramethylsilane (TMS) as internal reference or the residual solvent peak (7.16 ppm for ^1H and 128.1 ppm for ^{13}C). X-ray diffraction patterns were obtained from synthesis powders with a modified Statton camera using Nickel-filtered Cu Kα radiation of wavelength 0.1542 nm and they are not calibrated.

The functionalized *p*-*tert*-butyldimethylsilyloxybenzaldehyde (*p*-TBDMSOB) was prepared according to procedure reported by Kim et al. [7,8]. To a suspension of 14.65 g (0.12 mol) of 4-hydroxybenzaldehyde in 200 mL of CH_2Cl_2, 17.0 mL (0.12 mol) of triethylamine were added and the mixture was stirred at room temperature for 30 min. A 0.6 M solution of *tert*-butyldimethylsilyl chloride (18.09 g, 0.12 mol) in CH_2Cl_2 was then added dropwise. The mixture was kept at room temperature under stirring for 12 h, and the reaction was stopped by adding 75 mL of water. The organic phase was separated, washed repeatedly with water, dried over anhydrous $MgSO_4$, filtered and concentrated to yield 27.7 g (98%) of a yellow oily liquid. *p*-TBDMSOS was obtained from *p*-TBDMSOB by the methodology employed by Ito et al. [12], based on the Wittig olefination [13,14]. A solution of 27.89 g (0.07 mol) of methyltriphenylphosphonium iodide in 100 mL of dry THF was placed in a 500 mL three-necked round-bottom flask equipped with a reflux condenser and a dropping funnel, and 7.74 g (0.07 mol) of potassium *tert*-butoxide were added. The suspension was stirred and kept at 0 °C for 1 h, when the mixture turned an intense yellow color. A solution of 13.59 g (0.06 mol) of *p*-TBDMSOB in 100 mL of THF was then added dropwise and the mixture was stirred overnight, filtered and washed thoroughly with THF. The collected organic fraction was concentrated, yielding a reddish viscous liquid which was purified by flash chromatography: mobile phase, hexane.

p-TBDMSOS was copolymerized with styrene as indicated above. The copolymer product was deprotected by acid hydrolysis to the corresponding copolymer consisting of styrene and *p*-hydroxystyrene units, P(S/*p*-HOS). The deprotection was performed following a previously reported procedure [12,15,16]. In brief, silylated homo- or copolymers (0.2 g) were dissolved in THF (30 mL), acidified with concentrated HCl (5 mL), and the mixture was refluxed for 4 h. The resulting hydroxylated copolymers were recovered by precipitation with cold methanol and dried under vacuum at 60 °C.

3. Results and discussion

Table 1 shows the results obtained in the copolymerization of styrene/(*p*-*tert*-butyldimethylsilyloxystyrene) for initial

Table 1
Styrene/*p*-*tert*-butyldimethylsilyloxystyrene, S/(*p*-TBDMSOS), copolymerization initiated by $Ph_2Zn-CpTiCl_3-MAO$[a]

P(S/TBDMSOS)	S/*p*-TBDMSOS (mol%)[b]		Molecular weight		Reaction results		
	Feed	Copolymer	M_n[c]	M_w[c]	Yield (%)	A[d]	A/A_0[d]
100/0	100/0	100/0	–	–	35.4	60.8	1.00
95/5	94.4/5.6	96.0/4.0	19,300	36,800	30.1	56.0	0.92
90/10	90.5/9.5	91.0/9.0	22,200	39,500	31.3	60.6	0.99
85/15	85.1/14.9	86.0/14.0	16,300	30,600	18.9	39.4	0.65
80/20	79.3/20.7	78.0/22.0	10,300	24,500	17.7	38.9	0.64
75/25	74.9/25.1	75.0/25.0	2700	19,500	3.6	8.1	0.13
50/50	49.1/50.9	48.0/52.0	7200	42,400	2.9	7.9	0.13

[a] Polymerization conditions: solvent: toluene; t: 6 h; T: 60 °C. Total volume = 20 mL; [S] + [*p*-TBDMSOS] = 2.0 mol L^{-1}; [MAO] = 0.33 mol L^{-1}; $[Ph_2Zn] = [CpTiCl_3] = 2.0 \times 10^{-4}$ mol L^{-1}.

[b] Composition in the feed and in the copolymer as determined by NMR.

[c] Average molecular weights determined by GPC in THF. s-PS data are not given because of the non-solubility of this polymer in THF.

[d] Activity (A) expressed in (kg copolymer)·(mol metallocene)$^{-1}$ (h)$^{-1}$ and relative activity (A/A_0) referred to that of styrene arbitrarily defined as equal to 1.

comonomer molar ratios ranging from 0 up to 50%. Composition results obtained by NMR analysis reveal that the molar ratios of the feeds were essentially maintained in the respective resulting copolymers for all of the compositions analyzed. The molecular weights of the resulting copolymers were fairly high but diminished significantly when the content of the copolymer in the silylated monomer attained 25%, which was accompanied by a noticeable increase in polydispersity. Yield data indicate that conversion to copolymer also decreased as the proportion of *p*-TBDMSOS in the initial feed increased. Accordingly, the catalyst activity steadily decayed from the reference value of 1 assigned to homopolymer s-PS to below 50% for the copolymers with higher contents in *p*-TBDMSOS.

Fig. 1 shows the ^{1}H NMR spectra obtained for the whole set of P(S/*p*-TBDMSOS) copolymers prepared in this work. The copolymer composition was calculated by integration of the methine and methylene main chain peaks appearing at 2.1 and 1.5 ppm, respectively, and the methyl peaks of the *tert*-butyldimethylsilyl group appearing at 0.2 and 1.05 ppm. The tacticity of the resulting copolymers is reflected in the complex signal appearing around 45 ppm in the ^{13}C NMR spectrum, which arises from the stereotopic main chain methylene. In Fig. 2, the spectral region containing the CH_2 signal is enlarged

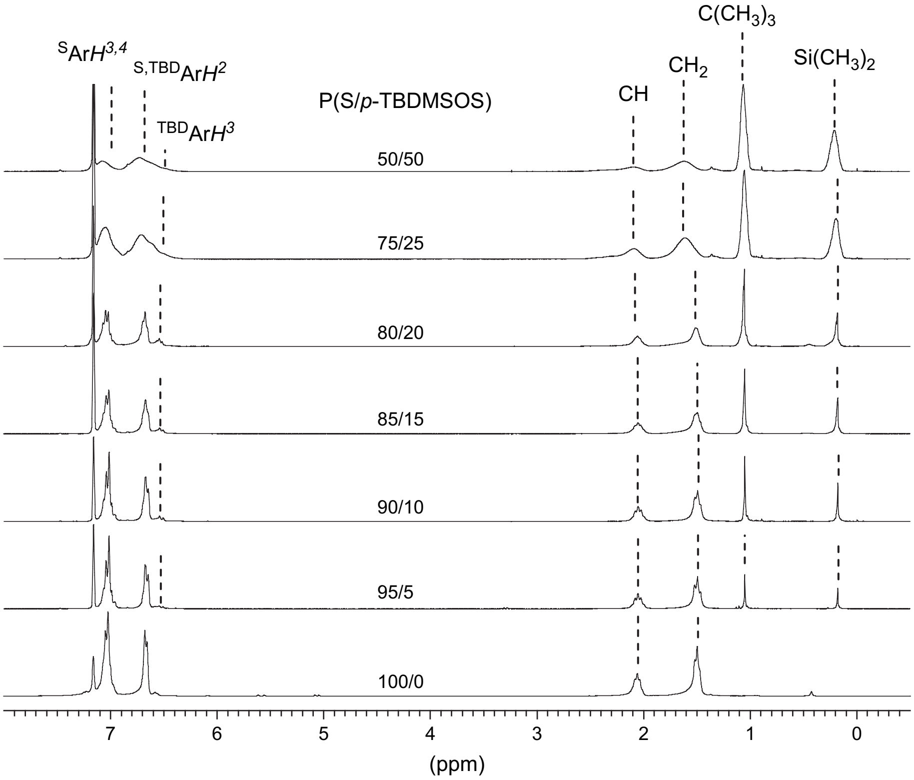

Fig. 1. ^{1}H NMR spectra in C_6D_6 at 70 °C of P(S/*p*-TBDMSOS) copolymers.

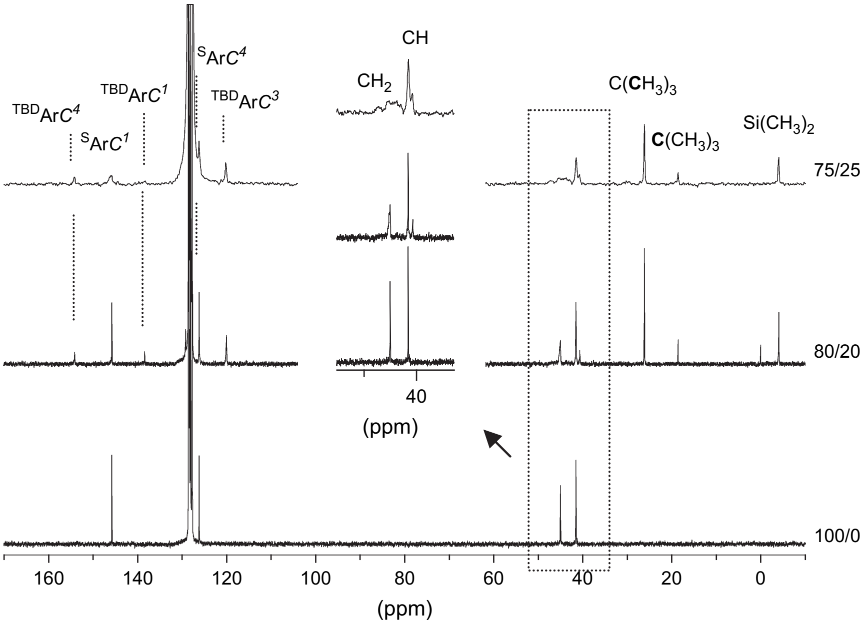

Fig. 2. ^{13}C NMR spectra in C_6D_6 at 70 °C of P(S/*p*-TBDMSOS) copolymers. Inset: Region of methylene and methine main chain carbons.

and compared to copolymers with 80/20 and 75/25 compositions, as well as for homopolymer s-PS. The higher complexity and broadness of the signal displayed in the spectrum of 75/25 copolymer are taken as a clear evidence of its atactic nature. On the contrary, a signal composed of sharp peaks with a definition comparable to those observed for syndiotactic polystyrene is seen in the spectrum of 80/20 copolymer indicating that a stereoregular microstructure is present for this composition.

The DSC and TGA traces of some selected P(S/*p*-TBDMSOS) copolymers are shown in Fig. 3. All show high thermal stability with onset decomposition temperatures near to 390 °C that decreased significantly with increasing content in the substituted comonomer. Decomposition takes place in one stage at a maximum rate temperature near 420 °C, with complete evaporation of the decomposition products. In some cases, a weak weight loss was seen at low temperature (~100 °C), which is thought to be due to humidity or due to small amounts of residual monomers present in the copolymer that is being analyzed.

Slope changes accompanied by enthalpy relaxation peaks characteristic of glass transition are clearly seen on the first heating DSC traces in all cases. The influence of comonomer composition on T_g is practically undetectable in contrast with the effect observed on crystallinity. The DSC traces of 90/10 and 80/20 copolymers do not show any melting peak, which must be taken as indicative of their amorphous nature.

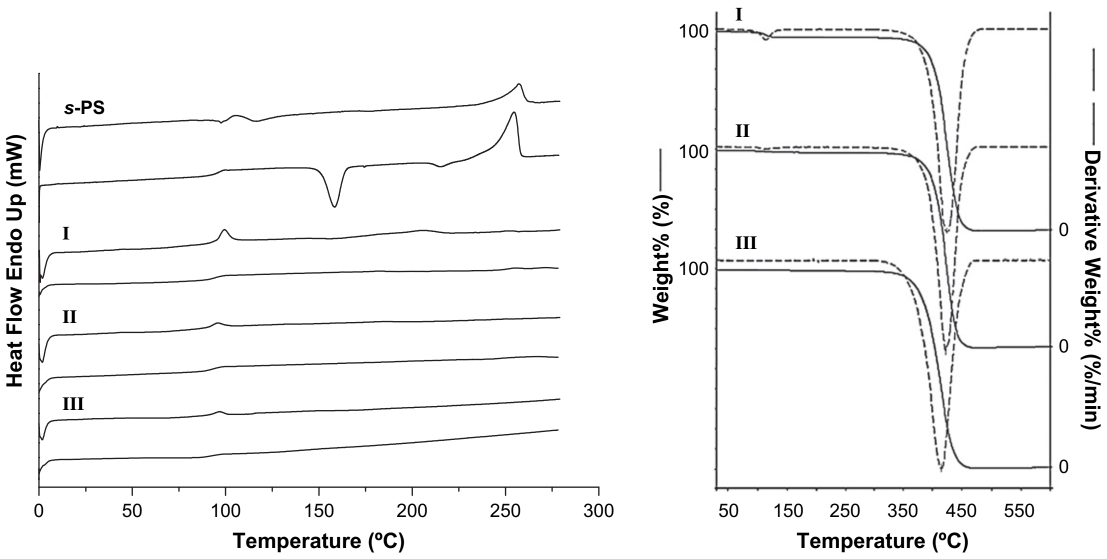

Fig. 3. DSC (first and second runs) and TGA traces of P(S/*p*-TBDMSOS) copolymers for the following comonomer molar ratios: (I) 95/5; (II) 90/10; (III) 80/20. The DSC traces recorded from s-PS homopolymer have been included for comparison.

Table 2
Thermal properties and X-ray spacings of protected P(S/*p*-TBDMSOS) and unprotected P(S/*p*-HOS) copolymers

	DSC			TGA			X-ray spacings[c] (Å)						
	T_m (°C)	ΔH_m (J/g)	T_g (°C)	T_d (10%)	T_d[a] max	W[b] (%)							
P(S/p-TBDMSOS)													
100/0	257	31	96	395	432	2	11.1m	8.7m	6.3vw	5.2m	4.4s	3.9m	–
95/5	205	17	94	388	425	0	10.7w	8.7vw	–	5.0vw	4.4m	3.9w	–
90/10	–	–	94	390	422	1							
85/15	–	–	94	393	429	2							
80/20	–	–	93	378	418	1							
75/25	–	–	93	383	420	0							
50/50	–	–	93	387	430	1							
P(S/*p*-HOS)													
95/5	250	25	101	386	422	0	10.7m	8.7vw	6.7w	5.5w	4.4s	3.8m	–
90/10	249	26	103	384	421	0	10.7m	8.7vw	6.7w	5.5w	4.4s	3.8m	–
80/20	239	12	113	385	421	0	10.4m	8.9m	–	5.7m	4.6s	3.8vs	3.2vw

[a] Temperature of maximum degradation rate.
[b] Remaining weight at the end of decomposition step.
[c] Bragg spacings measured in powder samples; visual intensities denoted as m: medium; s: strong; w: weak and vw: very weak.

A similar behavior should be reasonably expected for copolymers with higher contents in the substituted comonomer (≥75%), a prediction additionally supported by the atactic nature of these copolymers. Only the 95/5 P(S/*p*-TBDMSOS) copolymer corresponding to a comonomer ratio in the feed of 94.4/5.6 was found to be slightly crystalline with a $T_m = 205$ °C and a melting enthalpy of 17 J g^{-1}. The sterical effect of *p*-TBDMSOS on chain packing should be invoked to explain the fact that crystallization is fully repressed in the syndiotactic P(S/*p*-TBDMSOS) copolymers when concentration in these units is higher than ca. 5%. Table 2 summarizes thermal properties observed for these copolymers.

^{1}H NMR spectra of copolymers P(S/*p*-HOS) prepared by hydrolysis are shown in Fig. 4. The full disappearance of the methyl group signals corresponding to the $Si(CH_3)_2C(CH_3)_3$ protecting group (viz. $Si(CH_3)_2$ and $C(CH_3)_3$ protons at 0.26 and 1.15 ppm, respectively, in these spectra), indicates that hydrolysis of the starting copolymers has been almost completed.

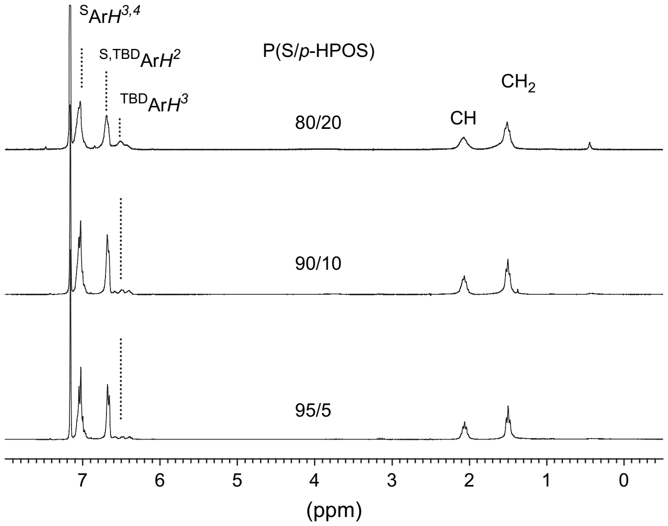

Fig. 4. ^{1}H NMR spectra of P(S/*p*-HOS) copolymers obtained after acid hydrolysis of the corresponding P(S/*p*-TBDMSOS).

The thermal analysis (Fig. 5) of the hydroxylated copolymers P(S/*p*-HOS) afforded results clearly different from those obtained for the parent protected copolymers. TGA revealed that P(S/*p*-HOS) copolymers continue to be thermally stable showing decomposition temperatures not far from those observed for P(S/*p*-TBDMSOS) displaying a similar weight loss profile. On the other hand, the DSC analysis showed that all the prepared hydroxylated copolymers are semicrystalline, with T_m and T_g higher than that of the copolymers from which they are derived. They display well defined endothermic peaks at T_m values ranging from 239 to 250 °C, which are very close to that of unsubstituted s-PS. Apparently, removal of the bulky *p-tert*-butyldimethylsilyloxy group allows crystallization of the copolymers. As expected, melting temperature and enthalpy of P(S/*p*-HOS) copolymers were observed to decrease as the *p*-hydroxystyrene unit content in the copolymer increased. Conversely the corresponding T_gs tend to increase indicating that although the copolymers crystallized more defectively, their mobility in the amorphous phase became more restricted as a result of the increased density of hydrogen bonds.

The X-ray diffraction analysis confirmed DSC results and afforded additional insight into the influence of copolymerization on the crystalline structure of the copolymers. The Bragg spacings measured for the copolymers are compared in Table 2 and a selection of powder diffraction patterns together with the pattern of s-PS homopolymers is shown in Fig. 6 for illustration. As it is seen, P(S/*p*-TBDMSOS) copolymers containing 10% or more of *p*-TBDMSOS did not yield discrete scattering as should be expected for polymers in the amorphous state. On the other hand, semicrystalline patterns displaying rather sharp rings were obtained from P(S/*p*-TBDMSOS) copolymer with a content of 5% in *p*-TBDMSOS. This result evidences the strong distorting influence of the bulky *p*-TBDMSO group on the packing of PS chains, as it was pointed out above. On the contrary, hydroxylated copolymers produced

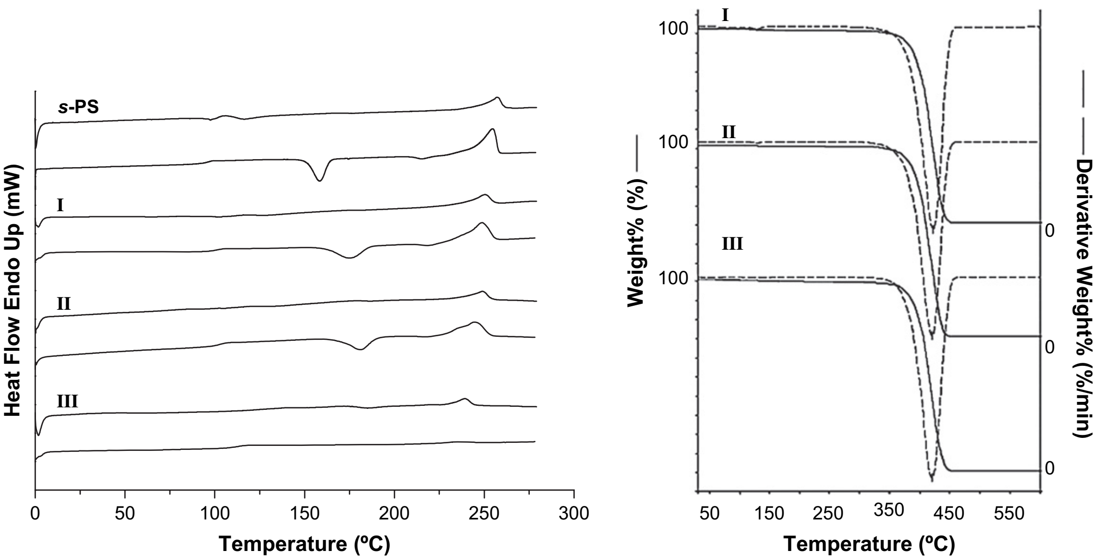

Fig. 5. DSC (first and second runs) and TGA of P(S/*p*-HOS) copolymers obtained from P(S/*p*-TBDMSOS) copolymers with the following nominal comonomer molar ratios: (I) 95/5; (II) 90/10; (III) 80/20. The DSC traces recorded from s-PS homopolymer have been included for comparison.

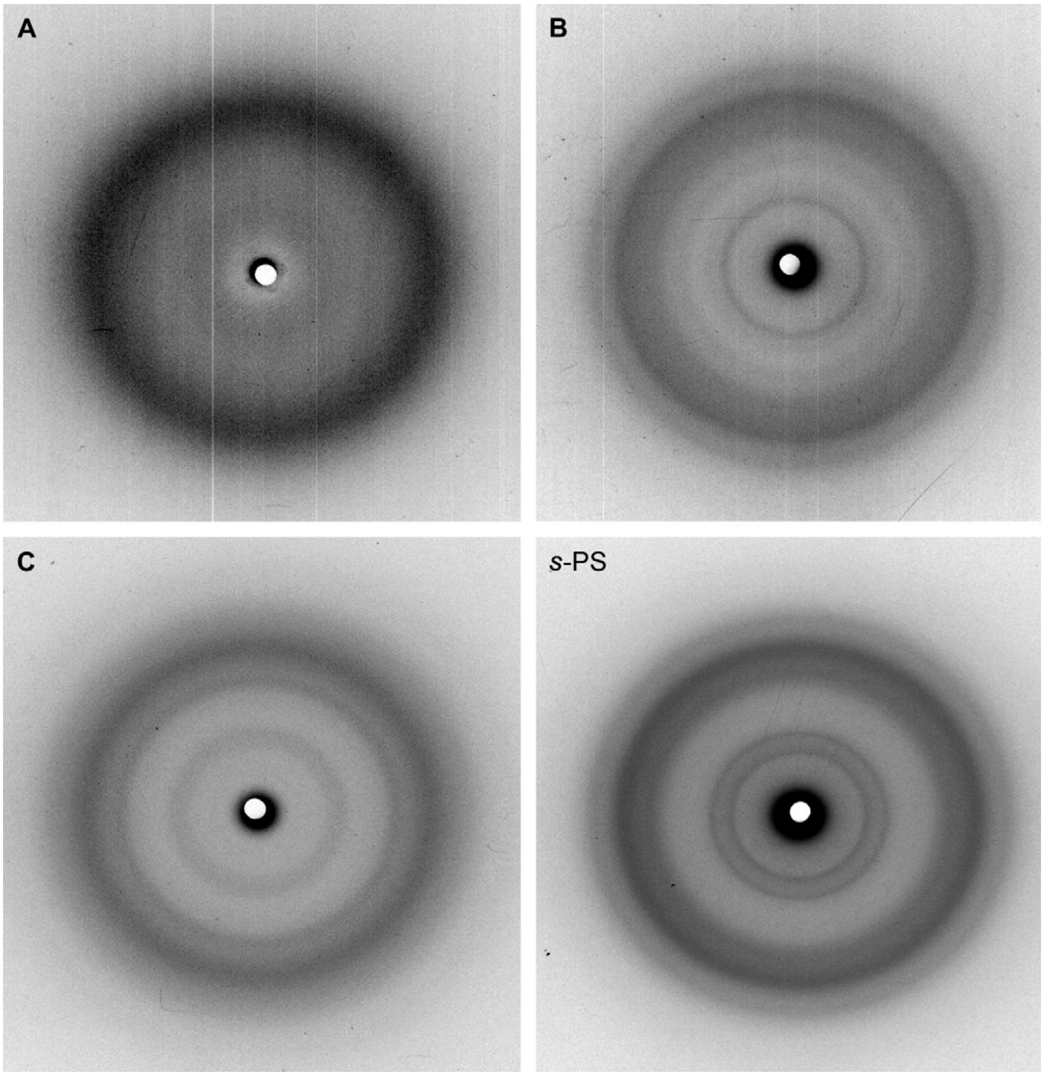

Fig. 6. Powder X-ray diffraction patterns of s-PS and copolymers. A: P(S/*p*-TBDMSOS) (90/10); B: P(S/*p*-HOS) 90/10; C): P(S/*p*-HOS) (80/20) and s-PS.

semicrystalline patterns for all the compositions examined. Obviously the comparatively small OH group is much less disturbing than the *p*-TBDMSO group so that hydroxylated s-PS copolymers are able to crystallize for a wide range of compositions. Comparison of the Bragg spacings for the semicrystalline copolymers and s-PS leads to the conclusion that the crystal structure of the homopolymers is essentially preserved in the P(S/*p*-HOS) copolymers with hydroxylated comonomer contents below 20%. As expected, the deviations observed in Bragg spacings are greater as the S/*p*-HOS ratio decreased. This result can be interpreted as the crystallites in these copolymers are made of homogeneous segments of s-PS, the substituted units being rejected to the amorphous phase. P(S/*p*-HOS) containing 20% of hydroxylated unit deserves particular consideration since spacing deviations are much larger. Such deviations could be explained by assuming that the *p*-HOS units are now entering in the crystalline phase and induce a dimensional change in the original crystal lattice. This is in agreement with the lower melting temperature and enthalpy observed for this polymer. Nevertheless, the occurrence of a new crystal structure different from that of s-PS should not be discarded.

4. Conclusions

According to the results shown above we can conclude that:

(a) Ph_2Zn–$CpTiCl_3$–MAO is an effective initiator system for the copolymerization of styrene/(*p*-*tert*-butyldimethylsilyloxystyrene), the resulting copolymers having a composition essentially similar to that of the correspondingly used feeds and a stereoregular microstructure for copolymers containing less than 25% comonomer.

(b) The acidic treatment of the poly(styrene-*co*-*p*-*tert*-butyldimethylsilyloxystyrene) promotes the complete hydrolysis of *p*-TBDMSOS groups leading to hydroxylated copolymers poly(styrene-*co*-*p*-hydroxystyrene), which cannot be obtained in high molecular weights by direct copolymerization of styrene and *p*-hydroxystyrene.

(c) The hydroxylated copolymers are semicrystalline displaying higher melting temperature and enthalpy than the protected copolymers and they adopt the crystal structure of s-PS, which becomes significantly distorted when the content in hydroxylated styrene units is 20%.

Acknowledgments

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