Synthesis and Characterization of Syndiotactic Styrene−Ethylene Block Copolymers

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ABSTRACT: Six samples of styrene−butadiene block copolymers (sPS−B **1**−**6**) containing a range of styrene molar fractions (x_S = 0.9−0.16) were prepared using MAO-activated $CpTiCl_3$ and converted to the corresponding styrene-1-butene-ethylene terpolymers (sPS−PE, **1h**−**6h**) through the selective hydrogenation of the unsaturated butadiene segments with *p*-toluenesulfonhydrazide. The monomer compositions and chemical microstructures of the sPS−PE copolymers were determined by ^{1}H NMR (x_S = 0.93−0.1) and ^{13}C NMR, respectively. The chemical shift assignments of the monomer tetrads (SSSS, SSEE, EESE, EEbE, EEEE, SEES, EEES; S = styrene, E = ethylene, b = 1-butene) were also determined by ^{13}C NMR as well as the average monomer block lengths (n_S = 72−4; n_E = 2−51). The block structure of the sPS−PE copolymers was further confirmed by DSC (differential scanning calorimetry), WAXD (wide-angle X-ray diffraction), and solid-state CP-MAS ^{13}C NMR (cross polarization magic angle spinning) analysis. The sPS−PE samples with high styrene content (x_S = 0.93−0.43) exhibit melting points in the range of 242−200 °C, and the sPS homosequences are observed in the crystalline "δ-clathrate" form. At low styrene content and short average sPS block lengths (x_S = 0.1; n_S = 4) the styrene domains are largely amorphous. Crystalline blocks of polyethylene were identified in the samples with long average block lengths (n_E = 21−51) by means of X-ray powder diffraction and solid-state CP-MAS ^{13}C NMR. In general, the initial crystallinity of the polyethylene blocks is lower than would be expected on the basis of the chemical composition of samples **1h**−**6h** but can be increased with thermal treatment, which produces the polyethylene orthorhombic crystalline form.

Introduction

Styrene−ethylene (S−E) copolymers synthesized using single-site, homogeneous Ziegler−Natta catalysts are being increasingly studied for their interesting properties and for the practical applications expected for these materials. For example, S−E diblock copolymers have been used as compatibilizing agents for blends of polystyrene and poly-α-olefin.[1] Recently, hydrogenated styrene−butadiene copolymers have been investigated as compatibilizing agents for blends of syndiotactic polystyrene (sPS) and several olefin homo- and copolymers.[2]

Heterogeneous Ziegler−Natta catalysts commonly employed in the synthesis of isotactic poly-α-olefins are not generally suitable for the synthesis of S−E copolymers. In addition to low activity, these catalysts only incorporate small amounts of styrene, primarily as isolated units.[3] The discovery of homogeneous, Ziegler−Natta systems based on stereorigid *ansa*-zirconocenes and half-sandwich group 4 metal metallocenes[4] allowed S−E copolymers to be obtained for the first time in 1990.[5] Over the past decade, S−E copolymers have been synthesized with a variety of compositions and structures, and with properties ranging from amorphous elastomers to crystalline thermoplastics.[6] Unfortunately, sPS and/or polyethylene (PE) are frequently obtained as byproducts, making the characterization of the copolymer difficult.

The first report on the synthesis of the S−E copolymers using group 4 metal metallocenes was made by our laboratories in the early 90's.[5] This research demonstrated that styrene−ethylene copolymerizations can be successfully carried out using MAO-activated $CpTiCl_3$ at different Al/Ti ratios and with a variety of monomer feed compositions. The polymer products consist of a mixture of PE and *pseudo*-random S−E copolymers that contain a maximum of 35 mol % styrene. The microstructure, as determined by ^{13}C NMR, consists of isolated styrene units and isolated SES triads, spanned by polyethylene sequences. Analysis by X-ray powder diffraction revealed the presence of crystalline PE sequences with melting points in the range of 110−122 °C. This corresponds to an average methylene block length $(CH_2)_n$ of n = 11−17.[7]

Kakugo et al. first reported the synthesis of isotactic poly(styrene-*alt*-ethylene), which is obtained as a mixture with sPS, using the "Cp-free" compound, 2,2′-thiobis(6-*tert*-butyl-4-methylphenoxy)titanium dichloride and MAO as the catalyst system.[8] This S−E copolymer was reported to have a melting point of 145 °C. Since this discovery, the same material has been obtained by several researchers with MAO-activated C_2 and C_s symmetric *ansa*-zirconocenes.[9] In particular, Oliva et al. succeeded in obtaining high molecular weight isotactic alternating S−E copolymers that could be stretched into fibers. The structure of the fibers was determined by X-ray diffraction and found to consist of a *zigzag* planar chain conformation in which the phenyl groups are perpendicular to the main chain axis.[10]

Constrained geometry catalysts have also been successfully employed in the synthesis of *pseudo*-random S−E copolymers.[11] The open ligand environment readily allows the incorporation of bulky comonomers, but precludes the formation of styrene homopolymers. Equally important is the fact that ethylene homo-

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Table 1. Data for SPS−B (1−6) and SPS−PE (1h−6h) Copolymers

samples	copolymer composition in diads (molar fraction)[a]	copolymer composition in molar fractions [b]	average monomer block lengths[c]	mp[d] (°C)	samples	copolymer composition in triads (molar fraction)[e]		copolymer composition in molar fractions[f]	average monomer block lengths[g]	mp[d] (°C)
1	SS = 0.89 SB + BS = 0.02 BB = 0.09	$x_S = 0.90$ $x_{B+V} = 0.10$	$n_S = 90$ $n_{B+V} = 10$	$T_{m(S)} = 242$	**1h**	SSS = 0.93 EEE = 0.01 EES = 0.03	SSE = 0.03 SES = n.d. ESE = n.d.	$x_S = 0.93$ $x_E = 0.07$	$n_S = 72$ $n_E = 2$	$T_{m (S)} = 242$ $T_{m(E)} =$ n.d.
2	SS = 0.79 SB + BS = 0.12 BB = 0.09	$x_S = 0.85$ $x_{B+V} = 0.15$	$n_S = 14$ $n_{B+V} = 3$	$T_{m(S)} = 226$	**2h**	SSS = 0.59 EEE = 0.25 EES = 0.08	SSE = 0.06 SES = n.d. ESE = 0.02	$x_S = 0.66$ $x_E = 0.34$	$n_S = 14$ $n_E = 9$	$T_{m(S)} = 226$ $T_{m(E)} = 58$
3	SS = 0.60 SB + BS = 0.12 BB = 0.28	$x_S = 0.66$ $x_{B+V} = 0.34$	$n_S = 11$ $n_{B+V} = 6$	$T_{m(S)} = 212$	**3h**	SSS = 0.46 EEE = 0.37 EES = 0.08	SSE = 0.06 SES = n.d. ESE = 0.02	$x_S = 0.54$ $x_E = 0.46$	$n_S = 10$ $n_E = 11$	$T_{m(S)} = 212$ $T_{m(E)} = 60$
4	SS = 0.46 SB + BS = 0.16 BB = 0.38	$x_S = 0.54$ $x_{B+V} = 0.46$	$n_S = 7$ $n_{B+V} = 6$	$T_{m(S)} = 200$	**4h**	SSS = 0.36 EEE = 0.48 EES = 0.08	SSE = 0.04 SES = n.d. ESE = 0.04	$x_S = 0.43$ $x_E = 0.57$	$n_S = 7$ $n_E = 14$	$T_{m(S)} = 200$ $T_{m(E)} = 65$
5	SS = 0.18 SB + BS = 0.14 BB = 0.68	$x_S = 0.25$ $x_{B+V} = 0.75$	$n_S = 4$ $n_{B+V} = 11$	$T_{m(S)} =$ n.d.	**5h**	SSS = 0.14 EEE = 0.71 EES = 0.08	SSE = 0.03 SES = n.d. ESE = 0.05	$x_S = 0.20$ $x_E = 0.80$	$n_S = 4$ $n_E = 21$	$T_{m(S)} =$ n.d. $T_{m(E)}) = 76$
6	SS = 0.12 SB + BS = 0.08 BB = 0.80	$x_S = 0.16$ $x_{B+V} = 0.84$	$n_S = 4$ $n_{B+V} = 21$	$T_{m(S)} =$ n.d.	**6h**	SSS = 0.07 EEE = 0.86 EES = 0.04	SSE = 0.01 SES = n.d. ESE = 0.02	$x_S = 0.10$ $x_E = 0.90$	$n_S = 4$ $n_E = 51$	$T_{m(S)} =$ n.d. $T_{m(E)} = 84$

[a] S = styrene; B = 1,2- and 1,4-butadiene. In all copolymer samples the butadiene homosequences always include about 11 mol % of 1,2 butadiene. [b] The styrene and butadiene molar fraction (x_S and x_B) were determined by integrating the appropriate ^{1}H NMR resonances (see Experimental Section). [c] The average block lengths have been calculated on the basis of the following relationships: $n_S = [2SS/(SB + BS)] + 1$; $n_B = [2BB/(BS + SB)] + 1$ (see ref 15). [d] $T_{m(S)}$ = melting point of sPS homosequence; $T_{m(E)}$ = melting point of PE homosequence. [e] S = styrene; E = ethylene; b = 1-butene; n.d. = not detected. [f] The styrene and ethylene molar fraction (x_S and x_E) were determined by integrating the appropriate ^{1}H NMR resonances (see Experimental Section). [g] The average block lengths have been calculated using the equations of Scheme 2.

polymers are also not observed. However, these catalysts are only capable of producing S−E copolymers that contain up to 50 mol % of stereoirregular styrene units.

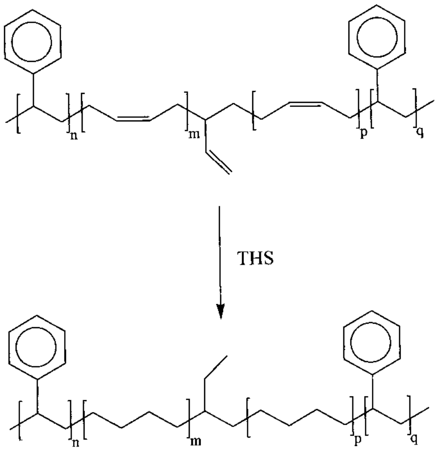
Recently, Xu et al. synthesized an isotactic poly(styrene-*alt*-ethylene) copolymer using $[\{(\eta^5:\eta^1\text{-}tert\text{-butyl-}(\text{dimethylfluorenylsilyl})\text{amido})\}\text{TiMe}]^+$.[12] The S−E copolymer was reported to have a melting point of 118 °C, a glass transition temperature (T_g) of 30 °C, and a weight-average molecular weight (M_w) in the range of 60 000−80 000.

To date, no S−E copolymers synthesized with homogeneous group 4 metallocene catalysts contain syndiotactic SS diads, even when the styrene composition approaches 50 mol % or syndio-specific styrene polymerization catalysts (e.g., $CpTiX_3$/MAO; X = halide, alkoxy;[13] $(C_5Me_5)Ti(CH_2Ph)_3/B(C_6F_5)_3$[14]) are employed. It has been suggested that the species generated with MAO-activated $CpTiX_3$, which promotes S−E copolymerization, is not the same species that polymerizes styrene to syndiotactic polymer.[13,14] As a result, the properties of S−E copolymers that contain blocks of sPS remain unexplored.

We recently described a procedure for synthesizing styrene−butadiene block copolymers (sPS−B), which contain blocks of sPS, using MAO-activated $CpTiCl_3$.[15] These copolymers contain highly stereoregular syndiotactic polystyrene segments spanned by polybutadiene (BR) blocks. The BR blocks consist of primarily *cis*-1,4 butadiene units with some isolated 1,2-butadiene. The molar concentration of the 1,2-butadiene groups was consistently found to be about 11 mol % of the total polybutadiene in the copolymer and independent of the amount of polybutadiene contained in the copolymer.

Here we describe the chemical conversion of sPS−B samples to the corresponding styrene-1-butene-ethylene terpolymers (sPS−PE) through the selective hydrogenation of the unsaturated polybutadiene segments. The full characterization of these novel S−E copolymers, which contain blocks of sPS, is also described.

Scheme 1



Results and Discussion

Six sPS−B copolymers samples (**1**−**6**; Table 1) containing a range of styrene molar fractions (x_S = 0.9−0.16) were prepared using MAO-activated $CpTiCl_3$, as described previously.[15] Selective hydrogenation was accomplished by treating these samples with *p*-toluenesulfonhydrazide (THS) in refluxing toluene. This quantitatively converted the sPS−B copolymers into the corresponding styrene−1-butene−ethylene terpolymers (sPS−PE, **1h**−**6h**; Table 1). The general structure of sPS−PE is pictured in Scheme 1.

The *cis*-diimide, produced in situ by the thermal decomposition of THS, readily reduces the unsaturated *cis*-1,4- and 1,2-butadiene copolymer segments, producing polyethylene sequences with isolated ethyl branches, while leaving the aromatic groups of the styrene comonomer intact.[16] The styrene molar fractions in samples **1h**−**6h** (x_S = 0.93−0.1; Table 1) were determined by integrating the appropriate ^{1}H NMR resonances (see Experimental Section). By comparing the ^{1}H NMR spectra of samples **1**−**6** with those of the corresponding hydrogenated samples (**1h**−**6h**), it was determined that the hydrogenation reaction is quantitative and that the copolymer samples remain intact.

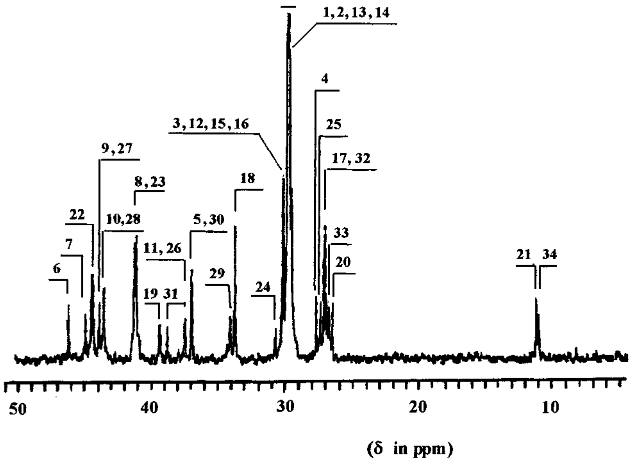


Figure 1. Aliphatic region of the ^{13}C NMR solution spectrum (125 °C, 1,1,2,2-tetrachloroethane-d_2) of the sPS−PE sample **3h**. The ^{13}C signals are labeled according to the numbering scheme used in Table 2.

A thorough investigation of the microstructure of copolymers **1h**−**6h** by ^{13}C NMR (Figure 1) permitted the resonances of the monomer tetrads (SSSS, SSEE, EESE, EEbE, EEEE, SEES, EEES; S = styrene, E = ethylene, b = 1-butene; Table 2) to be assigned. The assignments reported in Table 2 were based in part on the results of DEPT (distortionless enhancement polarization transfer) NMR experiments and by comparing the observed ^{13}C NMR chemical shifts with those reported in the literature. In particular, the ^{13}C NMR resonances for the EESE sequence (lines 2−6, Table 2) have been previously assigned in S−E copolymers synthesized using the CpTiCl$_3$/MAO catalyst system.[5] Furthermore, the resonances for the EEbE tetrad (lines 14−21, Table 2) have been assigned in styrene−1-butene−ethylene terpolymers produced by hydrogenating emulsion styrene−butadiene copolymers.[17] In general, S−E copolymers produced by metallocenes and emulsion styrene−butadiene copolymers synthesized with free radical initiators do not contain syndiotactic styrene homosequences. As a consequence, the chemical shifts of the ^{13}C NMR resonances of the SSEE tetrad, where the SS diad is syndiotactic, have not been reported in the literature. Sato and Tanaka quantified the difference that the stereochemical configuration (*m* or *r*) makes in the NMR chemical shifts of the SS diad by using the 6,8,10,12,14-pentaphenylnonadecane as a model.[18] All of the possible combinations of the chiral methines were synthesized and analyzed by ^{13}C NMR. The authors reported the chemical shifts of the carbons that are diagnostic of the SSEE tetrad (lines 8−11) based on their model compounds. The chemical shifts of the same carbons in the sPS−PE copolymers were found to be in agreement with Sato and Tanaka's results. It can be concluded from these results that both the original sPS−B samples (**1**−**6**) and the sPS−PE samples (**1h**−**6h**) contain isolated blocks of sPS.

Table 2. ^{13}C NMR Chemical Shifts of the Aliphatic Carbons Diagnostic for the Different Tetrads in the SPS−PE Copolymers

line	sequence[a]	observed chem shifts (ppm)	expected chem shifts (ppm)	ref
1	EEEE	29.63	29.63	5
2	E$_2$ESEE	29.63	29.63	5
3	EE$_1$SEE	30.11	30.08	5
4	EE$_2$SEE	27.85	27.54	5
5	EES$_1$EE	36.83	36.89	5
6	EES$_2$EE	46.00	45.94	5
7	S$_1$SEE	44.8	44	18
8	S$_2$SEE	41.18	41.05	18
9	SS$_1$EE	43.79	43.65	18
10	SS$_2$EE	43.42	43.26	18
11	SSE$_1$E	37.32	38	18
12	SSE$_2$E	30.11	30.08	5
13	SSEE$_1$	29.63	29.63	5
14	E$_1$EbEE	29.63	29.63	17
15	E$_2$EbEE	29.88	29.83	17
16	EE$_1$bEE	30.11	30.11	17
17	EE$_2$bEE	26.9	26.91	17
18	EEb$_1$EE	33.64	33.64	17
19	EEb$_2$EE	39.26	39.24	17
20	EEb$_3$EE	26.34	26.31	17
21	EEb$_4$EE	10.96	10.82	17
22	SS$_1$S	44.27	44.2	c)
23	SS$_2$S	41.06	41.1	c)
24	SEE$_1$S	30.57	33.15	5
25	SEE$_2$S	27.55	27.54	5
26	SE$_1$ES	37.32	38	18
27	S$_1$EES	43.79	43.65	18
28	S$_2$EES	43.42	43.26	18
29	Eb$_1$bE	33.97	33.96	17
30	Eb$_2$bE	36.83	36.87	17
31	Ebb$_1$E	38.66	38.92	17
32	E$_2$bbE	26.92	26.91	17
33	Eb$_3$bE	26.58	26.58	17
34	Eb$_4$bE	10.75	10.62	17

[a] To label the position of a particular carbon atom in a given sequence, the C_{ith} carbon atom of the ethylene (E), 1-butene (b), and styrene (S) units is correspondingly labeled as E_i, b_i, and S_i. The numbering is assigned according to the following scheme: E = $-C_1-C_2-$; b = $-C_1-C_2(C_3-C_4)-$; S = C_1-C_2-Ph.; e.g., b$_4$ stands for the C$_4$ carbon of the b unit. [b] Chemical shift values calculated and/or observed in model compounds, as reported in the corresponding references. [c] Chemical shift values observed in the sPS homopolymer (see, e.g.: Ishihara, N.; Seimiya, T.; Kuramoto, M.; Uoi, M. *Macromolecules* **1986**, *19*, 2464).

The chemical shifts reported in Table 2 can be used to calculate the methylene block lengths ($L_{\mathrm{CH_2}}$).[17] Samples **1h**−**6h** exhibit $(CH_2)_n$ sequences where n is odd (n = 1, 5, and longer). Even values (n = 2, 4, and longer) are not observed. For example, the $S_{\gamma\gamma}$[19] signal, which is diagnostic for $(CH_2)_n$, n = 5, is observed at 30.57 ppm. However, the $S_{\alpha\beta}$, and $S_{\beta\gamma}$ resonances which are diagnostic for $(CH_2)_n$, n = 2, 4, expected at 34.2−34.9 and 28.2 ppm, respectively, are not observed. This suggests that styrene and 1,2-butadiene units undergo a regioregular insertion during the polymerization process. In the syndiospecific polymerization of styrene with half-sandwich titanocene catalysts (activated with MAO) it is known that styrene insertion proceeds in a 2,1, or secondary, fashion in both the initiation step (styrene insertion into Ti−CH$_3$)[20] and subsequent propagation steps.[21] In the homopolymerization of butadiene with the same catalyst system it is known that the vinyl butadiene units also arise from a 2,1 insertion.[22] It is therefore likely that in the copolymerization of styrene and butadiene with CpTiCl$_3$/MAO, both the styrene and the vinyl butadiene units are incorporated via a regioregular 2,1 insertion (Scheme 1).

When the microstructure of the copolymer is defined at the triad level the average block lengths of the monomer homosequences (n_{S} and n_{E}) can be calculated using the equations reported in Scheme 2.[23]

Using these equations, the n_{S} and n_{E} block lengths can be calculated, assuming the concentrations of the different triads proportional to the corresponding resonances (Table 2). The values are reported in Table 1. The n_{S} values found in the sPS−PE samples **1h**−**6h** are in good agreement with the corresponding values

Scheme 2

$$n_S = \frac{\Sigma_i S_i}{\Sigma S_i} = \frac{[SSS] + [ESS] + [SSE] + [ESE]}{[ESE] + 1/2\,([ESS] + [SSE])}$$

$$n_E = \frac{\Sigma_i E_i}{\Sigma E_i} = \frac{[EEE] + ([EES] + [SEE]) + [SES]}{[SES] + 1/2\,([SEE] + [EES])}$$

determined in the sPS−B samples **1**−**6** and confirm that the ^{13}C NMR assignments made for both of the copolymer samples are correct. The presence of ethyl side branches in the polyethylene sequences of the hydrogenated copolymer samples produces n_E values that are lower than would be expected based on the mole fraction of polyethylene found in the copolymer.

The blocklike nature of the copolymer samples **1h**−**6h** is confirmed by thermal analysis (DSC). For example, inspection of the DSC profiles of sample **3h** ($n_S = 10$ and $n_E = 11$; Table 1) reveals the presence of two endothermic peaks, one at 212 °C and the other at 60 °C. These peaks can be assigned to the melting of the sPS and PE crystalline domains, respectively. The melting points of the sPS blocks in samples **1h**−**6h** range from 242 (**1h**, $n_S = 72$) to 200 °C (**4h**, $n_S = 7$). These values are lower than those found for highly syndiotactic high molecular weight sPS ($M_w = 200\,000$; $T_m = 273$ °C) or low molecular weight sPS ($M_w = 32\,000$; $T_m = 250$ °C).[24] It is noteworthy that the melting points of the sPS blocks observed in the hydrogenated samples (**1h**−**6h**) are identical to those observed in the corresponding sPS−B samples (**1**−**6**; Table 1). This suggests that replacing the amorphous polybutadiene domains with semicrystalline polyethylene does not induce significant morphological changes in the crystalline sPS domains of the sPS−PE copolymers.

The melting temperatures of the PE blocks were found to be in the range of 58 (**2h**, $n_E = 9$) to 84 °C (**6h**, $n_E = 51$). These values are significantly lower than that of highly crystalline PE ($T_m = 134$ °C) but are higher than the values found for the PE blocks in hydrogenated emulsion styrene−butadiene copolymers ($T_m = 42$ °C).[17]

Syndiotactic polystyrene exhibits a complex polymorphic behavior in the solid state. Four crystalline forms of sPS, known as α, β, γ, and δ, have been reported in the literature.[25] The α and β forms are found in a "*zigzag*" or "*all trans*" conformation,[26] whereas the γ and δ forms exhibit the 2(2/1) helix conformation.[27] The polymorphic behavior of sPS is further complicated by the fact that it is possible to produce clathrated forms when the α, γ, and δ crystalline forms are treated with either THF, or halogenated and/or aromatic solvents. Syndiotactic polystyrene homopolymers that are synthesized in, or recovered from toluene and dried under vacuum at 80 °C have been obtained in the δ clathrate form, as shown by X-ray.[28]

The α and β crystalline forms can be distinguished from the γ and δ forms by means of the solid-state CP-MAS ^{13}C NMR spectroscopy.[29] In the α and β forms of sPS all methylene carbons of the polymer backbone are spectroscopically equivalent, and a single resonance is found at 48.1 ppm in a 1:1 ratio with the methine carbon resonance found at 42.5 ppm. In the γ and δ forms, the 2(2/1) helix produces two methylene carbon environments which can be distinguished by solid state ^{13}C NMR. One of the methylene resonances is found at 37.3 ppm and the other at 40.3 ppm. Note that the latter resonance overlaps with the methine signal, which is also found at 40.3 ppm. In some cases, the δ clathrate form can be differentiated from the γ and δ forms by the presence of signals due to the clathrate solvent.

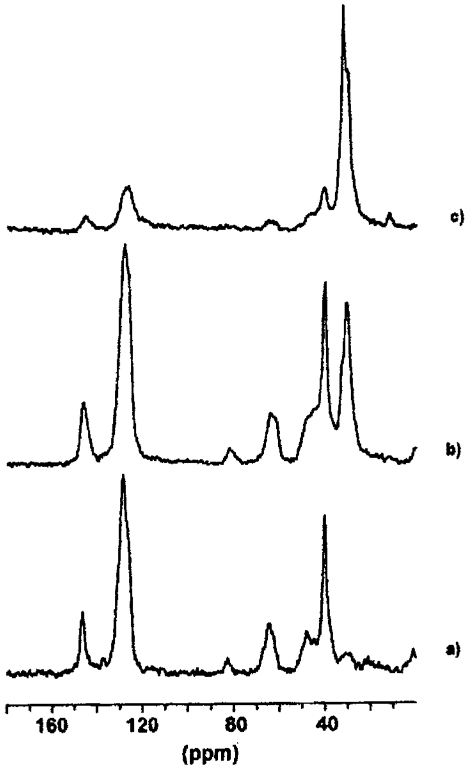


Figure 2. Solid state ^{13}C NMR CP MAS spectra: (a) sample **1h**, $x_S = 0.93$, $x_E = 0.07$; (b) sample **3h**, $x_S = 0.54$, $x_E = 0.46$; (c) sample **5h**, $x_S = 0.20$, $x_E = 0.80$.

The chemical, physical, and mechanical properties of sPS−PE copolymers will be influenced by the crystalline form taken by the sPS component. A preliminary investigation of samples **1h**, **3h**, and **5h** by solid-state CP-MAS ^{13}C NMR and WAXD demonstrates that the δ clathrate form persists and that the overall crystallinity of the sPS fraction decreases as the amount of sPS in the copolymer decreases.

Sample **1h**, which has a high styrene molar fraction ($x_S = 0.93$) and long average syndiotactic block lengths ($n_S = 72$), exhibits CP-MAS ^{13}C NMR resonances that are diagnostic for the 2(2/1) helix conformation of the δ crystalline form of sPS (Figure 3a). Furthermore, the X-ray powder profile of sample **1h** exhibits signals at $2\theta = 7.9$, 10.1, 17.3, 20.0, 23.2, and 27.2° which are consistent with the toluene δ clathrate crystalline form (Figure 4a). This is expected as the sPS−B polymerizations were performed in toluene. A DSC endothermic peak at 242 °C confirms the presence of crystalline sPS.

The CP-MAS ^{13}C NMR spectrum of sample **3h** ($x_S = 0.54$; $n_S = 10$) is similar to that of sample **1h**, except for the presence of an additional broad resonance centered at 32 ppm which is due to amorphous blocks of PE (Figure 3b). Furthermore, a shoulder at 33.4 ppm is also observed which is diagnostic for the presence of crystalline blocks of PE.[30] Accordingly, two endothermic peaks are observed by DSC, one at 212 °C corresponding to the melting point of crystalline blocks of sPS and one at 60 °C for the crystalline PE homosequences (Table 1). The ΔH values calculated for the melting of the sPS (6.6 J/g) and PE (23 J/g) blocks suggest that both domains are of low crystallinity. The X-ray powder

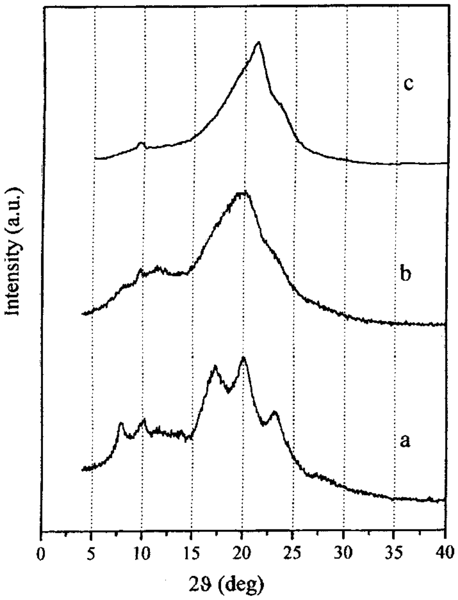


Figure 3. X-ray powder spectra: (a) sample **1h**, $x_S = 0.93$, $x_E = 0.07$; (b) sample **3h**, $x_S = 0.54$, $x_E = 0.46$; (c) sample **5h**, $x_S = 0.20$, $x_E = 0.80$.

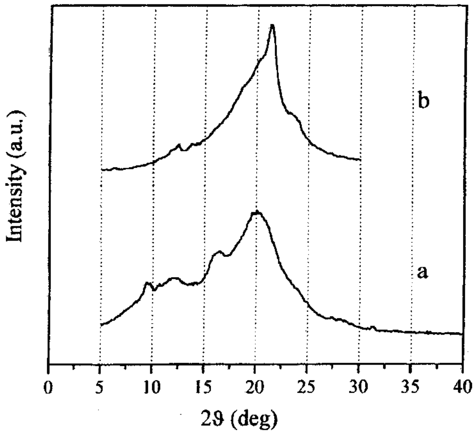


Figure 4. X-ray powder spectra: (a) sample **3h** after treatment for 18 h at 60 °C; (b) sample **5h** after heating at 110 °C, followed by slow cooling to room temperature (cooling rate = 2 °C/min).

profile of sample **3h** exhibits broad, low intensity signals at $2\theta = 7.9$ and 10° and a shoulder at $2\theta = 17°$, which confirms the presence of the toluene δ clathrate form of sPS (Figure 4b). To increase the crystallinity, sample **3h** was treated at 60 °C for 18 h and subsequently analyzed by X-ray. The X-ray powder diffraction pattern of the thermally treated sample (Figure 4a) exhibits broad signals at $2\theta = 9.5$, 12.1, and 16.3° which are indicative of the presence of imperfect crystals in the sPS γ form. The PE domains remain primarily amorphous as documented by the broad signal centered at $2\theta = 20°$. It has been well-established that thermal treatment converts the δ clathrate form into the γ form and subsequently into the α form.[25]

Sample **5h**, which has a low styrene content ($x_S = 0.1$) and short sPS average block lengths ($n_S = 4$; Figure 3c), is largely amorphous. The line shapes of the ^{13}C NMR signals due to the polystyrene methylene and methine carbons are similar to that observed for amorphous sPS and a polystyrene melting point was not detected by DSC. However, PE crystallinity can be inferred from the sharp ^{13}C NMR signal at 33.4 ppm and the corresponding endothermic peak observed at 76 °C by DSC. The X-ray powder profile of sample **5h** only exhibits a broad signal centered at $2\theta = 20°$ (Figure 4c). The crystallinity of this sample was increased by heating a film of sample **5h** from 25 to 110 °C at a heating rate of 5 °C/min, followed by cooling to ca. 25 °C at a cooling rate of 2 °C/min. After thermal treatment, two sharp signals at $2\theta = 21.3$ and 23.5° could be detected by X-ray which are diagnostic for the presence of the orthorhombic form of crystalline PE (Figure 4b).

Conclusion

The synthesis and characterization of novel S−E copolymers (**1h**−**6h**) containing blocks of crystalline sPS with varying average block lengths is reported. Crystalline blocks of PE were found in the samples **2h**−**6h** where the average ethylene block lengths are in the range of $n_E = 9{-}51$. Crystalline sPS was observed in samples **1h**−**4h** where $n_S = 72{-}7$. In general, the initial crystallinity of samples with high PE content is low, which is due to the presence of *n*-ethyl side branches. The crystallinity of the PE domains can be increased by thermally treating the samples. Upon thermal treatment, the orthorhombic PE crystalline form is produced. The presence of long PE blocks does not appear to affect the morphology of the sPS blocks. The sPS blocks are observed in the 2(2/1) helical conformation, as confirmed by solid-state NMR. X-ray analysis confirms that the sPS is in the δ clathrate form. The behavior of the sPS blocks in samples **1h**−**6h** is similar to that of homo-sPS.

Samples **1h**−**6h** constitute a new series of thermoplastic materials in which the crystallinity and the melting points of the sPS and PE blocks can be carefully controlled by regulating the amount of each monomer in the copolymer.

Experimental Section

General Procedures and Materials. All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques or an MBraun drybox, unless otherwise stated. Commercial grade toluene (Carlo Erba) was treated with sulfuric acid, washed with saturated bicarbonate solution and water, dried over calcium chloride, and distilled over sodium. *p*-Toluenesulfonhydrazide was purchased from the Aldrich Chemical Co. and used without further purification.

Synthetic Procedure for sPS−B. The sPS−B samples **1**−**6** were prepared according to the reported procedure.[15] The following general procedure describes the synthesis of sPS−B.

A three-necked flask (250 mL), equipped with a mechanical stirrer (central neck), was charged with toluene (100 mL), styrene (50 mL), and solid MAO (0.6 g) under nitrogen. The solution was thermostated at 25 °C for 15 min. Once thermal equilibrium was achieved the desired partial pressure of butadiene was introduced and given 30 min to reach equilibrium. The polymerization was initiated when $CpTiCl_3$ (6 mg, 30 mmol, Al/Ti molar ratio = 400), dissolved in toluene (2 mL), was introduced into the reactor by syringe. The polymerization run was terminated by introducing ethanol (15 mL) into the reactor. The copolymer was coagulated in ethanol (200 mL) acidified with HCl to which the antioxidant Wingstay K (0.5−1.0 g) had been added. The copolymer was recovered by filtration, washed with fresh ethanol, and dried in vacuo at room temperature to constant weight.

Synthetic Procedure for sPS−PE. The sPS−PE copolymer samples (**1h**−**6h**) were obtained by selectively hydrogenating the putative unsatured sPS−B copolymer samples (**1**−**6**) using *cis*-diimine produced in situ by the thermal decomposition of *p*-toluenesulfonhydrazide (THS) in refluxing toluene.

A general procedure for the hydrogenation of sPS−B is reported below.

A toluene solution (120 mL) of sPS−B copolymer (2−3 wt %) was treated with 2 equiv of THS for each butadiene unit (olefin unsaturation) in a round-bottom flask (250 mL) equipped with a reflux condenser and a Teflon stirbar. The mixture was gently refluxed for 8 h. The initially white reaction mixture turned into a yellow solution. The reaction solution was cooled to room temperature, and the *p*-toluensulfinic acid side product was removed by filtration. The colorless toluene filtrate was treated with ethanol (300 mL), and the hydrogenated sPS−PE copolymer was recovered by filtration, washed with hot water in order to eliminate traces of *p*-toluensulfinic acid, and dried in vacuo at 80 °C to constant weight. ^{1}H NMR analysis of the reaction product indicated that the hydrogenation of the olefin double bond was quantitative.

Differential Scanning Calorimetric (DSC). DSC measurements were carried out on a Mettler calorimeter in a flowing nitrogen atmosphere at a heating rate of 10 °C/min.

X-ray. Wide-angle X-ray diffraction (WAXD) patterns in the range $2\theta = 4-40°$ were obtained with an automatic Philips instrument using nickel-filtered Cu Kα radiation.

Solution ^{1}H NMR and ^{13}C NMR. The copolymer samples (25 mg) were dissolved in 1,1,2,2-tetrachloro-1,2-dideuterioethane (0.4 mL, 20 wt %) in a 5 mm (o.d.) NMR tube and analyzed at 125 °C with a Bruker AM250 spectrometer (250 MHz for ^{1}H and 62.89 MHz for ^{13}C). The chemical shifts are referenced to TMS and were calculated by using the residual isotopic impurities of the deuterated solvents. All NMR chemical shifts are reported in ppm.

The monomer composition of samples **1**−**6** were determined by comparing the integrals of the following ^{1}H resonances (δ in ppm, $CDCl_3$, 25 °C): 7.07 and 6.56 (5*H*, m, $CH_2CH(C_6\mathit{H}_5)$); 5.58 (1*H*, m, $CH_2CH_2(C\mathit{H}{=}CH_2)$; 5.38 (2*H*, m, $CH_2C\mathit{H}{=}C\mathit{H}CH_2$). The monomer composition of the **1h**−**6h** copolymers were determined by comparing the integrals of the following ^{1}H resonances (δ in ppm, 1,1,2,2-tetrachloroethane-d_2, 125 °C): 7.07 and 6.56 (5H, m, $CH_2CH(C_6\mathit{H}_5)$); 1.7 (1H, m, $CH_2C\mathit{H}(C_6H_5)CH_2$); 1.15 (2H, bs, $-C\mathit{H}_2C\mathit{H}_2$); 0.80 (3H, t, CH_2-$CH(CH_2C\mathit{H}_3)$. The area of the aromatic protons (7.0−6.4 ppm; 5H) and methyl protons (0.80 ppm; 3H) was assumed proportional to the styrene and 1-butene content, respectively, whereas the area of the ^{1}H signals in the range 2−0.9 ppm was assumed proportional to the ethylene (4H), styrene (3H), and 1-butene (5H) content, respectively.

The following ^{13}C NMR acquisition parameters were used: relaxation delay between scans = 2 s; acquisition time = 0.34 s; flip angle = 45° (corresponding to 2 μs); number of transients = 20 K; broad band decoupling mode.

Solid State CP-MAS ^{13}C NMR. Copolymer samples (ca. 250 mg) were charged in a zirconia rotor (o.d. 7 mm) and spun at 4500 Hz at the magic angle. Cross polarization method with high power decoupling was employed for generating the ^{13}C signal. The following acquisition parameters were used: relaxation delay between scans = 2s; spin locking time = 1 ms; number of transients = 1K. The chemical shifts are referenced to TMS and determined using the peak of crystalline polyethylene at 33.4 ppm as internal reference.

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