Alternating Ethylene–Styrene Copolymerization with a Methylaluminoxane-Free Half-Titanocene Catalyst

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ABSTRACT: Copolymerization of ethylene and styrene in the presence of the catalytic system η^5-C_5Me_5-$Ti(CH_2Ph)_3$–$B(C_6F_5)_3$ has been investigated. Independently from the feed composition, basically alternating ethylene–styrene copolymers are obtained, together with some polyethylene and syndiotactic polystyrene, from which the former can be separated by solvent extraction. NMR analysis of suitably ^{13}C-enriched end groups shows that the regiospecificity of styrene insertion in the initiation step is largely secondary. A tentative explanation for the preferentially alternating comonomer incorporation is proposed.

Introduction

The classical heterogeneous Ziegler–Natta catalysts are little effective in promoting copolymerization of ethylene (E) and styrene (S), affording, with low productivity, polymers having a substantially polyethylenic structure with a low content of styrene comonomer (mainly as isolated units).[1] The development of the homogeneous, methylaluminoxane-based Ziegler–Natta catalysts has also allowed the synthesis of E–S copolymers with various compositions and structures. Kakugo *et al.*[2] reported that a catalyst based on 2,2′-thiobis(4-methyl-6-*tert*-butyl-phenoxy)titanium dichloride and methylaluminoxane (MAO) affords a fractionable mixture of syndiotactic polystyrene and alternating E–S copolymer. The authors stressed the role of sulfur as essential to obtain the alternating copolymer, since the latter was not produced by using a similar compound having a CH_2 instead of a S bridge as catalyst precursor.

Subsequently, a patent[3] disclosed the E–S copolymerization promoted by catalysts based on bridged amido–monocyclopentadienyl titanium complexes, such as [dimethylsilyl(phenylamido)(tetramethyl-η^5-cyclopentadienyl)]titanium dichloride, and MAO. The copolymers obtained were defined "pseudorandom", meaning that they do not contain any regioregularly arranged S–S sequences, even at styrene contents as high as 47%. In this case, the "constrained geometry" of the catalyst precursor, caused by the Cp–Si–N chelate ligand, was suggested to play a decisive role.[3]

However, copolymerization of ethylene and styrene in the presence of simple catalytic systems, such as $CpTiCl_3$–MAO, had been previously reported in a paper from our laboratory.[4] The results of the copolymerization were shown to depend on the reaction conditions and, in particular, on the Al/Ti mole ratio: at high Al/Ti ratio, a mixture of polyethylene and syndiotactic polystyrene, or at most block copolymers, is produced, while at low Al/Ti ratio, E–S copolymers similar to the above-mentioned "pseudorandom" ones, containing up to 35% of styrene units, can be obtained.[4] The latter finding was tentatively explained by hypothesizing that reaction between $CpTiCl_3$ and MAO might afford different active species promoting, respectively, either homopolymerization or copolymerization of the two monomers.

Thus, the use of particular catalyst precursors, while not essential, could increase the selectivity toward the generation of the active species affording E–S copolymers. Actually, similar E–S copolymers were recently prepared also with typical *ansa*-metallocene catalysts, such as [isopropylidene(1-cyclopentadienyl)(9-fluorenyl)]zirconium dichloride–MAO.[5]

However, the copolymerization mechanism, particularly in the presence of unbridged half-titanocene catalysts, needs further clarification, as also pointed out by Brintzinger *et al.* in a recent review.[6] As a matter of fact, a recent report denied the production of E–S copolymer in the presence of $CpTiCl_3$–MAO.[7] In this paper, we report the alternating E–S copolymerization in the presence of the MAO-free catalytic system Cp^*-$TiBz_3$–$B(C_6F_5)_3$, (Cp^* = pentamethylcyclopentadienyl, Bz = benzyl), which is known to be extremely active in the homopolymerization of both the monomers[8] and appears as a simpler and better defined system than the MAO-based ones.[9]

Results

Several E–S copolymerization runs were carried out under variable conditions in the presence of the catalytic system Cp^*TiBz_3–$B(C_6F_5)_3$. The main results are summarized in Table 1, while details of the polymerizations are reported in the Experimental Section.

Runs 1–4 were performed at increasing temperatures in toluene with ethylene at atmospheric pressure and decreasing styrene concentrations to keep the feed composition approximately constant. The runs were initiated by injecting simultaneously solutions of the catalyst precursors into the reaction vessels containing the solution of the monomers and a small amount of $Al(i\text{-}C_4H_9)_3$ as a scavenger, thermostated at the desired temperature, and terminated after low conversion of the monomers, so that the variation of their concentration was negligible. The copolymerization products were analyzed by ^{13}C NMR. The sample obtained at 0 °C (sample 1) essentially consists of polyethylene (only a strong resonance is observed at δ 29.7), while those obtained at 25, 50, and 75 °C (samples 2–4) show a more complex composition. The aliphatic region of the ^{13}C NMR spectrum of sample 3 is displayed in Figure 1 as an example. According to the literature data,[2,4] the resonances observed are diagnostic of the presence of long methylene sequences (EEE), styrene homosequences in a syndiotactic arrangement (SSS), and ES sequences. The spectra of samples 2 and 4 show the

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Table 1. Ethylene–Styrene Copolymerization Conditions and Results

run	reaction conditions[a]	temp, °C	[styrene] in the feed, mol/L	yield, g	comp of copolym products,[b] % w/w PE	E–S	s-PS
1	i	0	1.1	0.30	>90		
2	i	25	0.80	0.45	63	22	15
3	i	50	0.65	0.53	12	63	25
4	i	75	0.50	0.35	29	41	30
5	ii	0	1.1	0.23	>90		
6	ii	25	0.80	0.20	62	20	13
7	iii	50	0.65	trace			
8	iv	50	0.65	0.32	15	61	24
9	i	50	0.20	0.25	34	57	9
10	i	50	0.40	0.35	33	58	9
11	i	50	1.2	0.49	6	72	22
12	i	50	2.0	1.0	8	20	72
13	v	50	0.65	0.38	nd[c]	nd	nd

[a] Reaction conditions: (i) Cp*TiBz$_3$, 25 μmol; B(C$_6$F$_5$)$_3$, 25 μmol; Al(i-C$_4$H$_9$)$_3$, 25 μmol; total volume (toluene + styrene), 26 mL; ethylene pressure, 1 atm; time, 15 min. (ii) As in (i), but Cp*TiBz$_3$ and B(C$_6$F$_5$)$_3$ were premixed in 10 mL of toluene and aged 5 min at 50 °C. (iii) As in (i), but no Al(*i*-C$_4$H$_9$)$_3$ was added. (iv) As in (iii), but Cp*TiBz$_3$, 50 mmol; B(C$_6$F$_5$)$_3$, 50 mmol. (v) As in (i), but Al(^{13}CH$_3$)$_3$ (0.06 mmol) was added, and time was 5 min. [b] Estimated from ^{13}C NMR spectra (see Experimental Section). [c] Not determined.

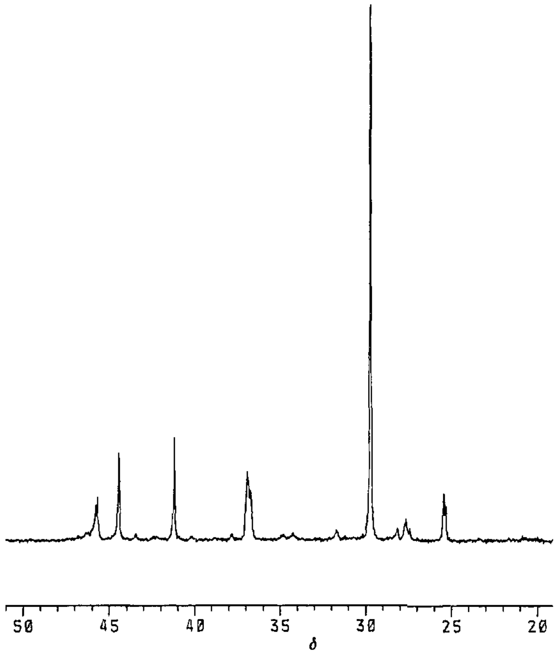

Figure 1. Aliphatic region of the ^{13}C NMR spectrum of a raw copolymerization product prepared with Cp*TiBz$_3$–B(C$_6$F$_5$)$_3$ (sample 3). Spectrum recorded in C$_2$D$_2$Cl$_4$ at 120 °C. TMS scale.

same resonances, but with different relative abundances (see Table 1), and in both cases, the resonances due to ES sequences are less intense.

Samples 1–4 were fractionated by stirring with THF at room temperature: sample 1 was almost insoluble, while samples 2–4 dissolved to the extent of ~15, ~40 and ~25%, respectively. The THF-soluble fractions (samples 2s, 3s, and 4s), analyzed by NMR, were very similar: the aliphatic region of the ^{13}C NMR spectrum of sample 2s is displayed in Figure 2 as an example. Three main resonances centered at δ 45.4, 36.7, and 25.3 ppm are assigned, respectively, to the T$_{\delta\delta}$, S$_{\alpha\gamma}$, and S$_{\beta\beta}$ carbons of an E–S alternating copolymer.[2,4] Minor resonances at δ 29.7 and 27.5 are attributed to the S$_{\delta\delta}$ and S$_{\beta\delta}$ carbons, respectively.

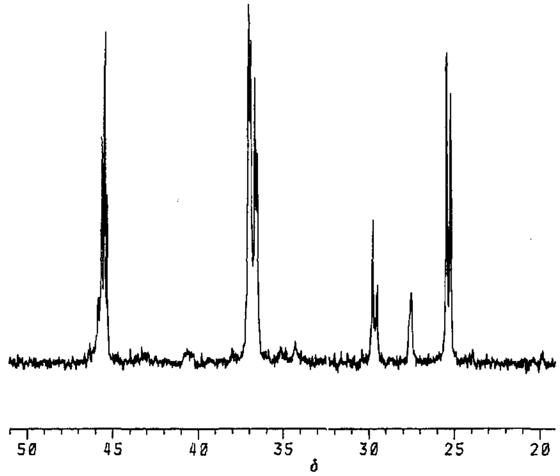

Figure 2. Aliphatic region of the ^{13}C NMR spectrum of a THF-soluble fraction of a copolymerization product prepared with Cp*TiBz$_3$–B(C$_6$F$_5$)$_3$ (sample 2s). Spectrum recorded in CDCl$_3$ at 25 °C. TMS scale.

Table 2. Relative Abundance of the Backbone Carbons in the E–S Copolymer Fractions Obtained at Increasing Concentration of Styrene in the Feed

δ, ppm from TMS	carbon[a]	area of the resonances sample 9s	sample 10s	sample 3s	sample 11s	sample 12s
25.2, 25.4	S$_{\beta\beta}$	0.15	0.16	0.18	0.20	0.21
27.5	S$_{\beta\delta}$	0.06	0.07	0.07	0.04	0.03
29.4, 29.7	S$_{\gamma\delta}$, S$_{\delta\delta}$	0.09	0.09	0.07	0.03	0.04
34.3, 35.1	S$_{\alpha\beta}$	0.03	0.03	0.04	0.05	0.06
36.5, 36.6, 36.9, 37.0	S$_{\alpha\gamma}$	0.42	0.41	0.42	0.43	0.42
45.3, 45.4, 45.6	T$_{\delta\delta}$	0.23	0.22	0.22	0.23	0.22

[a] S = secondary carbon, T = tertiary carbon; the Greek letter indicates the nearest tertiary carbon. [b] The areas are normalized to unity.

Runs 5 and 6 were carried out under conditions similar to those of runs 1 and 2, but precontacting the catalyst precursors in the absence of the monomer and ageing the system 5 min at 50 °C before initiating the polymerization. The products obtained have a structure indistinguishable from that of samples 1 and 2. Run 7, performed under conditions similar to those of run 3, but in the absence of Al(*i*-C$_4$H$_9$)$_3$, produced only traces of polymer. However, use of a twofold concentration of the catalyst precursors (run 8) resulted in a polymer productivity and composition analogous to those of run 3.

Runs 9–12 were performed at a constant temperature of 50 °C and 1 atm of ethylene pressure, but with increasing styrene concentrations. The compositions of the raw copolymerization products, determined by ^{13}C NMR analysis as described in the Experimental Section, resulted strongly dependent on the feed composition (see Table 1): in particular, the E–S copolymer fraction increases with increasing concentration of styrene, although at very high S/E ratio (run 12), the production of syndiotactic polystyrene becomes favored. On the contrary, NMR analysis of the THF-soluble fractions (samples 3s and 9s–12s) showed little change in the composition of the E–S copolymers, all having a substantially alternating structure (see Table 2): e.g., the relative abundance of the S$_{\beta\beta}$ carbons ranges between 15 and 21%, while the mole fraction of styrene in the copolymers (calculated from the ^{13}C NMR spectra as reported previously[5b]) ranges between 0.46 and 0.49.

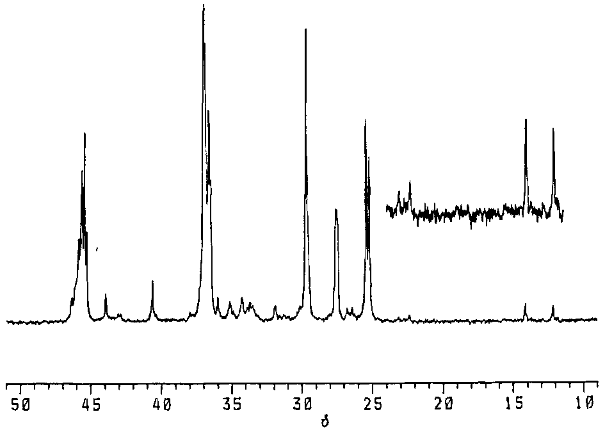

Figure 3. Aliphatic region of the ^{13}C NMR spectrum of a THF-soluble fraction of a copolymerization product prepared with $Cp^{*}TiBz_3-B(C_6F_5)_3-Al(^{13}CH_3)_3$ (sample 13s). ^{13}C-enriched end groups are displayed in the vertical expansion. Spectrum recorded in $CDCl_3$ at 25 °C. TMS scale.

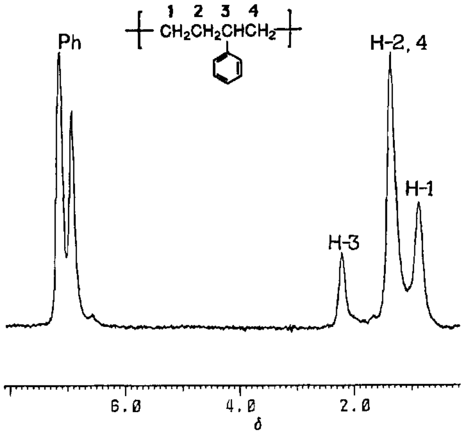

Figure 4. ^{1}H NMR spectrum of an alternating ethylene–styrene copolymer (sample 11s). The resonances are assigned according to the scheme. Spectrum recorded in $CDCl_3$ at 25 °C. TMS scale.

Finally, run 13 was carried out as run 3, but adding ~0.06 mmol of 75% ^{13}C-enriched $Al(CH_3)_3$ to the catalytic system. In the ^{13}C NMR spectrum of the THF-soluble fraction (see Figure 3) additional resonances due to ^{13}C-enriched end groups are detected. According to a previous paper,[5b] they can be attributed to the following end groups: $\cdots CH(C_6H_5)CH_2{}^{13}CH_3$ (δ 12.1, a), $\cdots CH_2CH_2{}^{13}CH_3$ (δ 14.1, b), and $\cdots CH_2CH(C_6H_5){}^{13}CH_3$ (δ 22.3, c), arising in the initiation step, respectively, from 2,1 insertion of styrene (a), insertion of ethylene (b), and 1,2 insertion of styrene (c) into the $Ti-{}^{13}CH_3$ bonds of the active species generated by methyl exchange with $Al(^{13}CH_3)_3$. End groups a and b are in a ~1:1 relative abundance, while end group c, which is hardly detectable after 130 000 scans, is at most 4 times less abundant.

Discussion

As summarized in the Introduction, several Ti or Zr compounds, having different structural and electronic features, when activated with MAO, afford catalysts able to promote the binary copolymerization of ethylene and styrene.[2–5] Although different E–S copolymers are produced by the different catalysts, all of them share a common feature, i.e., a structure lacking SS sequences (excepting, in certain cases, for some $\cdots(Ph)CHCH_2CH_2CH(Ph)\cdots$ sequences, possibly deriving from regioirregularly arranged SS units), even when the molar fraction of styrene in the copolymer approaches 0.5. While this finding is not surprising for catalysts which are not able to promote homopolymerization of styrene, like the previously quoted "constrained geometry"[3] or metallocene-based[5] systems, it seems less straightforward for catalysts which are also able to produce syndiotactic polystyrene, like Kakugo's catalyst,[2] and $CpTiCl_3-MAO$.[4]

The above-reported results obtained in the presence of the $Cp^{*}TiBz_3-B(C_6F_5)_3$ catalyst show some peculiar features which shed some light on the copolymerization mechanism.

First, little, if any, E–S copolymer, is obtained at temperatures <25 °C (even when the catalytic system is preaged at 50 °C in the absence of the monomers), while significant amounts of copolymer, although mixed with syndiotactic polystyrene and polyethylene, are obtained at temperatures ≥50 °C. This suggests that the species promoting the copolymerization results from a reaction requiring higher temperatures and the presence of the monomer(s). The role of $Al(i\text{-}C_4H_9)_3$ should not be essential, since some E–S copolymer is obtained also without using any Al compound, provided that the catalyst concentration is high enough to scavenge impurities in the reaction medium.

Second, the copolymeric fractions obtained are always almost perfectly alternating E–S copolymers, at least in the explored range of feed compositions. In fact, the ^{1}H (see, e.g., Figure 4) and ^{13}C NMR spectra of the THF-soluble fractions of samples obtained in runs 2–12 are very similar to those of the poly(ethylene-*alt*-styrene) synthesized by Suzuki *et al.*[10] by hydrogenating 1,4-poly(1-phenylbutadiene) or 1,4-poly(2-phenylbutadiene). The splittings, due to tacticity effects, of the ^{13}C resonances of the $T_{\delta\delta}$, $S_{\alpha\gamma}$, and $S_{\beta\beta}$ backbone and phenyl *ipso* carbons (see Table 2) indicate that the copolymers are substantially atactic.[10] This structure is different from that of the alternating E–S copolymer reported by Kakugo *et al.*,[2] who observed a unique stereochemical placement of the phenyl substituents and proposed an isotactic structure on the basis of the (tentative) diad and triad assignments by Suzuki *et al.*[10] The present copolymers also differ significantly from those obtained in the presence of catalysts based on either bridged amido–monocyclopentadienyltitanium derivatives or *ansa*-zirconocenes and MAO. In fact, the latter systems afford copolymers in a wide range of compositions depending on the E/S ratio in the feed: however, significant styrene incorporation in the copolymer requires high styrene concentrations in the feed, and, in these conditions, the polymerization activity is greatly reduced. As a consequence, no alternating copolymers are produced, but only copolymers containing a significant amount of sequences of five methylenes or longer, as indicated by the areas of the resonances of the $S_{\delta+\delta+}$ and $S_{\beta\delta+}$ carbons. In contrast, the $Cp^{*}TiBz_3-B(C_6F_5)_3$ catalytic system is apparently more prone to incorporate styrene, possibly owing to the less crowded coordination sphere, and so substantially alternating copolymer fractions are obtained even with low styrene concentrations in the reaction medium.

Third, the regiospecificity of styrene insertion seems higher than for other systems, as suggested by the low relative abundance of the $S_{\alpha\beta}$ carbons (cf, e.g., the 15% of tail-to-tail enchainments observed in copolymers obtained with "constrained-geometry" catalysts[3]) and confirmed by the analysis of the ^{13}C-enriched end groups, indicating that secondary insertion is largely prevailing (>4:1) over primary insertion in the initiation step.

A prevailingly (although to a lesser extent) secondary insertion of styrene has been also observed in E−S copolymers prepared with an *ansa*-zirconocene catalyst.[5b] The preference for 2,1 insertion must be related to electronic reasons, since polymerization of α-olefins promoted by the same catalysts is known to proceed via 1,2 insertion, mainly due to steric factors.[11] As previously suggested for styrene homopolymerization,[12] also on the basis of the structure of model compounds,[13] it is likely that the benzyl-type growing chain end deriving from 2,1 insertion of styrene is bound to the electron-deficient metal center also through the phenyl π-system (η^n-coordination,[13] $n \geq 2$). Thus, the tendency of the active species to incorporate alternatively the two monomers could be related to the bonding mode of the last inserted monomer unit (η^1 for E, η^n for S) affecting the competitive monomer coordination: the coordination constant of (electron richer) styrene would be larger than that of ethylene toward the (more coordinatively unsaturated) $Ti^*CH_2CH_2\cdots$ propagating complex, while ethylene would compete favorably for the coordination to the (more sterically hindered and less coordinatively unsaturated) $Ti^*(\eta^n\text{-}CH(C_6H_5)CH_2\cdots$ propagating complex. A similar interpretation was suggested for alternating copolymerization of 1,3-butadiene and α-olefins: [14] of course, it remains to be clarified if similar mechanisms are operating in the copolymerization of ethylene with either styrene or 1,3-butadiene, although there is experimental evidence that the polymerization mechanisms of styrene and conjugated diolefins with half-titanocene catalysts are closely related.[15] Other effects, e.g., the coordination of the counterion and/or of more than one monomer molecule, could also play a role and deserve further investigation.

As to the authentic structure of the catalyst, a combined NMR and ESR monitoring of the reaction between Cp^*TiBz_3 and $B(C_6F_5)_3$ at 25 °C has previously shown[16] that the initially formed $[Cp^*TiBz_2]^+$ $[BzB(C_6F_5)_3]^-$ ionic complex decomposes to a Ti(III) species, possibly $[Cp^*TiBz]^+$ $[BzB(C_6F_5)_3]^-$, whose concentration greatly increases by addition of styrene. It has been suggested, also on the basis of kinetic homopolymerization results,[17] that the former complex is only able to promote polymerization of ethylene, while the latter is active in the syndiospecific polymerization of styrene. The results reported in this paper support this hypothesis and suggest that a third, possibly intermediate, complex is responsible for the alternating E−S copolymerization. Attempts to identify the structure of such a species, including further ESR experiments, are in progress and will be reported subsequently.

Experimental Section

Materials. Polymerization grade ethylene (SON) was used without further purification. Toluene (Carlo Erba) was refluxed over metallic sodium and distilled under a nitrogen atmosphere. Styrene (Carlo Erba) was purified by distillation under reduced pressure over CaH_2. Cp^*TiBz_3, $B(C_6F_5)_3$, and $Al(^{13}CH_3)_3$ were prepared according to published procedures.[18−20]

Copolymerizations. The copolymerization runs were carried out at atmospheric pressure in 100-mL glass flasks provided with a magnetic stirrer. The reactor was charged under nitrogen sequentially with toluene, styrene, and $Al(i\text{-}C_4H_9)_3$ (when specified); the inert gas was removed and the polymerization mixture was saturated with ethylene (which was continuously fed during the run) and thermostated at the desired temperature in an oil bath. The reaction was initiated by injecting simultaneously into the flask toluene solutions (1 mL each) of Cp^*TiBz_3 and $B(C_6F_5)_3$. The copolymerizations were stopped by injecting methanol, the reaction mixtures were poured into methanol, and the polymers were recovered by filtration, washed with fresh methanol, and dried in vacuo. The concentration of ethylene in solution at 50 °C and 1 atm was experimentally measured and was found to be ~0.1 M.

Analysis of the Copolymerization Products. The raw copolymerization products as well as the THF-soluble fractions were analyzed by NMR on an AM 250 Bruker spectrometer operating in the Fourier transform mode. The spectra were recorded either in $C_2D_2Cl_4$ at a temperature of 120 °C (in the case of the raw polymers) or in $CDCl_3$ at 25 °C (in the case of the soluble fractions) and referenced vs TMS on the basis of the residual solvent resonances (for $C_2D_2Cl_4$ at 120 °C, δ 74.05).

The raw copolymerization products were fractionated by stirring with THF 8−10 h at room temperature. The extraction was not exhaustive, since variable amounts of E−S copolymer remained in the extraction residue: however, conventional extraction with boiling solvents (THF or $CHCl_3$) in a Kumagawa extractor was less selective, leading to the dissolution of some polyethylene and syndiotactic polystyrene. For this reason, the composition of the copolymerization products was evaluated from the areas of suitable ^{13}C NMR resonances, using, e.g., the equation

$$\%\ \mathrm{w/w\ (polyethylene)} = 0.5A(S_{\delta+\delta+}) \times PM(\mathrm{E})/\{[0.5A(S_{\delta+\delta+}) \times PM(\mathrm{E})] + [A(S_{\alpha\gamma}) \times PM(\mathrm{ES})] + [A(S_{\alpha\alpha}) \times PM(\mathrm{S})]\}$$

where PM(E), PM(ES), and PM(S) are the molecular weights of the repeating units of polyethylene, poly(ethylene-*alt*-styrene), and polystyrene, respectively. Similar equations are used for determining the weight percent of alternating E−S copolymer and syndiotactic polystyrene. These equations provide a reasonable estimate, since the contribution of the E−S copolymer to the area of the $S_{\delta\delta}$ resonance can be neglected.

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