

Characterization of Morphology in Chemically Modified Styrene-*b*-(Ethylene-*co*-Butylene)-*b*-Styrene by Solid-State Nuclear Magnetic Resonance

Emilia P. Collar,¹ Jesús M. García-Martínez,¹ Leoncio Garrido²

¹Departamento de Física e Ingeniería, Instituto de Ciencia y Tecnología de Polímeros, Consejo Superior de Investigaciones Científicas, Juan de la Cierva 3, 28006 Madrid, Spain

²Departamento de Química Física, Instituto de Ciencia y Tecnología de Polímeros, Consejo Superior de Investigaciones Científicas, Juan de la Cierva 3, 28006 Madrid, Spain

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ABSTRACT: Multiphase triblock styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene (SEBS) copolymers chemically modified with maleic anhydride (MAH) in the presence of a radical initiator by reactive extrusion were studied by solid-state ¹H-NMR and ¹³C-NMR. In the experiments performed, the concentrations of MAH and initiator were kept constant, whereas the temperature profile in the extruder was varied. Samples with known extents of grafting and crosslinking were analyzed with NMR with techniques based on proton spin diffusion to investigate the microphase structure of the modified copolymers. The ¹³C-NMR results show that the size of the rigid domains was about 15 nm

and was not significantly changed by the modification. Alterations in the rubbery phase were illustrated by measured changes in proton spin-spin (T_2) relaxation times. The fraction of protons having intermediate mobilities increased slightly in modified SEBS with respect to that observed in unmodified copolymers. These results were found to be independent of the extruder temperature profiles used, at least in the range studied. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2656–2664, 2008

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INTRODUCTION

The modification of polymers is a very active area of research because of its significance to industrial polymers.^{1,2} The design of polymer materials for new applications and the improvement of their performance for existing ones often require blends of two or more polymers and mixtures of polymers and inorganic components that lead to heterogeneous structures. Also, the increasing availability of recycled plastics is generating mixtures of incompatible polymers that require aid to facilitate their processing and obtain end products with adequate properties. In any of these scenarios, the physical and mechanical properties of the polymer materials depend not only on the intrinsic properties of their components but on how intimately they are mixed.

Since the early 1980s, it has been widely accepted that the achievement of desired performance in a heterogeneous polymer system requires the optimization of molecular interactions across the interphase between its components. Numerous efforts to improve the compatibility between phases are ongoing; one of

the most intensively pursued efforts is the reduction of interfacial tension, broadening the interphase by means of interfacial agents obtained by the chemical modification of well-known polymers.

An example of the latter is the multiphase triblock copolymer styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene (SEBS). These copolymers are used as interfacial agents in blends of, for example, polyolefins with polystyrene.^{3–6} Furthermore, to enhance the properties of SEBS as a compatibilizer and extend its application, the chemical modification of the copolymers by grafting polar groups has been studied.^{7,8} However, the complexity of chemical modification, including unwanted degradation processes and flow dynamics imposed by the reactor where the reaction takes place, coupled with the low yield of grafting generally achieved prompt the need to perform more research to obtain a better understanding of these processes.⁹ In this regard, the characterization of the morphology of these reactant polymer systems by determination of the critical dimensions of domains and interfacial regions and how the chemical modification alters the raw polymer microstructure is crucial. For this purpose, various techniques can be used.

Solid-state NMR has been shown to be a powerful tool for the characterization of microheterogeneities in polymer systems, particularly when they are lacking

Correspondence to: L. Garrido (lgarrido@cetef.csic.es).

long-range order.^{10,11} This is because of the sensitivity of intrinsic NMR properties (e.g., chemical shifts, relaxation times) to the local chemical environment and to changes in molecular mobility. Moreover, NMR methods offer the advantage of not requiring any special procedure to prepare the sample to be measured; this allows the study of changes caused by processing on the microphase structure of the heterogeneous polymer systems. In this article, we describe the characterization by solid-state ¹H-NMR and ¹³C-NMR of SEBS chemically modified with maleic anhydride (MAH) in the presence of a radical initiator by reactive extrusion. At room temperature, this thermoplastic elastomer consists of rigid domains (polystyrene) dispersed in a rubbery matrix (ethylene-1-butylene copolymer). To get a better understanding of the possible changes in morphology induced by chemical modification, well-characterized samples were analyzed with NMR with techniques based on proton spin diffusion to investigate the domain structure of the modified copolymers.

EXPERIMENTAL

Experimental samples of triblock copolymers of SEBS with a styrene content of 30% (mol/mol) and a weight-average molecular weight of 81,000 g/mol were provided by Repsol YPF (Madrid, Spain) and were used as received. Also, for the NMR experiments, a reference sample consisting of SEBS (Aldrich, Gillingham, UK) with 29% styrene units and a weight-average molecular weight of 89,000 g/mol was used.

The coreactant, MAH (Panreac, Castellar del Vallés, Spain), and the radical initiator used in the chemical modification were used as received. A 50/50 blend of the thermal stabilizers Irganox 1010 and B225 (Novartis, Barcelona, Spain) was added to the reaction media to minimize undesired degradation processes.

The samples of chemically modified SEBS with grafted MAH chosen for this study were obtained by reactive extrusion. Reactive dry blends of coreactants, initiator, and thermal stabilizers were fed into a twin-screw extruder (Collin ZK50, SEMSA, Barcelona, Spain) operating at 100 rpm and with two temperature profiles: 185–215°C [high-temperature profile (HTP)] and 160–195°C [low-temperature profile (LTP)]. Five experiments were performed at each temperature profile, and the concentrations of MAH and initiator were kept constant and equal to 4 and 2% w/w, respectively.

After they were dried at room temperature, pellets of MAH grafted with SEBS were washed in boiling xylene (Panreac), precipitated with methanol (Panreac), and filtered. The solid fraction [nonsoluble (crosslinked) and precipitated copolymer] thus

recovered was dried *in vacuo* to a constant weight, and the chemical modification (i.e., amount of grafting and crosslinking) was characterized.

The extent of succinic anhydride grafted in the modified copolymers was determined by the hot titration method described elsewhere.¹² In addition, the amount of undesired crosslinking reactions induced in SEBS during the chemical modification was assessed by the extraction of modified copolymer samples placed in standard meshed metallic cells in boiling xylene for 3 h. The nonsoluble fraction was determined by the weighing of the material remaining in the cells after they were dried *in vacuo* for 48 h.

The solid-state ¹H-NMR and ¹³C-NMR measurements were performed in a Bruker Avance 400 spectrometer (Bruker Analytik GmbH, Karlsruhe, Germany) equipped with a 89 mm wide bore and a 9.4-T superconducting magnet (proton and ¹³C Larmor frequencies at 400.13 and 100.61 MHz, respectively). All reported data were acquired at a temperature of 295 K, with a standard Bruker double-resonance 4-mm cross-polarization (CP)/magic-angle spinning (MAS) NMR probe head with 90° ¹H and ¹³C pulse lengths between 3.1 and 4.2 μs. The MAS spinning rates were 4.0 and 6.5 kHz for the ¹H and ¹³C experiments, respectively, with the exception of those performed with static samples to measure proton $T_2(H)$ relaxation time. The ¹³C detection experiments were carried out with 4-mm zirconia rotors (ca. 60 mg of sample). Proton spin-lattice relaxation times in the rotating frame [$T_{1\rho}(H)$'s] were measured with a ¹H-¹³C CP pulse sequence with increasing proton spin locking times. We accumulated 1000–2000 scans for each spectrum with contact times of 5 ms and repetition delays of 5 s.

The proton detection experiments were performed with a small amount of sample (a few milligrams) placed in 12-μL zirconia rotors to avoid preamplifier saturation and to keep a homogeneous radio frequency field over the sample volume. Proton spin-lattice relaxation time (T_1) and spin-spin relaxation time (T_2) measurements of the rubbery component were performed with inversion recovery (IR) and Hahn spin-echo pulse sequences, respectively.

Proton spin diffusion was measured with a dipolar filter pulse sequence¹³ consisting of twelve 90° ¹H pulses to saturate the rigid (polystyrene) phase. We varied the strength of the filter by changing the pulse spacing between 2 and 40 μs, and the number of cycles of the filter sequence was repeated from one to six times. After the filter was applied, a phase cycling pulse stored the magnetization alternately along +z and -z to minimize the T_1 effect, and because this was not very effective at long mixing times (t_m 's), the data were corrected by the factor $\exp(t_m/T_1)$. For experiments with ¹³C detection, 2000 scans were averaged with a contact time of 1 ms and a repetition

TABLE I
Extent of Grafting and Crosslinking and ^1H -NMR Relaxation Times
in the Raw and Modified SEBS

Sample reference	Grafting (mmol of MAH/g of SEBS)	Crosslinking (% w/w)	$T_1(H)$ (ms)	$T_2(H)$ (μs) ^a
SEBS-r ^b	0.0	0.0	500 (3)	229 (5)
SEBS	0.0	0.0	535 (5)	255 (4)
HTP-1	0.020	1.61	481 (5)	185 (2)
HTP-2	0.039	1.06	487 (5)	212 (3)
HTP-3	0.039	0.88	485 (5)	194 (3)
HTP-4	0.118	5.72	491 (4)	192 (2)
HTP-5	0.108	52.6	500 (3)	183 (2)
LTP-1	0.039	1.31	484 (5)	204 (3)
LTP-2	0.034	0.90	490 (5)	211 (3)
LTP-3	0.039	1.19	486 (5)	229 (4)
LTP-4	0.088	5.85	487 (5)	201 (2)
LTP-5	0.098	16.5	485 (3)	188 (3)

Standard deviations are in parentheses.

^a Proton spin–spin relaxation times corresponding to the rubbery (olefinic) phase.

^b Block copolymer obtained from Aldrich and used as a reference.

delay of 3 s. For those with ^1H detection, 24 scans were averaged with a repetition delay of 3 s.

All free induction decays were processed with the spectrometer manufacturer's software. The spectra were externally referenced to tetra methylsilane (Scharlau, Sentamerat, Spain).

RESULTS AND DISCUSSION

The functionalization of SEBS could be achieved by the reactive extrusion of the copolymer with MAH in the presence of an initiator producing free radicals. The modification aimed at increasing the polarity of the olefinic domain without changing the styrenic phase significantly. At the same time, degradation and crosslinking reactions should have remained at conversions as low as possible. In this context, to characterize the products resulting from the modification of the SEBS block copolymers, chemical analysis and solid-state NMR were used.

Chemical analysis

The results obtained by chemical analysis of the modification achieved in samples of the SEBS copolymers included in this study are shown in Table I. Although for each temperature profile and in all cases the same set of starting reaction conditions was used, a significant variability in the degree of grafting and crosslinking among the analyzed samples was observed. However, the results were in agreement with the outcome that could be anticipated for these processes with the unsteady character of the graft reaction considered.¹²

Proton relaxation time measurements

The proton spin–lattice relaxation times in the laboratory frame $T_1(H)$ and in the rotating frame $T_{1\rho}(H)$ are related to the spin diffusion process and can be used to estimate the domain structure of heterogeneous polymer systems.¹¹ Because $T_{1\rho}(H)$ and $T_1(H)$ usually have values of a few and several hundred milliseconds, respectively, each relaxation time provides information about the morphology of these systems at different scales. The relaxation measurements in the block copolymers studied (see the results in Table I) showed that the $T_1(H)$ data fit well to a monoexponential, which suggested the apparent presence of one component. The observed values represented an average of the values reported for styrene homopolymer and olefinic rubbers of similar structure.¹⁴ The averaging was caused by the phenomenon of spin diffusion. On the other hand, the results of the $T_{1\rho}(H)$ measurements (see Table II) showed that protons in the rigid phase behaved differently from those in the rubbery phase, which suggested the presence of a heterogeneous system at the $T_{1\rho}(H)$ scale. With these results, if we considered the

TABLE II
 $T_{1\rho}(H)$ Values of the SEBS Block Copolymers

Sample reference	$T_{1\rho}$ (ms)	
	Rigid phase	Rubbery phase
SEBS-r ^a	5.34 (0.08)	2.44 (0.04)
SEBS	4.9 (0.2)	2.5 (0.1)
HTP-2	5.75 (0.07)	2.50 (0.05)
LTP-2	5.3 (0.2)	2.50 (0.05)

Standard deviations are in parentheses.

^a Block copolymer obtained from Aldrich and used as a reference.

early stages of the spin diffusion process and assumed that it started uniformly and varied linearly across the interphase, it was possible to estimate the minimum size of the domains present with the equation

$$\langle x^2 \rangle = (4/3)Dt \quad (1)$$

where $\langle x^2 \rangle$ represents the mean square displacement, D is the spin diffusion coefficient, and t is the time-scale represented by the relaxation measurement.¹⁵ With the fact that the relaxation measurements showed a homogeneous system from the T_1 perspective and a heterogeneous one from spin-lattice relaxation time in the rotating frame ($T_{1\rho}$), and with the assumption of a value of D for the rigid domains of $0.8 \times 10^{-15} \text{ m}^2/\text{s}$,¹⁰ the estimated upper and lower limits of the styrene domains were 23 and 2.4 nm, respectively. These results were similar to those reported for SEBS block copolymers of different origin elsewhere.¹⁶ It was noteworthy that the modification of SEBS with MAH did not significantly alter the values of $T_1(H)$ and $T_{1\rho}(H)$, at least with the experimental conditions used in this study.

Measurements of $T_2(H)$ were used to study the interface of multiphase styrenic block copolymers.¹⁷ In this study, the relaxation measurements of $T_2(H)$ of protons associated with the olefinic phase showed a decrease in the values of T_2 corresponding to modified SEBS with a high extent of crosslinking and grafting compared with those measured in unmodified SEBS, as shown in Table I. The results observed in modified SEBS show a reduction of segmental mobility in the rubbery phase caused, most likely, by the presence of crosslinks and grafted MAH. However, no correlation was found between the observed reduction in the values of T_2 and the extent of crosslinking, as shown in Figure 1. These results suggest that the crosslinks were not randomly or homogeneously distributed throughout the rubbery phase.

Proton spin diffusion

The difference in molecular mobility (glass-transition temperature) between the two phases present in the SEBS block copolymers allowed us to use proton spin diffusion to investigate the structural organization of the various domains involved. To accomplish this goal, two approaches can be followed. One approach involves a ^{13}C detection scheme with CP to transfer magnetization from the abundant spins, ^1H , to the rare ones, ^{13}C . This transfer of magnetization is very efficient within the rigid domains and, consequently, allows the study of the styrenic phase. However, the use of a CP time, typically on the order of several hundred microseconds (in our case, 1 ms), to transfer the magnetization from the protons

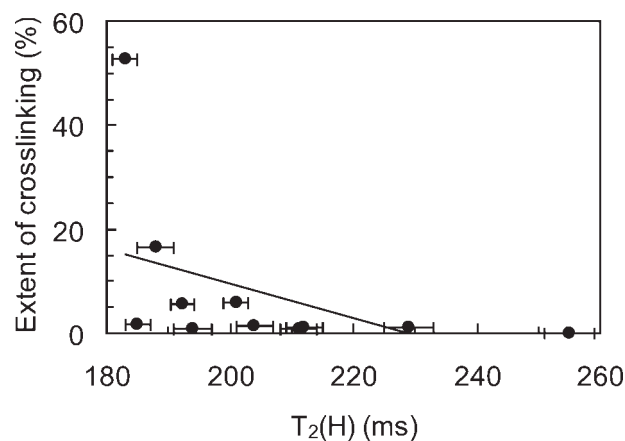


Figure 1 Graph illustrating the variation of $T_2(H)$ corresponding to the mobile fraction of protons with the extent of the crosslinking as a result of the chemical modification of SEBS by reactive extrusion in the presence of MAH.

to the carbons masks the initial part of the spin diffusion process and, as a result, hampers the determination of information about the interfacial region. A second approach consists of a ^1H detection scheme, which allows observation without delays of the spin diffusion phenomenon and provides a more accurate picture of the interphase. Moreover, the high sensitivity of ^1H -NMR facilitates the detection and quantitative analysis of the mobile component. Therefore, using both strategies to study the copolymers of interest provides a more complete picture of the phase structure.

Figure 2 shows typical ^{13}C -NMR spectra obtained in a spin diffusion experiment corresponding to samples of SEBS [Fig. 2(a)] and modified SEBS HTP-2 [Fig. 2(b)] at various t_m 's (spin diffusion times). After the initial selection of the magnetization corresponding to the rubbery phase (ethylene-1-butylene copolymer, peaks between 20 and 40 ppm), the buildup of the magnetization associated with the rigid phase (polystyrene blocks, peaks at 140 and 127 and between 40 and 50 ppm) with increasing t_m was observed.

The size of the domains in heterogeneous polymer materials can be calculated from the time course of the magnetization transfer between the rubbery and rigid phases, in our case, between the polyolefin and polystyrene blocks of SEBS. It has been shown that a good estimate for the size of the dispersed phase (d_{dis}) and the interdomain distance (d) can be obtained by the extrapolation of the initial buildup rate to the plateau value in the spin diffusion recovery curves.¹⁰ d_{dis} for a binary system ab is given by

$$d_{\text{dis}} = \left(\frac{\rho_{\text{Ha}}\Phi_a + \rho_{\text{Hb}}\Phi_b}{\Phi_a\Phi_b} \right) \left(\frac{4\varepsilon\Phi_{\text{dis}}(\sqrt{D_a D_b})}{\sqrt{\pi}(\rho_{\text{Ha}}\sqrt{D_a} + \rho_{\text{Hb}}\sqrt{D_b})} \right) \sqrt{t_m} \quad (2)$$

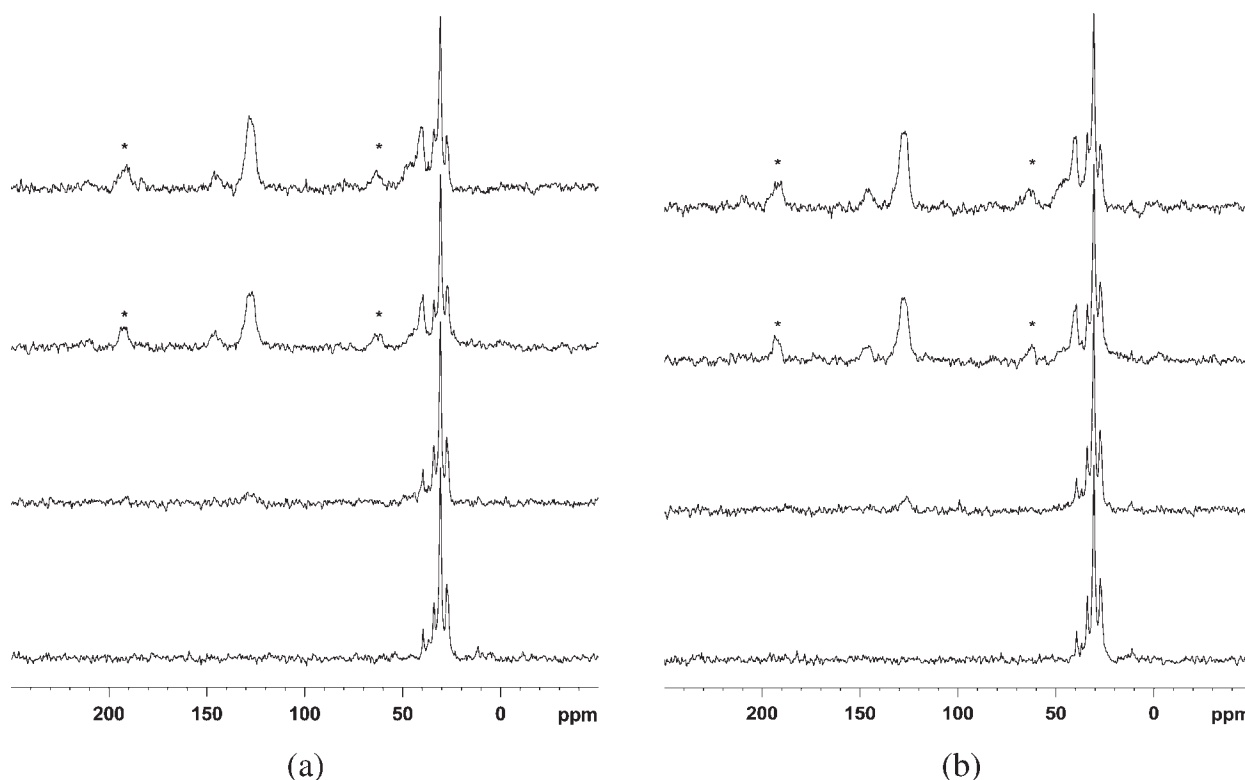


Figure 2 Solid-state ^{13}C -NMR spectra after application of the dipolar filter corresponding to (a) SEBS and (b) modified SEBS HTP-2 at t_m 's of (from bottom to top) 0.25, 4, 100, and 200 ms. A buildup of the magnetization associated with the carbons in the rigid phase (polystyrene blocks) with increasing t_m was observed. Asterisks indicate spinning sidebands.

where ρ_{Ha} and ρ_{Hb} are the proton densities, Φ_a and Φ_b are the volume fractions, Φ_{dis} is the volume fraction of the dispersed phase, D_a and D_b are the spin diffusion coefficients, and ε is the dimensionality of the phase structure, a geometric factor equal to 1, 2, or 3 for planar, cylindrical, or spherical structures, respectively.

d is given by

$$d = \frac{d_{\text{dis}}}{\Phi_{\text{dis}}^{1/\varepsilon}} \quad (3)$$

Figure 3 illustrates the variation of the normalized magnetization corresponding to the samples of unmodified and modified SEBS as function of the square root of t_m . For each sample, we corrected the effect of T_1 on the measured intensities, multiplying by the factor $\exp(t_m/T_1)$. Also, for each curve, we normalized the data by setting the highest value of the magnetization to 1. All samples exhibited similar behavior. No difference was observed between untreated and treated samples nor between those processed at high- or low-temperature profiles. The extrapolation of the slope observed at early diffusion times intercepted the plateau value at t_m equal to the so-called characteristic spin diffusion time (t_m^*). With D values of $0.8 \times 10^{-15} \text{ m}^2/\text{s}$ for rigid domains and $0.05 \times 10^{-15} \text{ m}^2/\text{s}$ for rubbery domains^{10,18} and

a dimensionality of two, characteristic of SEBS systems,^{19,20} the domain size and period were calculated with eqs. (2) and (3). The results are shown in

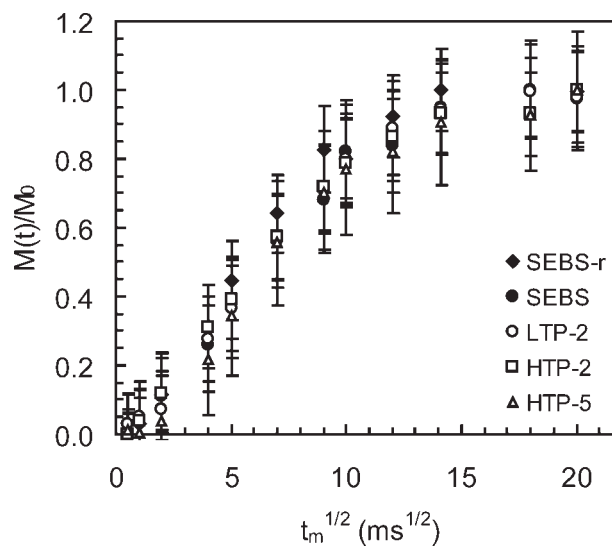


Figure 3 Plot of the normalized change in magnetization associated with the rigid phase of SEBS after application of the dipolar filter. The extent of modification and the temperature profile in the extruder did not alter significantly the behavior of the magnetization transfer in the samples studied. The standard deviations were calculated by measurement of the root mean square (rms) in each spectrum.

TABLE III
Dimensions of Rigid (Styrenic) Domains and d Values in the SEBS Copolymers

Sample reference	$t_m^{*0.5}$ (s ^{0.5})	Rod diameter (nm)	Interrod distance (nm)
SEBS-r ^a	0.358	14.1	25.7
SEBS	0.392	15.4	28.2
LTP-2	0.392	15.4	28.2
HTP-2	0.389	15.3	28.0
HTP-5	0.397	15.6	28.5

^a Block copolymer obtained from Aldrich and used as a reference.

Table III, and as indicated earlier, no significant differences between the treated and untreated samples were observed. The calculated values of the domain size of the styrenic (dispersed) phase were within the limits estimated from spin lattice relaxation measurements, and the values of d_{dis} and d agreed well with the results obtained previously by others with NMR¹⁴ and techniques such as small-angle X-ray scattering, transmission electron microscopy, and atomic force microscopy.^{19,20} Although apparently the rigid domains did not seem to be perturbed, the involvement of styrenic chain segments located at the interphase could not be ruled out because, as mentioned earlier, of the ¹³C experiments lack of sensitivity to detect changes occurring in that region. This issue was also explored with the application of two-dimensional heteronuclear experiments to investigate these samples. Two-dimensional wideline-separation spectroscopy (WISE) was used in the study of heterogeneous polymer systems to correlate high-resolution ¹³C chemical shifts to the proton line width to qualitatively assess the mobility of each component.²¹ The results of WISE experiments performed on raw and modified SEBS (data not shown) did not reveal any significant changes in the proton line shapes associated with carbons in styrenic or olefinic domains.

The ¹H detected spin diffusion allows one to observe the signal decay associated with the olefinic regions right after the magnetization gradient is established in the polymer system of interest. Although the proton signal of the styrenic domains decays very rapidly ($T_2 \approx 12 \mu\text{s}$)¹⁷ due to the lack of molecular mobility and was not observed in these experiments, changing the strength of the dipolar filter could unveil detailed information about the rubbery domains and the interface and, indirectly, about the rigid domains. The strength of the dipolar filter could be modulated by changes in the number of cycles that the filter was repeated (n_c) and the time between the radio frequency pulses (τ). In the experiments performed, we increased the strength of the dipolar filter by either increasing n_c while keeping τ constant or by increasing τ and keeping n_c con-

stant. Figure 4 illustrates typical examples of the variation of the normalized magnetization associated with samples LTP-1 [Fig. 4(a)] and HTP-1 [Fig. 4(b)] with increasing values of t_m and n_c varied from 1 to 6 at $\tau = 10 \mu\text{s}$. Similarly to the ¹³C detected spin diffusion experiments and for each sample, the data were corrected for the T_1 effect by the factor $\exp(t_m/T_1)$, and the initial value of the magnetization (M_0) was set to 1 for each curve. The reduction of the NMR signal followed similar patterns when $n_c \geq 4$, independently of the temperature profile set in the extruder and the extent of the modification. Figure 5 shows the decrease in the proton magnetization associated with the olefinic regions with increasing t_m , with τ varied from 2 to 40 μs and with n_c kept equal to 1, for the samples indicated previously, LTP-1 [Fig. 5(a)] and HTP-1 [Fig. 5(b)]. With these

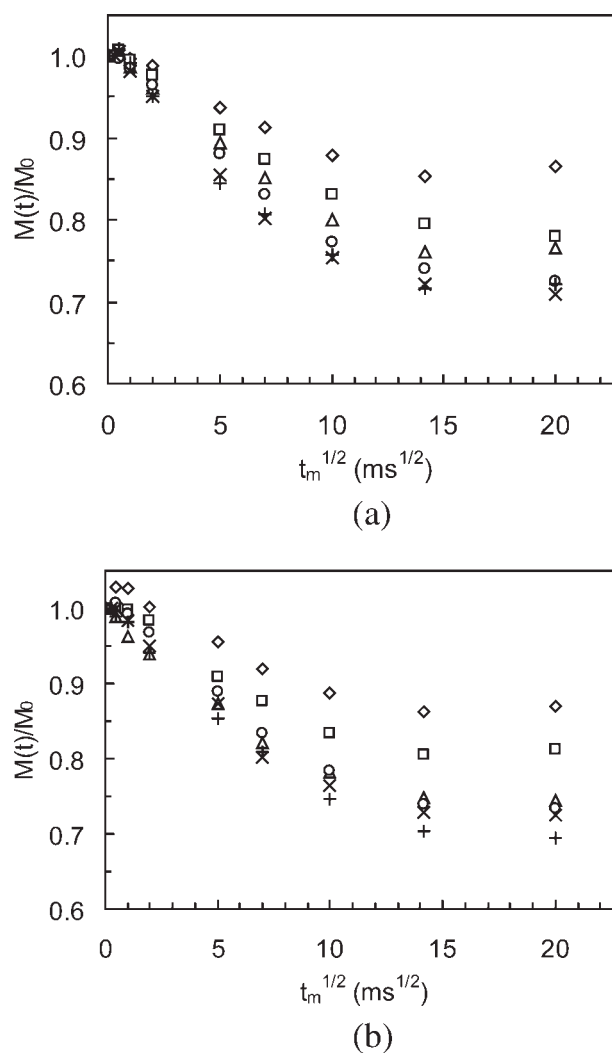


Figure 4 Variation of the normalized proton signal intensity corresponding to the olefinic regions in samples (a) LTP-1 and (b) HTP-1 as a function of the square root of t_m , with $n_c = (\diamond)$ 1, (\square) 2, (\triangle) 3, (\circ) 4, (\times) 5, and $(+)$ 6 and $\tau = 10 \mu\text{s}$.

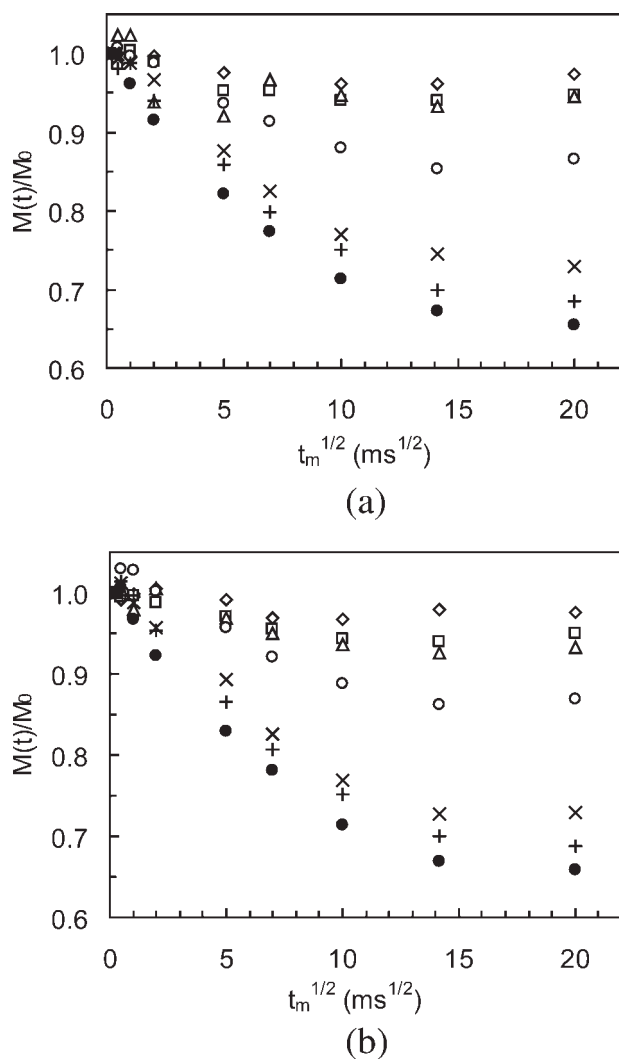


Figure 5 Variation of the normalized proton signal intensity corresponding to the olefinic regions in samples (a) LTP-1 and (b) HTP-1 as a function of the square root of t_m , with $\tau = (\diamond) 2$, $(\square) 4$, $(\triangle) 6$, $(\circ) 10$, $(\times) 20$, $(+)$ 30, and (\bullet) 40 μs and $n_c = 1$.

conditions, the essentially T_2 selective nature of the dipolar filter experiment was easily visualized. At short values of τ , only highly rigid segments of the polystyrene blocks were saturated, and therefore, a small amount of the magnetization stored in the rubbery phase was transferred to the rigid phase to reach equilibrium. As τ increased, the filter strength increased, and segments of polymer chains with intermediate mobility, such as those at the interface or crosslinks, were also saturated, and more magnetization from the rubbery phase needed to be transferred to reach the equilibrium conditions. Thus, alterations in the fraction of intermediate and highly mobile protons could systematically be detected and evaluated.²² In the systems subject to study here, we observed that for each sample, the residual magnetization changed very slightly when $\tau \geq 20 \mu\text{s}$ and

reached a plateau value at about that value corresponding to the stoichiometric ratio between protons in the rigid and rubbery phases. The proximity of the curves observed at high values of τ were indicative of a relatively sharp interface between styrenic and olefinic domains, as has been found in unmodified SEBS^{17,19} and other styrene–olefin block copolymers.^{14,22}

Figure 6 illustrates the variation of the normalized proton magnetization corresponding to the olefinic regions of SEBS samples modified at high-temperature [Fig. 6(a)] and low-temperature [Fig. 6(b)] profiles in the extruder. As a reference, each graph includes the values obtained for unmodified SEBS. The values of τ and n_c used in the dipolar filter were 10 μs and 6, respectively. In all cases, the results corresponding to samples with the highest extent of modification (i.e., high values of grafting and cross-linking) exhibited magnetization curves below those

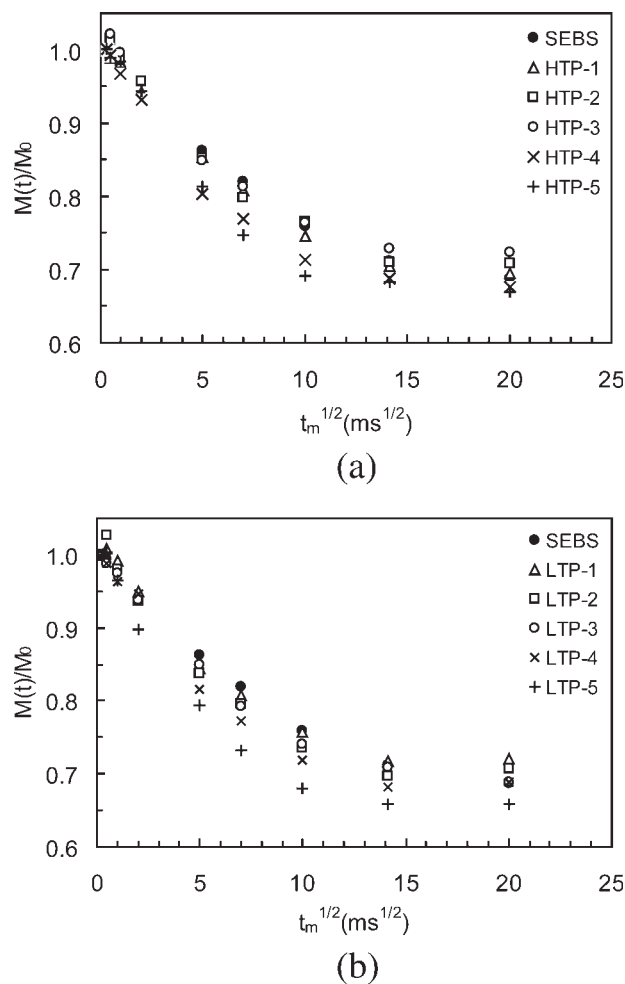


Figure 6 Plot of the change in normalized magnetization associated with the rubbery phase versus the square root of the diffusion time in samples processed at (a) high- and (b) low-temperature profiles in the extruder. The samples having higher extent of modification exhibited slightly steeper initial slopes and lower plateau values.

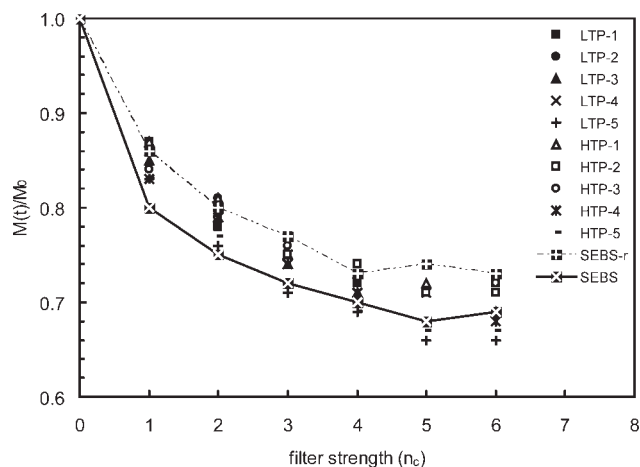


Figure 7 Variation of the normalized proton magnetization corresponding to the olefinic region in samples of SEBS as a function of filter strength (n_c) for $\tau = 10 \mu\text{s}$ and $t_m = 400 \text{ ms}$. The modified SEBS copolymers exhibited a small reduction in the fraction of rigid component compared to the untreated SEBS, which corresponded to an increase of the interfacial fraction. To facilitate the reader's visualization, the traces associated with the reference and raw (untreated) samples of SEBS are shown.

corresponding to slightly modified and unmodified SEBS. These results suggest an immobilization of the olefinic chain segments caused by the crosslinking and grafting of MAH to the polymer chains, which might have occurred in the bulk of the mobile phase and at the interphase.

To obtain more insight as to whether the polymer segments at the interphase were involved in the modification or not, the results obtained for all samples starting with a weak dipolar filter and increasing its strength were compared, as shown in Figure 7. By increasing the strength of the dipolar filter gradually, step by step, we were able to visualize the progressive transfer of magnetization stored in the rubbery phase to the rigid phase, incorporating regions with intermediate segmental mobility.

It was shown that a dipolar filter with $n_c = 1$ and $\tau = 10 \text{ ms}$ is sufficient for suppressing only the contribution of rigid polystyrene domains.²² Thus, at low filter strengths, $n_c = 1$, the reduction of the magnetization could be attributed to its transfer from the rubbery regions to the most rigid domains only (the polystyrene blocks). Then, an increase in n_c led to a decrease in the proton signal associated with the rubbery domains due to magnetization transfer to regions with increase mobility, that is, the interphase and olefinic chain segments at crosslinks. The remaining magnetization at equilibrium represented the fraction of the mobile component in the copolymers.

The results show that at low filter strength, the amount of rigid fraction in treated SEBS was reduced compared with that of the untreated SEBS. All treated samples with low extents of modification

showed similar behavior. For the samples with higher extents of crosslinking and grafting, the reduction in the amount of rigid component was less pronounced, and the value of the magnetization left at equilibrium indicated that the amount of mobile component was lower than in the unmodified SEBS. In proton spin diffusion experiments with an equivalent variation of the dipolar filter strength, that is, varied τ with constant n_c , similar behavior of the magnetization transfer was observed.

These results suggest that the modification took place mainly at the interphase. If the crosslinking and grafting of MAH had occurred in the bulk of the olefinic phase, a reduction in the amount of the most rigid component would have not been observed. On the contrary, an increase in the transfer of magnetization from the olefinic to the styrenic phase would have been observed in the modified SEBS with respect to that in unmodified copolymers at any strength of the dipolar filter. Also, this hypothesis was in agreement with the outcome of the T_2 relaxation measurements, which suggested a heterogeneous distribution of the crosslinks in the mobile domains.

The fact that the ^{13}C experiments did not show a significant change in the size of the rigid domains after the modification should not be surprising because the technique has limited sensitivity to changes occurring at the interphase; the experimental conditions were not set to discriminate well the regime with intermediate mobility from those with high and low molecular motion. Moreover, the ^{13}C measurements placed the emphasis on the polystyrene blocks, and it was estimated that for styrenic-olefinic block copolymers, the amount of styrenic segments in the interphase represents only about 20% of the macromolecular segments in that region.¹⁷

On the other hand, only a minor variation in the domain size seemed to be required to reproduce the behavior observed in the modified copolymers, as shown by the sample of block copolymer used as reference (also included in Fig. 7). A reduction in the rigid domain radius of 0.7 nm, from 7.7 nm in raw SEBS to 7.0 nm in SEBS-r, represented for cylindrical morphology, a decrease in volume of about 18%, which was proportionally close to the observed reduction in the fraction of styrenic domains, from 0.2 to about 0.15, at $n_c = 1$, as shown in Figure 7. Therefore, it might be said that the amount of polystyrene at the interphase, that is, that exhibiting an intermediate level of segmental mobility, increased as a result of the chemical modification.

CONCLUSIONS

The proton spin diffusion measurements on SEBS block copolymers with the ^{13}C -NMR detection

approach showed that the rigid phase with domain sizes of about 15 nm and d values of about 28 nm was not significantly perturbed by their chemical modification. Alterations in the olefinic component were illustrated by measured changes in the proton T_2 relaxation times that most likely occurred at the interface, particularly at low extents of modification. The results obtained with proton detection experiments show a reduction in the amount of the mobile phase with increasing crosslinking and grafting. In addition, the outcome of the experiments performed with varied dipolar filter strengths suggests that the modification of the copolymer chains might have primarily taken place at the interphase. These results were found to be independent of the extruder temperature profiles used, at least in the range studied.

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