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Polymer 41 (2000) 4389–4400

polymer

Grafting of diethyl maleate and maleic anhydride onto styrene-*b*-(ethylene-*co*-1-butene)-*b*-styrene triblock copolymer (SEBS)

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Received 18 March 1999; received in revised form 15 July 1999; accepted 27 September 1999

Abstract

In this paper a study of the bulk functionalization of styrene-*b*-(ethylene-*co*-1-butene)-*b*-styrene triblock copolymer (SEBS) with diethyl maleate (DEM) or maleic anhydride (MAH) and dicumyl peroxide (DCP) as initiator in a Brabender mixer is described. The determination of the functionalization degree (FD) by NMR analysis indicates that the FD values depend on the feed composition and in particular on the DEM/DCP ratio. All obtained products were fractionated by solvent extraction and characterized by IR, NMR and GPC. The results obtained show that the functionalization takes place with a very large preference at the aliphatic carbons of the polyolefin block. Moreover occurrence of degradation and chain extension reactions gives a functionalized product with a MWD larger than 1. Acetone extraction allows the isolation of styrene rich oligomers, thus the high MW functionalized polymer has a lower content of aromatic units than original SEBS.

The results are described with reference to reaction mechanism previously reported in case of the functionalization under similar conditions of polymonoalkenes. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: SEBS copolymer; Functionalization; Maleate grafting

1. Introduction

Thermoplastic elastomers have gained in the recent years a great importance for their technical properties and reuse possibility. In particular the styrene-*b*-(ethylene-1-butene)-*b*-styrene (SEBS) copolymer has been used to enhance the mechanical properties of polystyrene/polyolefin [1–3] blends where it segregates at the interface and reduces the interfacial tension.

Moreover SEBS functionalized with maleic anhydride (MAH), (SEBS-g-MAH) have been used as compatibilizers of immiscible polymers blends. Many reports are devoted to the study of the properties of polyamide/functionalized-SEBS blends [4–8] and in general an increase of mechanical properties is observed when SEBS-g-MAH as compatibilizer was used. This grafted copolymer seems to be a better compatibilizer than a similarly functionalized polyolefin such as EPR-g-MAH. Indeed the SEM and TEM analysis of PP/PA6 blends have shown a good dispersion of PP in the PA6 matrix where SEBS-*g*-MAH behaves also as a reinforcing filler.

Toughened poly(ethylene terephtalate) (PET) was obtained by reactive blending with 1–5 wt% of SEBS-*g*-MAH (with 2 wt% grafted MAH) [9,10]. The fracture strain of PET was increased by more than a factor of 10, consistent with in situ formation of a graft copolymer by reaction of PET hydroxyl end groups with MAH.

Also in the case of blends of polyamide 6 (PA6) with polycarbonate (PC) it was proposed that in the situ chemical reaction between the succinic anhydride groups of SEBS and the amine end group of PA6 during melt mixing induces the encapsulation of SEBS-*g*-MAH within the PC domains in PA6 rich blends [11,12]. Through this phase formation, the adhesion on the domain boundary between PA6 and PC are improved and thus also mechanical properties are enhanced.

At present very few studies were dedicated to the free radical functionalization of SEBS [13,14] and no molecular or mechanistic studies were reported.

Previous work on the functionalization reaction of aliphatic polyolefin [15,16] indicated that the presence of branched olefin units favored degradation over functionalization and crosslinking whereas this last was more effective for linear ethylene blocks. The observed effects allowed to propose a reasonable mechanism, and select proper conditions for the functionalization degree (FD) and keep undesired secondary reactions under control [17,18]. In the

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PII: S0032-3861(99)00696-5

present paper a similar study was extended to functionalization of SEBS with diethylmaleate (DEM) or MAH and dicumylperoxide (DCP) in the bulk using a Brabender mixer in order to evaluate the effect of the aromatic blocks in the process. The reactions were carried out at 220°C in inert gas atmosphere while varying feed composition in term of absolute and relative amounts of functionalizing monomer and peroxide in respect to the SEBS. The polymer after removal of low molecular weight products by acetone extraction was characterized by FT-IR and NMR to detect the FD, and the changes in composition. GPC analysis on the contrary provided information about degradation and broadening of MW distribution. Model experiments of functionalization with LLDPE and polystyrene as well as solid state NMR were used to detect preferential functionalization of aliphatic blocks with respect to polystyrene blocks. Thermal transitions of functionalized SEBS were then detected by DSC analysis. The collected data have allowed us to propose a description of the complex reaction mechanism and to get a better insight into the structure of the SEBS-*g*-DEM and SEBS-*g*-MAH copolymers.

2. Experimental

2.1. Materials

The block copolymer SEBS Europrene Sol TH 212 was supplied by Enichem Elastomeri and was employed without further purification. This polymer contains 19% by moles of styrene units and 32.4% of 1,2 butadiene, 48.6% of 1,4 butadiene units; $\bar{M}_w = 65\text{–}70 \times 10^3$ and $\bar{M}_w/\bar{M}_n = 1.03\text{–}1.11$.

Atactic polystyrene (PS) with $\bar{M}_n = 50 \times 10^3$ and $\bar{M}_w/\bar{M}_n = 2.5$ was supplied by Repsol and used without purification.

Linear low-density polyethylene (LLDPE) was supplied by Enichem and it is an ethylene 1-butene copolymer containing 14% by moles of 1-butene units.

Diethylmaleate (DEM, Aldrich) was purified by distillation; maleic anhydride (MAH Aldrich) was purified by recrystallization from benzene. Dicumyl peroxide (DCP, Aldrich) was used without further purification.

2.2. Functionalization reaction

Functionalization of SEBS was performed in a Brabender mixer (Plastograph) at 220°C operating under a nitrogen atmosphere. About 20 g of polymer was introduced in the mixer and after 3 min a mixture of DEM (or MAH) and DCP was added to the melt. The reaction was carried out for 16 min and the recovered polymer was extracted with boiling acetone. The amount of monomers used was varied from 1.8 to 8.7 mol with respect to 100 mol of polymeric units in the case of DEM and from 2 to 3.5 mol with respect to 100 mol of polymeric units in case of MAH. The amount of DCP is varied from 0.06 to 0.55 mol with respect to 100 mol of polymeric units.

The functionalization reaction of a mixture of LLDPE and atactic PS was performed using the same procedure, and the reaction products were dissolved in toluene and then precipitated by acetone addition. In this way, it was possible to separate PS and LLDPE after functionalization.

The functionalization of PS was also carried out in a Brabender mixer operating at a constant speed of 30 rpm. The mixing temperature was 190°C and the residence time was 25 min. The monomer (MAH or DEM) and the initiator (DCP) were added to the premelted polymer (3 min under nitrogen atmosphere). The functionalization products were first dissolved in tetrahydrofuran (THF) and then precipitated into methanol to remove the unreacted monomer and low-molecular weight products. The solid was completely dried by heating at 40°C for 20 h at 0.1 mmHg.

FT-IR (Perkin–Elmer mod. 1330) and NMR (Varian Gemini-200 and Bruker AMX-300WB) spectroscopies were used to analyze the extracted samples containing low molecular weight products as unreacted DEM, residues of DCP and oligomer fractions and the residue samples containing the functionalized polymers. ^{1}H NMR spectroscopy (using $CDCl_3$ as solvent) was used to determine the polymer composition after extraction and also for FD determination by comparing the area of the signals of 2-diethylsuccinic groups grafted to the polymer (at 4.2 ppm $-O-CH_2-CH_3$) with respect to the area of the signals of the polymer (from 7.4 to 6.3 aromatics and from 3 to 0.6 ppm aliphatic protons) [19].

The FD of samples functionalized with MAH was determined by titration with standard solution of KOH and HCl [20] in *n*-propanol.

Residues to acetone extraction dissolved in $CHCl_3$ (0.2% by wt) were analyzed by gel permeation chromatography (GPC) (PL-GPC210). Refraction index RI detector and 2XPL-gel 20 μm MIXED-A column were used.

The differential scanning calorimetry (DSC) analyses were performed under N_2 with a Perkin–Elmer DSC-7 equipped with a cooling system (CCA-7). The calibration was performed with Hg and In. Heating and cooling thermograms were carried out at standard rate of 20°C/min.

The solid-state NMR experiments were carried out on a Bruker AMX-300 WB spectrometer, equipped with a 4 mm cross polarization (CP)–magic angle spinning (MAS) probe, at the operating frequency of 75.47 MHz for ^{13}C.

3. Results

3.1. Preparation, fractionation and functionalization degree of the reaction products

The polymer after the functionalization reaction was treated with boiling acetone to remove low molecular weight

Table 1
Feed composition, obtained amount extracted with acetone and GPC analysis of the products in the functionalization reaction of SEBS

Run	Monomer	Monomer (% mol)	DCP (% mol)	Extracted with acetone (% wt)	Styrene units in the acetone residue (% mol)	FD (% mol)	$\bar{M}_n$ g mol^{-1}	$\bar{M}_w$ g mol^{-1}	$\bar{M}_w/\bar{M}_n$	E[a]
Europrene Sol TH 212	–	–	–	–	–	–	61,000	63,000	1.03	–
HSB01	–	0	0	1.2	18.6	–	61,000	72,000	1.18	–
HSB00	DEM	4.5	0	3.7	18.3	–	–	–	–	–
HSB03	–	0	0.11	2.9	16.0	–	34,000	64,000	1.88	–
HSB04	DEM	1.8	0.11	2.9	17.8	0.2	38,000	62,000	1.66	1.8
HSB16	DEM	1.8	0.16	4.1	17.0	0.1	–	–	–	–
HSB11	DEM	1.8	0.22	3.9	12.7	0.2	37,000	71,000	1.90	0.9
HSB17	DEM	1.8	0.28	4.8	15.6	0.4	31,000	89,000	2.87	1.4
HSB12	DEM	1.8	0.33	3.8	14.4	0.4	37,000	76,000	2.01	1.2
HSB08	DEM	3.6	0.11	6.1	14.3	0.6	42,000	63,000	1.50	5.5
HSB07	DEM	3.6	0.22	4.8	12.6	0.8	35,000	61,000	1.74	3.6
HSB09	DEM	3.6	0.33	6.1	13.2	0.7	27,000	55,000	2.04	2.1
HSB10	DEM	3.6	0.44	6.1	13.5	1.1	34,000	67,000	1.97	2.5
HSB13	DEM	3.6	0.55	4.9	12.6	1.1	31,000	80,000	2.58	2.0
HSB02	DEM	5.4	0.06	4.9	14.0	0.5	46,000	62,000	1.35	8.3
HSB06	DEM	5.4	0.22	6.7	13.0	1.2	38,000	60,000	1.58	5.5
HSB14	DEM	5.4	0.33	9.1	14.7	1.3	–	–	–	4.0
HSB15	DEM	4.5	0.55	6.1	14.9	1.6	23,000	79,000	3.43	2.9
HSB05	DEM	8.7	0.22	9.7	13.5	1.6	32,000	50,000	1.56	7.3
SEBA02	MAH	2.0	0.06	4.1	12.9	0.6	38,000	53,000	1.39	10
SEBA04	MAH	2.0	0.09	3.4	12.9	0.7	20,000	59,000	2.95	7.8
SEBA01[b]	MAH	2.0	0.13	3.0	13.3	0.8	–	–	–	6.1
SEBA03[b]	MAH	2.0	0.17	3.8	13.6	1.0	–	–	–	5.9
SEBA05	MAH	2.8	0.17	4.5	14.4	1.1	19,000	40,000	2.10	6.5
SEBA06	MAH	3.1	0.17	4.9	15.1	1.2	10,000	32,000	3.20	7.1
SEBA07	MAH	3.5	0.17	3.2	13.3	1.1	13,000	52,000	3.85	6.5
SEBA08	MAH	3.5	0.09	2.4	14.7	0.8	17,000	41,000	2.42	8.9
Kraton G 1901	MAH	–	–	–	16.1[c]	0.1	15,000	38,000	2.53	–

[a] E = mol of grafted monomer per mole of DCP.
[b] Product partially insoluble.
[c] Content of styrene before extraction is 18.3% by mol.

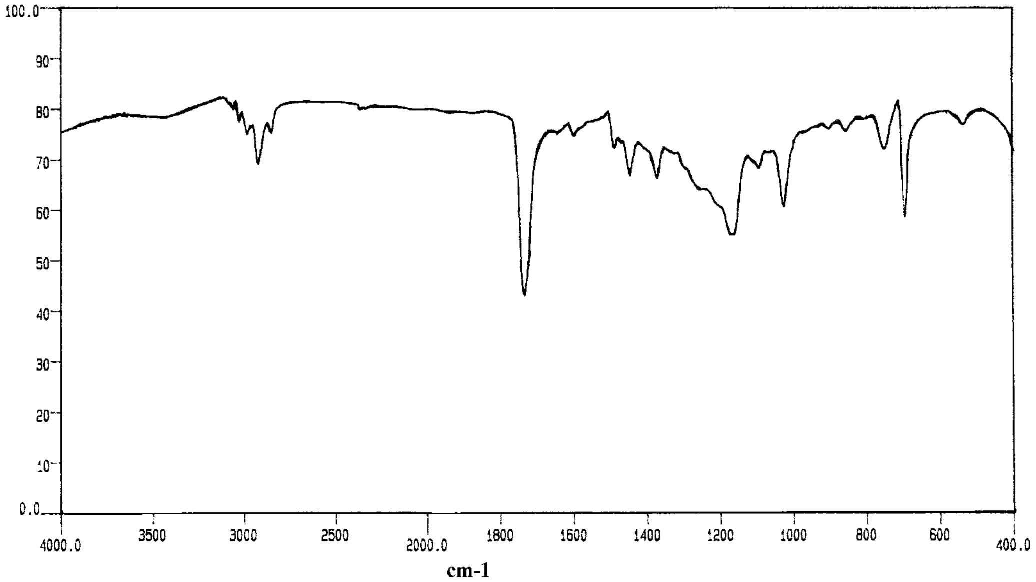

Fig. 1. IR spectrum of acetone soluble fraction extracted from SEBS after functionalization with DEM and DCP (run HSB06, Table 1).

products (unreacted monomer, DCP residues, oligomers and low MW polymeric fractions, if present).

The amount of the acetone-soluble fraction (Table 1) is, in general, larger than in the blank experiment (run HSB01), and increases with increasing the monomer (HSB06 6.7%, HSB05 9.7%) and the DCP content (HSB10 6.1%, HSB15 6.1%, SEBA06 4.9%) of the feed.

Both FT-IR and NMR analyses showed that the acetone fraction contains unreacted monomer, oligomers and low molecular weight polymeric fractions rather rich in styrene units (Figs. 1 and 2). This last material can be formed by chain scission reaction; thus the residue of the acetone extraction contains less styrene units than the starting polymer (Table 1).

In all experiments carried out with a variable amount of DEM (variable DEM/P molar ratio) and using a fixed DEM/DCP molar ratio (8.2 and 16.4, respectively) the FD increases almost linearly (runs HSB11, HSB10, HSB15

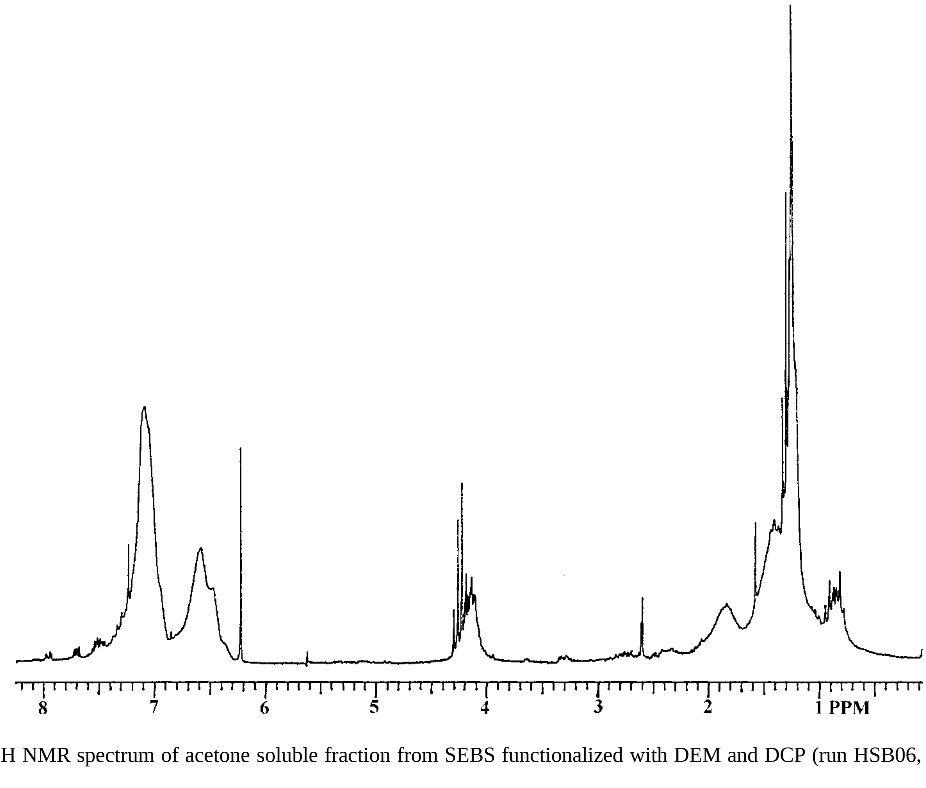

Fig. 2. ^{1}H NMR spectrum of acetone soluble fraction from SEBS functionalized with DEM and DCP (run HSB06, Table 1).

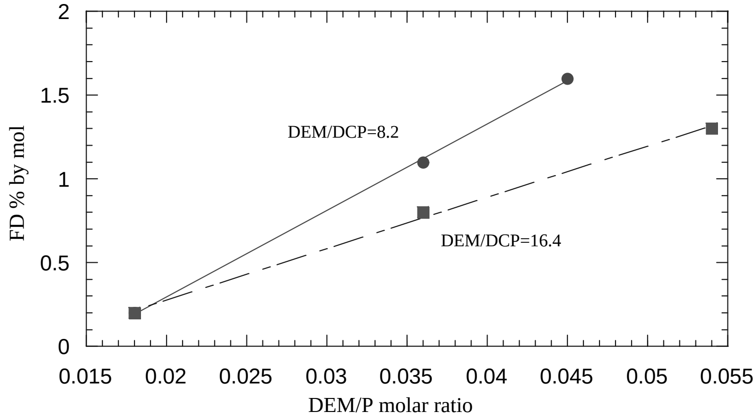

Fig. 3. Dependence of the FD on DEM/P molar ratio with fixed DEM/DCP molar ratios.

and runs HSB04, HSB07 and HSB14, respectively) (Fig. 3). FD also increases with DCP/DEM ratio (using a fixed DEM/P molar ratio of 0.054), but in a limited way as observed for aliphatic polyolefins (Fig. 4).

The data obtained in the case of the functionalization with MAH are similar to those with DEM but lower reagents concentration seems necessary to reach the same FD.

The efficiency of primary radicals for the grafting reaction *E* was evaluated as the mole of grafted DEM or MAH per mole of peroxide. *E* for SEBS is intermediate between that observed for polypropylene (PP) and ethylene/1-butene copolymer (LLDPE) [17] (Fig. 5). The higher efficiency for MAH with respect to DEM can be due to some homopropagation of grafted MAH and the “ene” reaction.

3.2. Functionalization of a mixture LLDPE/PS and PS

A mixture of 1-butene/ethylene copolymer (containing 14% by moles of 1-butene units) and atactic polystyrene in 80/20 units mole ratio as in SEBS was used. After functionalization with DEM and DCP under usual conditions, the reacted polyolefin and polystyrene were separated by acetone extraction. The FT-IR characterization (C=O bond at 1740 cm^{-1}) shows that only LLDPE is functionalized (Fig. 6); moreover $\bar{M}_n$ and $\bar{M}_w$ values of the recovered polystyrene are very similar to the starting ones ($\bar{M}_n$ from 51×10^3 to $55 \times 10^3 \bar{M}_w$ from 130×10^3 to 150×10^3).

When PS alone was submitted to functionalization, IR spectra provided evidence of the grafting reaction (Fig. 7) for both FPS2 and FPS3. For FPS2 (PS-*g*-DEM) it is possible to observe (Fig. 7a) the presence of the carbonyl stretching band at 1732 cm^{-1} while for FPS3 (PS-*g*-MAH) a new absorption band at 1778 cm^{-1} (Fig 7b), not observed in the spectrum of PS, is found. Once again this band is assigned to the carbonyl stretching of MAH grafted on PS. The GPC data (Table 2) indicate that the values of $\bar{M}_n$, $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$are nearly the same as those of PS before reaction thus excluding appreciable crosslinking and/or chain scission.

3.3. GPC analysis of the functionalized polymers

The insoluble acetone polymers derived from the functionalization runs were analyzed by GPC using $CHCl_3$ as the solvent (Table 1).

The curves of all functionalized samples are broader than

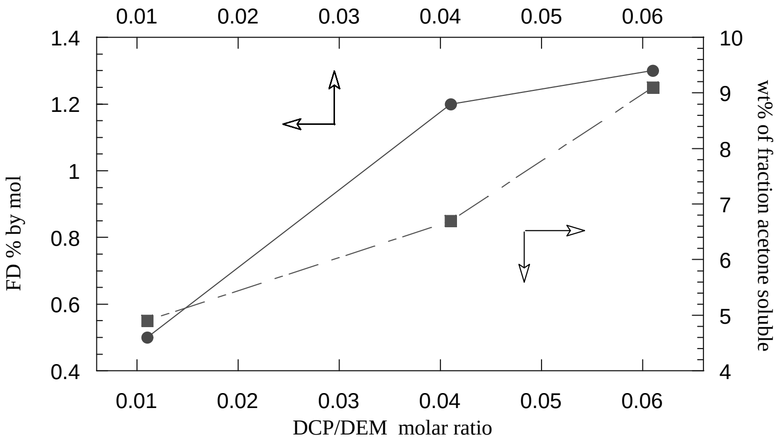

Fig. 4. Dependence of the functionazation degree (FD) and the amount of product soluble in acetone on the DCP/DEM ratio at fixed DEM/P molar ratio = 0.054.

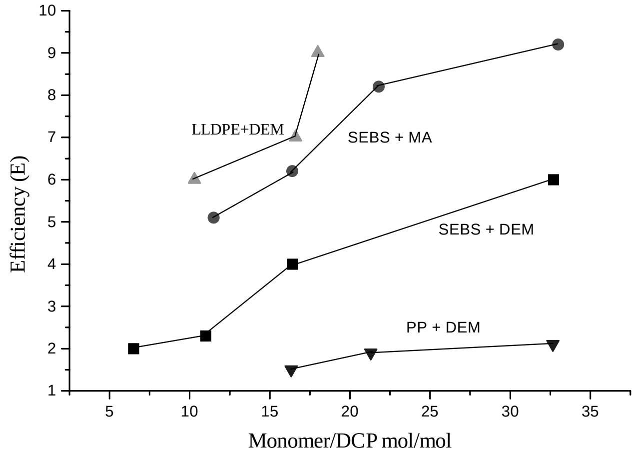

Fig. 5. Efficiency (E) = number of grafted monomers per mole of DCP with varying monomer/DCP ratio.

that of the SEBS before the treatment in Brabender, which has polydispersity ∽1. In particular new peaks are observed in the region of the low molecular weights.

In general we observed a decrease of $\bar{M}_n$ at all feed composition, and no variation of $\bar{M}_w$ this indicates that DEM hinders better crosslinking than degradation.

When the content in the feed of DCP is very high and the monomer/DCP ratio is very low (HSB17, HSB12, HSB13) also $\bar{M}_w$ increases. In this case probably the crosslinking (or chain extension) is not negligible because of the high concentration of primary radicals; accordingly the efficiency E is rather low (HSB17 $E = 1.4$, HSB12 $E = 1.2$, HSB13 $E = 2$). (Table 1)

A decrease of $\bar{M}_n$ and $\bar{M}_w$ values and higher values of the polydispersity (from 1.03 for the SEBS to 3.85 for SEBA07) are observed also with MAH. When the DCP/MAH ratio is higher than 0.065, partially insoluble polymers (SEBA01 and SEBA03) are formed (Table 1).

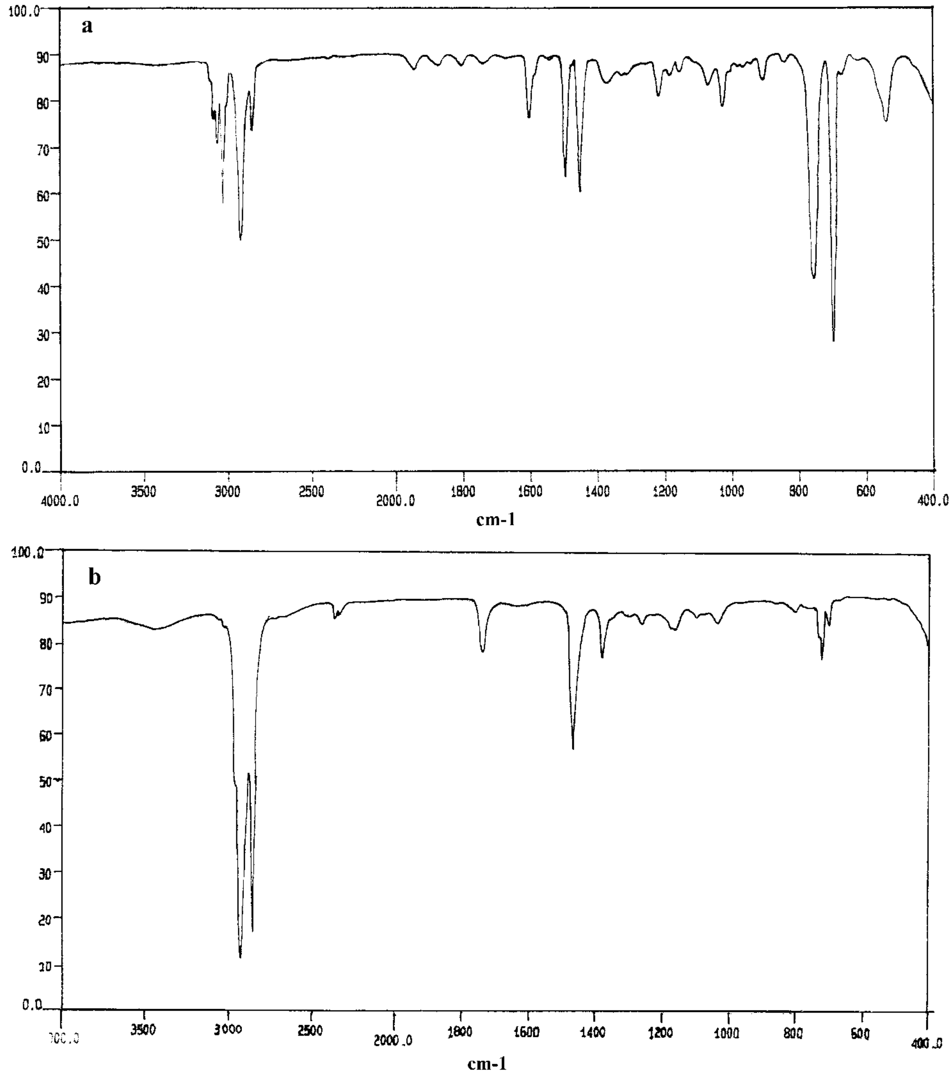

Fig. 6. IR spectra of: (a) acetone soluble; and (b) acetone insoluble polymers after the functionalization of a mixture LLDPE/PS.

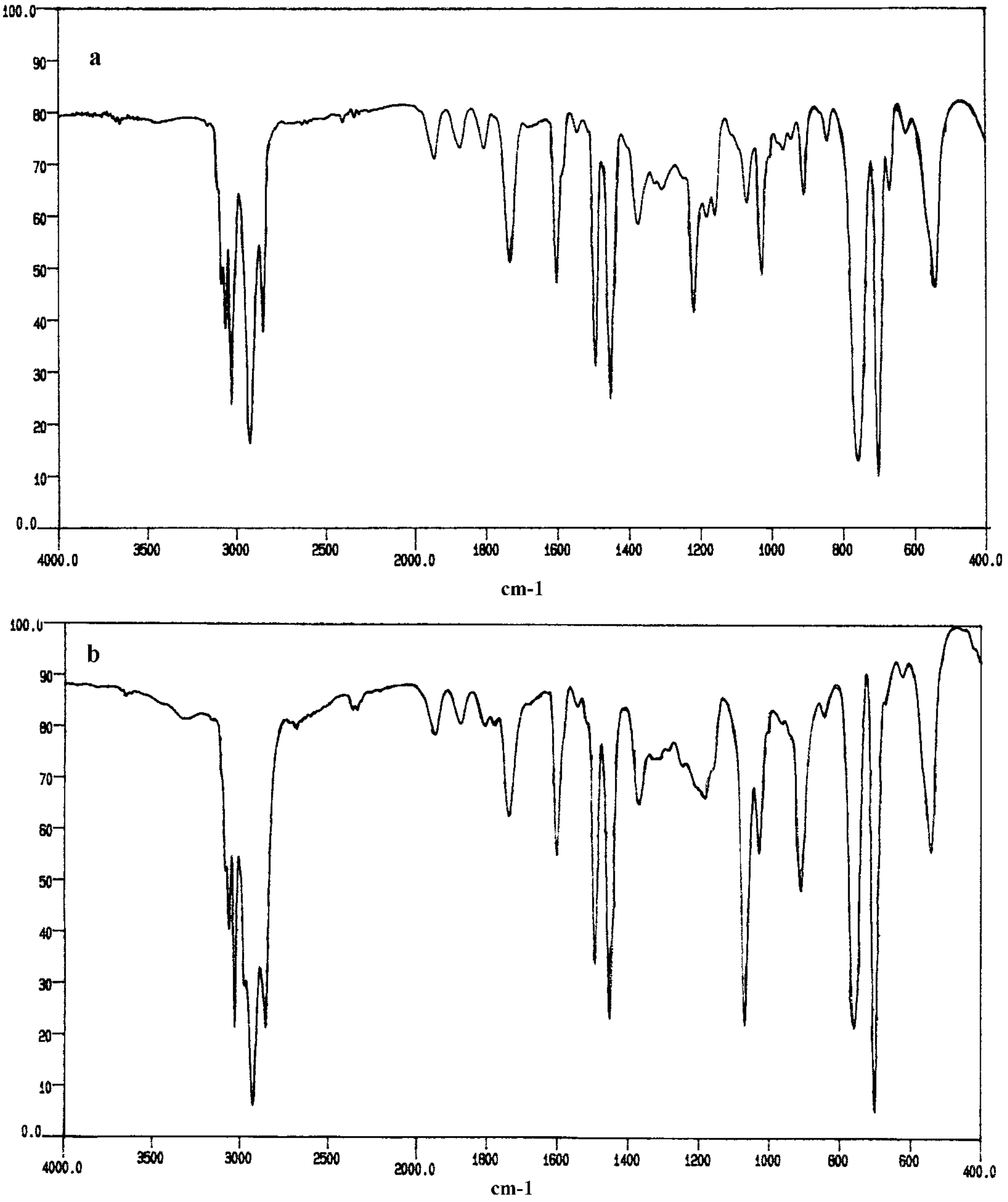

Fig. 7. IR spectra of functionalized PS: (a) PS-*g*-DEM (FPS2); (b) PS-g-MAH (FPS3).

Table 2
Feed composition and GPC analysis of the products in the functionalization reactions of PS

Run	Monomer	Monomer (% mol)	DCP (% mol)	FD (% mol)	$\bar{M}_n$ g mol^{-1}	$\bar{M}_w$ g mol^{-1}	$\bar{M}_w/\bar{M}_n$
PS	–	–	–	–	52,000	130,000	2.5
FPS1	–	–	0.04	–	55,000	109,000	2.0
FPS2	DEM	6.0	0.04	2.0[a]	55,000	150,000	2.7
FPS3	MAH	10.6	0.04	2.5[b]	63,000	158,000	2.5

[a] Determined by ^{1}H NMR analysis.

[b] Determined by titration with methanolic NaOH in THF solution.

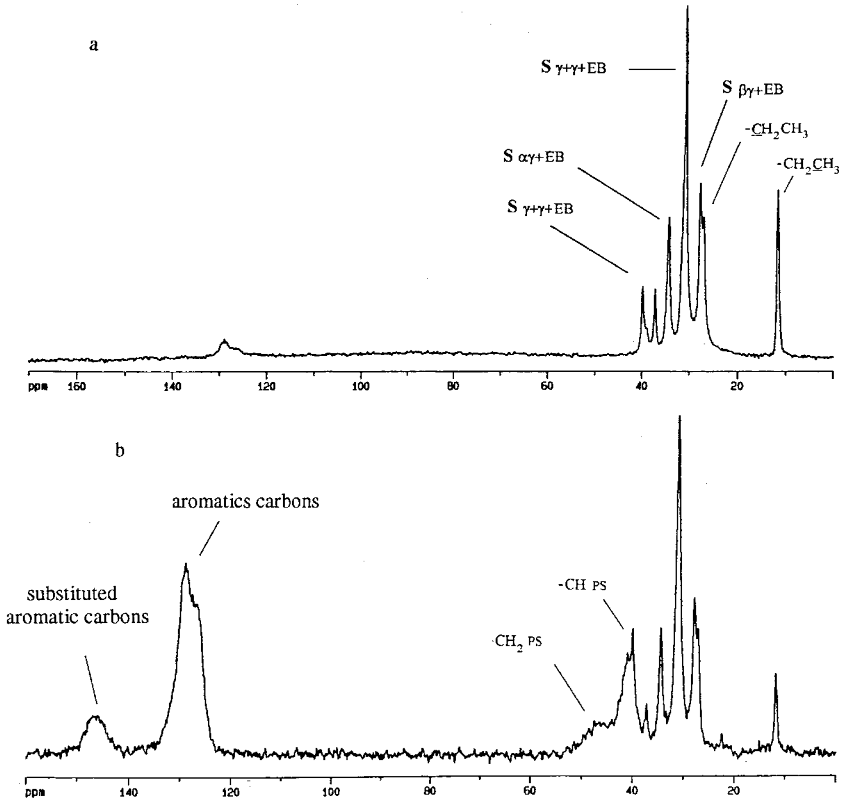

Fig. 8. Solid state NMR of SEBS: (a) ^{13}C–SPE–MAS; (b) ^{13}C–CP–MAS.

3.4. Characterization of the functionalized products by solid state NMR

The single pulse excitation (SPE) and CP combined with DD and MAS technique experiments were performed to obtain more information about the molecular structure functionalized SEBS.

Whereas the CP–MAS technique enhances the signals arising from rigid phases, a very short relaxation delay (1 s) was chosen to observe only the fast relaxing magnetization arising from mobile phases.

The SPE–MAS and CP–MAS spectra of SEBS, respectively, indicate as expected the presence of two phases (Fig. 8): the amorphous material consists essentially of the polyolefin alone (from 10 to 40 ppm in Fig. 8a), with the exception of the signal at 129 ppm ascribable to aromatic carbons, whereas the rigid phase includes polystyrene and polyethylene blocks (Fig. 8b). The assignments of the resonances as indicated in Figs. 8 and 9 are in agreement with the values reported in the literature [21].

From the comparison of the SPE–MAS spectra of SEBS (Fig. 8a) and HSB06 (Fig. 9a) it is possible to note the appearance of two additional peaks at 60 and 15 ppm. These peaks can be assigned to the ethyl carbons (–O–CH$_2$–CH$_3$) of diethyl succinate (DES) groups derived from DEM insertion [22]. The resonance of the other DES carbons are hidden by the more intense signals of ethylene and 1-butene units, which cover all the signals, included between 42 and 24 ppm.

In the ^{13}C–CP–MAS spectrum of the same sample obtained with 20 μs contact time the signals ascribable to carbons of grafted ester groups are not detectable; this result can confirm that the functionalization reaction occurs only onto the polyolefin block (Fig. 9b).

3.5. DSC analysis

The thermal transitions measured by DSC (Fig. 10) show the peculiar characteristics of these copolymers, which present two relaxations, α and β, corresponding to the glass transition of polystyrene and the relaxation of the elastomeric block, respectively. The nature of the β-relaxation depends on the crystallinity of the system [23]. The are three main transitions to be considered in the curve of SEBS after treatment in Brabender (sample HSB01). The glass transition temperature (T_g) of the –EB– block (number 1 in Fig. 10) appears around −57°C. Just after this first T_g it is possible to detect the onset of the melting behavior (number 2 in figure). The maximum of the curve has been taken as the melting temperature, T_m which is around 17°C. Both the broad range of melting and the small area of the melting endotherm ($\Delta H = 10.3$ J/g) indicate that there is a very small percentage of crystallinity in the system. Finally at the highest temperatures in the curve a second T_g is observable around 80°C related to polystyrene blocks.

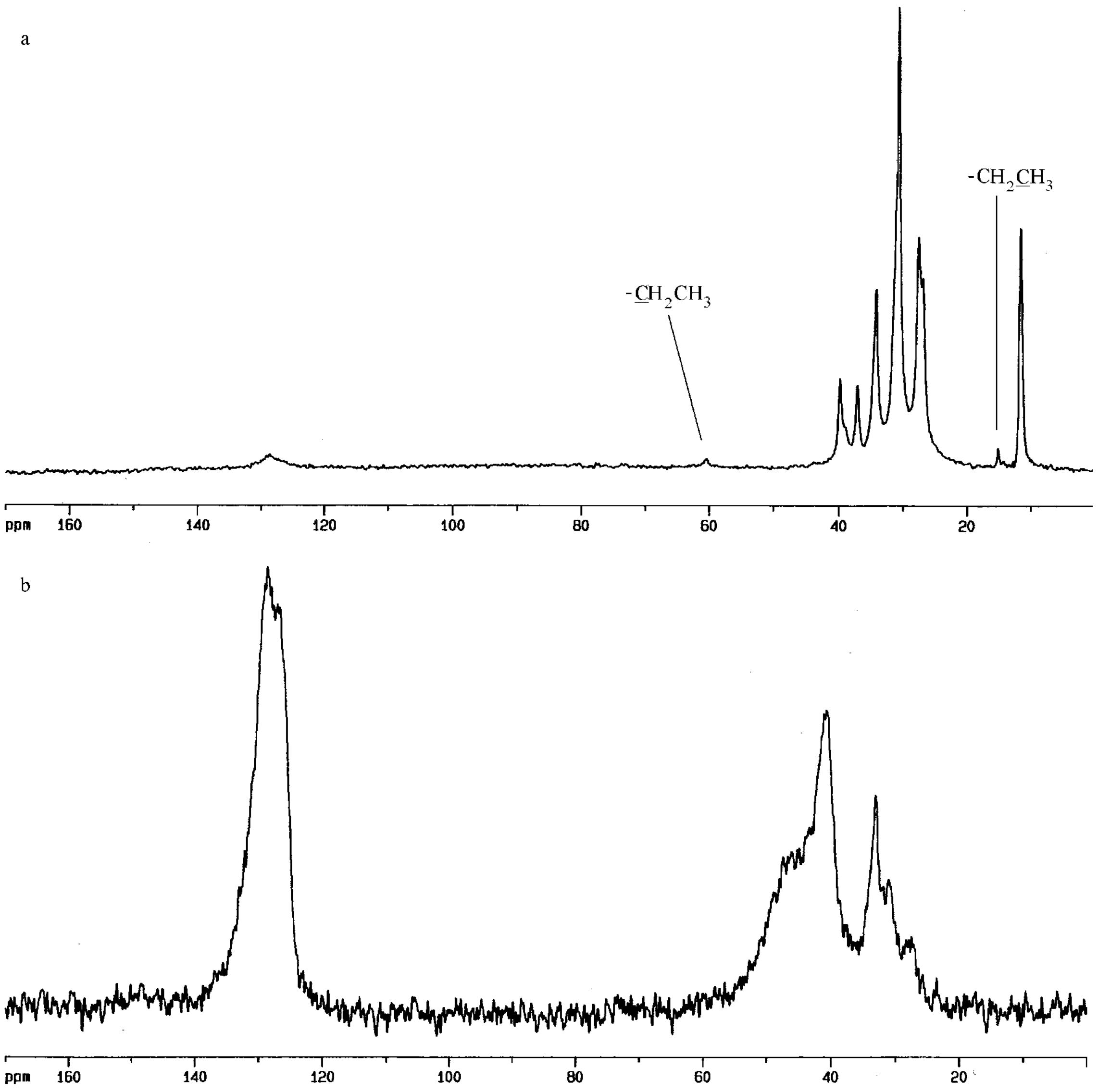

Fig. 9. Solid state NMR of SEBS-*g*-DEM (run HSB06): (a) ^{13}C SPE-MAS; (b) ^{13}C–CP–MAS.

The DSC curves of the samples functionalized with DEM (HSB06) or MAH (SEBA06) are very similar to those of SEBS after simple thermal processing (HSB01, HSB06, SEBA06, Table 3).

The glass transition of the –EB– block ($T_g\beta$) of SEBA06 functionalized with MAH (1.2% by moles) is weakly shifted at higher temperatures; probably the grafted polar groups undergo intermolecular interactions such as interchain hydrogen bonding involving the carboxylic side chain. These interactions seem to be stronger than in the case of samples with grafted ester groups; sample HSB06 with FD = 1.2 mol%) has the same $T_{g\beta}$ as unmodified SEBS.

The functionalized samples have lower crystallinity than SEBS and also lower $T_{g\alpha}$ due to the lower amount of styrene units.

4. Discussion

The reaction scheme reported in Fig. 11 represents an attempt to rationalize the results described in the previous section taking into account also previous information obtained in case of aliphatic polyolefins [19].

Primary radicals formed by peroxide decomposition are certainly able to extract hydrogen from both aliphatic and aromatic units of the SEBS macromolecules. This is shown by the possibility of functionalizing both ethylene/α-olefin copolymers (resembling aliphatic EB blocks) and polystyrene (resembling aromatic S blocks). Therefore reactions described in equations 4 and 5 should both occur.

The same probably holds for the equation in Ref. [6]. However, both in the case of SEBS and LLDPE/PS mixture, having the same composition as SEBS, only the aliphatic

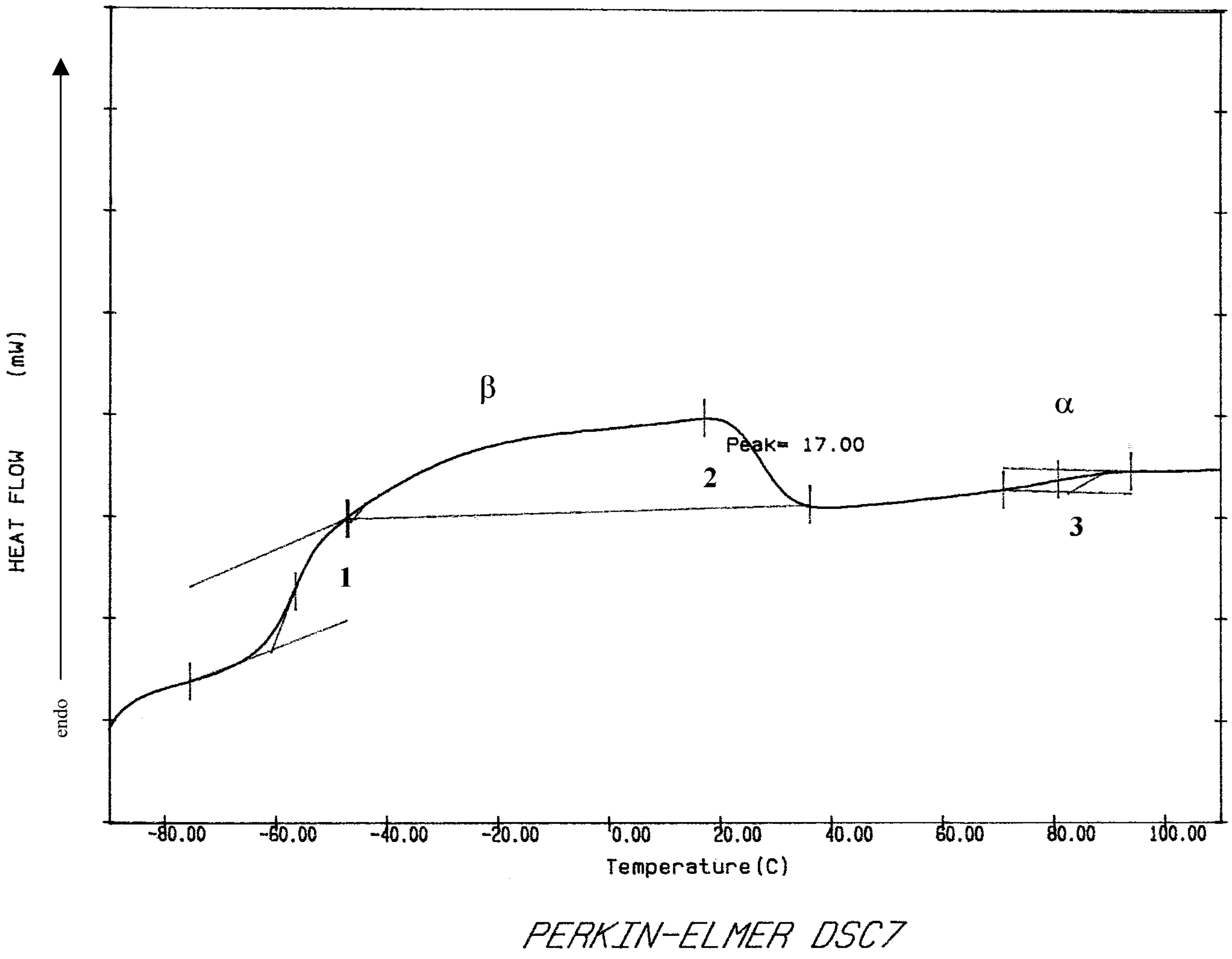

Fig. 10. DSC curve of SEBS-*g*-DEM (run HSB06).

radical appears to take part in the grafting reaction. So in the scheme only the equation in Ref. [7] represents the grafting (functionalization) reaction in spite of all radicals reported in Fig. 12 formed during the reaction. This conclusion is fourthly supported by solid state NMR data, which indicate that the carboxylate groups are located in the soft EB phase. Many transfer reactions can occur in this system; the one most significant to the present process is that described in the equation in Ref. [8]. Indeed this reaction regenerate frees radicals on SEBS. Its occurrence is confirmed by the fact that the grafting efficiency (number of functional groups per DCP molecule) is generally larger than 2 (Fig. 5) even with DEM, which predominantly gives monomeric grafting [22], whereas for MAH the same propagation was observed [24].

Table 3
DSC data of SEBS and functionalized SEBS

Sample	FD (mol %)	$T_{g\beta}$ (°C)	$T_{m\beta}$ (°C)	$T_{g\alpha}$ (°C)	$\Delta H_{T_{m\beta}}$ (J/g)
HSB01	–	− 57.7	17.0	80.3	10.3
HSB06	102	− 57.2	14.7	79.2	7.5
SEBA06	1.2	− 54.7	12.3	78.3	7.5

The FD and *E* values are in general higher (Fig. 5) in case of MAH. Probably there are two reasons for this result [24]: the MAH can homopolymerize during the functionalization reaction; indeed probably the values of FD and of efficiency (*E*) can be distorted by the presence of oligomers of MAH grafted onto the copolymer. The second is the possible occurrence of the ene reaction between the MAH and the double bonds formed by chain degradation. The anhydride is the most reactive because it is a dienophile stronger than the maleate [25].

E increases with increase of the DEM/DCP ratio and the absolute amount of DEM, which through reaction [7] hinders side reactions of macroradicals.

As far as degradation is concerned, the data of Table 1 show clearly that a certain chain breaking cannot be avoided, but only controlled to a certain extent by increasing the DEM/DCP ratio. Under the same conditions polystyrene does not undergo appreciable degradation (Table 2) and this suggests that chain breaking of SEBS involves the aliphatic

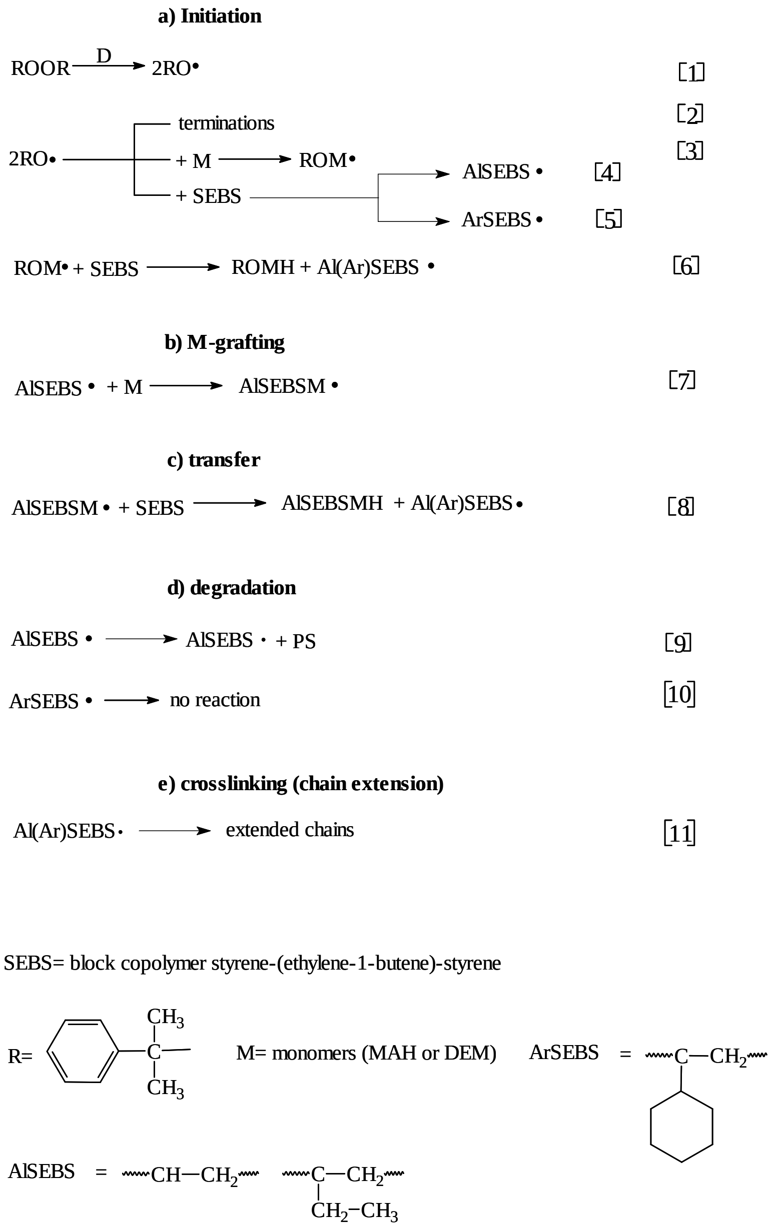

Fig. 11. Simplified reaction mechanism of the SEBS functionalization with MAH or DEM.

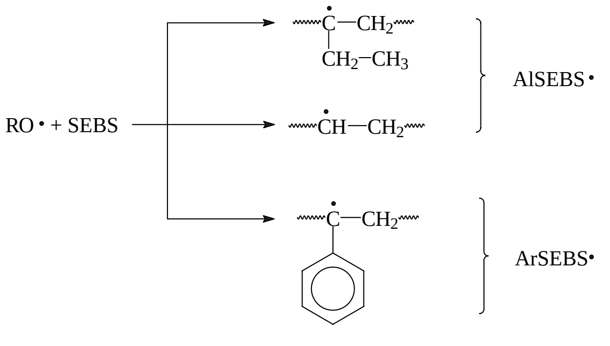

Fig. 12. Possible macroradicals formed by hydrogen abstraction from the units of SEBS macromolecules.

blocks (Fig. 13). When the free radical giving the degradation is close to the junction with the S-block, polystyrene chains are formed which are extracted with acetone and the residual insoluble polymer contains a lower amount of aromatic units (Table 1).

The complete solubility of the polymer after the reaction and the lack of an appreciable increase of molecular weight seem to exclude crosslinking and indicate that chain extension is limited. As these last reactions are bimolecular with respect to the SEBS free radical, evidently they give rise preferentially to reactions such as grafting, transfer and degradation, which are first-order with respect to the macromolecular radical.

The data collected up to now do not allow giving a definite

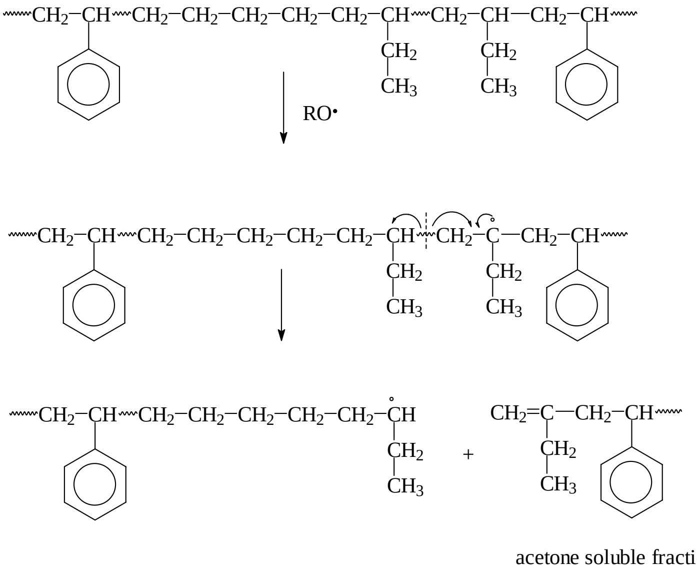

Fig. 13. Chain degradation by β-scission reaction producing polystyrene rich low molecular weight macromolecules.

explanation for the absence of functionalization of the styrene blocks.

The possibility of functionalizing polystyrene under similar conditions suggests that grafting of succinate groups on the styrene unit is possible. Therefore, both for the LLDPE/PS mixture and in SEBS the highly preferential selectivity of the grafting process for the aliphatic chain must be bored on kinetic grounds. The benzylic radicals are more stable than the aliphatic one and therefore less reactive toward the monomer. The radical formed after reaction of maleate (or MAH) is certainly favored with respect to the aliphatic radicals, but less than the benzylic radical. An additional contribution may be derived from the better compatibility of the monomer for the soft phase than for the hard one. However these points still need more data before a definitive interpretation can be given.

Acknowledgements

The authors express their thanks to Prof. Francesco Ciardelli and Prof. Mauro Aglietto for helpful discussion and Dr Marco Geppi for solid state NMR

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