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Functionalization of a styrene/butadiene random copolymer by radical addition of L-cysteine derivatives

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Abstract

The functionalization of a styrene/butadiene (20/80) random copolymer (SBR) is performed by radical-mediated addition of L-cysteine derivatives to the macromolecules' double bonds. The reaction carried out in solution and in the melt leads to SBR chain bearing amino and carboxylate functionalities through thiol addition to the vinyl double bonds of the 1,2-butadiene units with anti-Markovnikov regioselectivity. The addition yield (up to 5 wt%) and the occurrence of the crosslinking side reaction are investigated with reference to feed conditions and process parameters. The optical rotation of the reaction products confirms the addition of L-cysteine to SBR chain and provides a simple route to prepare optically-active polymers containing pendant amino acid residues.

Keywords: L-Cysteine ethyl ester; SBR copolymer; Functionalization of polymers

1. Introduction

The free-radical addition reaction of thiols supporting carboxy-, hydroxy-, epoxy-, siloxy-groups onto polybutadienes with different structure (PB), was widely studied since 1947 [1–6]. Pioneer works by Cunneen and coworkers [1–3] and by Oswald [4] showed the possibility to modify polybutadiene rubber by reaction of thiols with the double bonds both in presence of radical initiator or UV irradiation. Priola's and Pascault's groups [7–9] extended the study to the thiol addition reactions onto telechelic liquid polybutadienes (hydroxy-terminated HTPBD, or carboxy-terminated CTPBD), strategic materials for propellant or polyurethane formulation [10–14].

To better understand the mechanism and the key parameters of the reaction, low molecular weight (internal and terminal olefins [15–18] or butadiene oligomers [8,19–22]) and high molecular weight macromolecules (polybutadienes with well defined structure and different content of 1,2 and 1,4 (*cis* and *trans*) units [11,18,23]) were used as model compounds. The collected results showed the larger reactivity of vinyl double bonds than the internal ones thus highlighting a decrease of reactivity with increasing substitution on the double bonds; also, among the 1,2 bisubstituted olefins the *cis* isomers are more reactive than the *trans* ones. Besides the prevalence of the "anti-Markovnikov" isomer was clearly demonstrated and explained on the basis of the intermediate radical stability [24,25] or steric factors [22,26].

The process, mostly performed in solution, was carried out with diazo compounds, peroxides, and photosensitizers as activators [4,6–8,10,12,13]. The steric hindrance of thiol affected negatively the yield: thus complete addition was observed for *n*-butanethiol, whereas partial addition with slower kinetics was reported for 2,2-dimethyl propanethiol [11]. Moreover thiols with an ester group were more reactive than those with a free carboxylic group [2,6]. Different functional groups can be attached to the rubber by using different thiols. The addition of mercaptoacetic acid, thioglycolic acid

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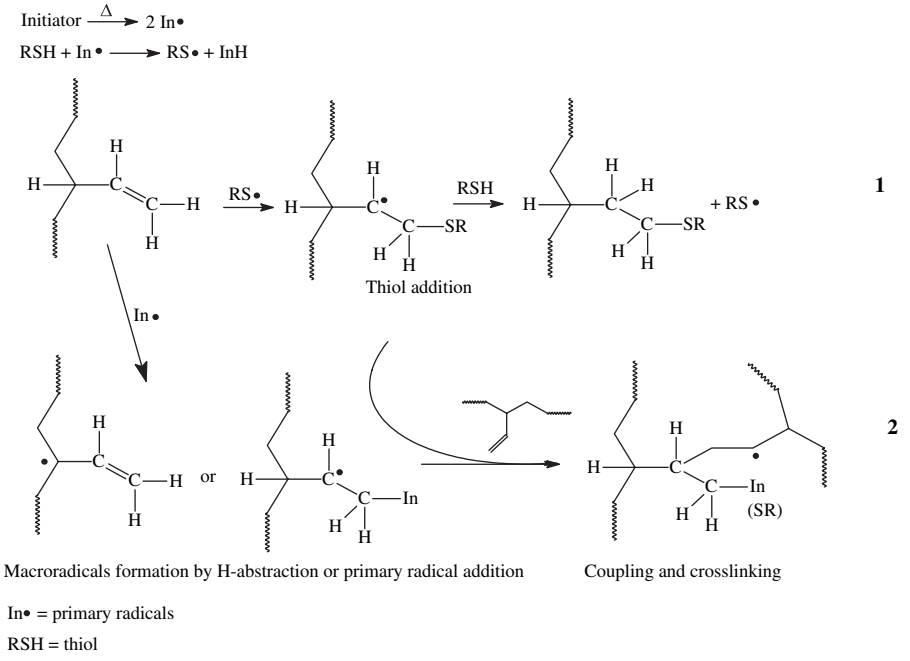

Scheme 1. Possible reactions occurring during the thiol radical addition to vinyl double bonds of SBR copolymer in the presence of free-radical initiator: (1) radical-mediated thiol addition reaction and (2) radical-induced crosslinking reaction.

[12] or mercaptoethanol [19] leads to carboxy- or hydroxy-functionalized rubber. Also other mercapto compounds, such as phosphonated thiols [14,27], fluorinated thiols [13], mercaptopropyltriethoxysilane [20,22], and thioacetic acid [28] were reacted to PB or ethylene-propylene diene rubber, (EPDM). Silane-modified PB was allowed to selectively crosslink [21,29] and the thioacetate-modified EPDM, after hydrolysis, was used in blends with sulphur-vulcanized nitrile rubber [28]. Very recently, the addition of alkanethiols [30] to terminal unsaturation of polypropylene (PP) was successfully used without apparently affecting the molecular weight. Contemporary Schlaad et al. [31] obtained functional block copolymers by reacting mercaptans with very different structure and functionalities: 3-mercaptopropionic acid and its methyl ester, 2-mercaptoethyl-diethylamine hydrochloride, 2-mercaptoethylamine hydrochloride, *N*-acetyl-L-cysteine methyl ester, 3-mercapto-1,2-propanediol, benzyl mercaptan and 1-mercapto-1*H*,1*H*,2*H*,2*H*-perfluorooctane were successfully added onto 1,2-polybutadienes and 1,2-polybutadienes based block copolymers characterized by low molecular weight with very high yield of grafting (typically 70–80%).

In the frame of the radical-mediated polymer modification, the addition to double bonds of thiol radical was considered a specific and selective reaction not directly involving the formation of polymeric alkyl radical species which – especially in the case of polyolefins – undergoes to side reactions depending on feed conditions and polymer structure [32–34]. Therefore the available literature about the thiol addition was generally focused to the obtainment of functionalized materials and only in few cases changes of molecular weight and formation of gel content were investigated [28]. Actually side reactions such as crosslinking take place, particularly in the presence of high percentage of vinyl groups and for high molecular weight polymers.

In a previous report we studied the addition of thiol bearing carboxy and ester groups (thioglycolic acid derivatives) to functionalize a random styrene/butadiene copolymer (SBR) and controlling at the same time the undesired side reactions [35]. The influence of reaction conditions was studied by changing feed with the aim to optimize the functionalization degree and minimize the formation of insoluble crosslinked polymer (Scheme 1).

In the present paper, taking into account the results of our previous study [35], the addition to SBR of L-cysteine ethyl ester (L-CysEt) was studied with the aim to introduce functionalities – as the resulting carboxy and amino groups of the L-CysEt-modified SBR (Fig. 1) – strategic for the blending of this very important elastomer with organic and inorganic substrates and give new composites for application in the field of rubber materials (tyres, gasket, etc.).

Moreover the chiral amino acid side groups can be useful for the blending of SBR with natural polymer containing

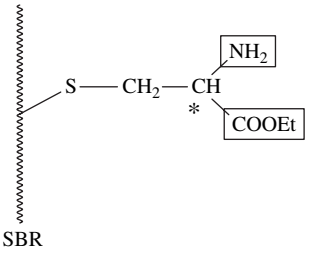

Fig. 1. Structure of L-CysEt-modified SBR with the inserted functional groups evidenced.

optically-active amino acid residues such as collagen and other proteins.

The reaction, initiated by α,α′-azobisisobutyronitrile (AIBN) was first studied in the case of low molecular weight olefins as models in order to evaluate the reactivity of L-CysEt towards double bonds with a different structure. Successively it was extended to SBR in toluene solution and in bulk by using a Brabender mixer. All the products were characterized by NMR and IR spectroscopies, GPC measurements, DSC analysis to highlight structural changes, modification extent and thermal property variations. Polarimeter was used to check the optical activity of polymers owing to the modification.

2. Experimental part

2.1. Materials

SBR copolymers were kindly supplied by EniChem Elastomeri S.p.A. (Ravenna): the SBR dry copolymer (SBR dry) contained 33 wt% of styrene (19.7 mol%) and 67 wt% of butadiene (about 49 mol% 1,2 units and 31.3 mol% 1,4 units); the oil extended SBR copolymer (SBR oil) had same polymer composition and contained 35 wt% of aromatic oil.

L-Cysteine ethyl ester (L-CysEt) was obtained by neutralization of L-cysteine ethyl ester hydrochloride (Aldrich): in a round bottom flask, under inert atmosphere, 5 g of L-cysteine ethyl ester hydrochloride (L-CysEt·HCl, 0.0269 mol) was solubilized in 100 mL of water and 53.9 mL of a 0.5 M solution of NaOH were added drop by drop (0.0269 mol) at room temperature; L-CysEt was extracted with ethyl acetate (four rates of 150 mL) and subsequently distilled under reduced pressure (49 °C, 0.1 mm).

IR (KBr): 3358 (s, N–H), 2254 (m, S–H), 1737 cm^{-1} (vs, C=O).

^1H NMR ($CDCl_3$): $\delta = 4.16$ (q, $-O-CH_2-CH_3$, $J = 7$ Hz), 3.6 (t, $-CH_2-CH(NH_2)-COOEt$, $J = 7$ Hz), 2.82 (d, $HS-CH_2-CH$, $J = 7$ Hz), 1.68 (broad, $-SH$, $-NH_2$), 1.26 ppm (t, $-O-CH_2-CH_3$, $J = 7$ Hz).

$[\alpha]_D^{25} = -54.7$ at C1 in chloroform.

The *N*-acetyl-L-cysteine methyl ester (Ac-L-CysMet, Aldrich, >99%) was used without any previous treatment.

$[\alpha]_D^{25} = -26.5$ at C1 in methanol.

1-Dodecene and a mixture of *cis* and *trans* 7-tetradecene (Fluka) were purified by distillation under reduced pressure (80 °C at 0.5 mm and 120–140 °C at 0.5 mm, respectively).

α,α′-Azobisisobutyronitrile (AIBN) (Carlo Erba) was purified by recrystallization from ethanol. All the solvents used were purified by standard procedures.

Benzoyl peroxide (BPO) (dibenzoyl peroxide, Luperox® A98, Aldrich, 97%) was used without purification.

2.2. Functionalization reactions

2.2.1. Addition of L-CysEt to low molecular weight olefins

Run 1: 10 mL of pure toluene, 3 mL (0.0136 mol) of 1-dodecene, 2.02 g (0.0136 mol) of L-CysEt and 0.0446 g (2.72×10^{-4} mol) of AIBN were introduced into a two-necked flask under nitrogen atmosphere and the resulting mixture was stirred and heated at 90 °C for 4 h and then cooled down to room temperature. The reaction product containing the unreacted olefin, the unreacted L-CysEt and the resulting thioethereal compounds was recovered by evaporation of solvent (toluene) and analyzed by IR and NMR spectroscopies. The addition product (thioethereal) was isolated by removing other products (essentially unreacted olefin and L-CysEt) by distillation under reduced pressure and the residue (2.41 g) was characterized by IR, ^1H NMR and GC–MS.

IR (KBr): 3358 (s, N–H), 2978, 2934 (vs, $-CH_2$, CH_3), 1737 cm^{-1} (vs, C=O).

^1H NMR: $\delta = 4.2$ ($-O-CH_2-CH_3$), 3.6 ($-S-CH_2-CH(NH_2)-COOEt$), 2.6–2.3 ($-CH_2-CH_2-S-CH_2-CH-$), 1.9 ($-NH_2$), 1.25 ($-O-CH_2-CH_3$) and ($-CH_2-CH_2-CH_2$, olefin), 0.85 ppm ($-CH_2-CH_2-CH_3$, olefin).

MS (70 eV): $m/z = 244$ ($M^+ - -COOEt$), 215 ($M^+ - -CH(NH_2)-COOEt$), 201 ($M^+ - -CH_2-CH(NH_2)-COOEt$), 102 ($M^+ - CH_3-(CH_2)_{11}-S-CH_2-$).

Run 2: into a two-necked flask were introduced under nitrogen atmosphere 4.5 mL (0.0203 mol) of 1-dodecene and 3.031 g (0.0203 mol) of L-CysEt. After stirring for 1 h, 0.0666 g (2.03×10^{-4} mol) of AIBN was added and the resulting mixture was heated at 90 °C for 4 h. The reaction product and the unreacted reagents were separated by distillation under reduced pressure and analyzed by IR and the residue (3.71 g) that consists in the addition product was characterized by IR and GC–MS.

Run 3: 10 mL of pure toluene, 6.6 mL (0.0260 mol) of an isomeric mixture of *cis* and *trans* 7-tetradecene, 3.88 g (0.0260 mol) of CysEt and 0.0853 g (5.2×10^{-4} mol) of AIBN were introduced into a two-necked flask under nitrogen atmosphere and the resulting mixture was stirred and heated at 90 °C for 4 h and then cooled down to room temperature. The separation of reagents and products was carried out as described as above; no residue was collected.

2.2.2. Addition of L-CysEt to SBR in solution

The following procedure is related to the sample 1, but was applied to all the runs reported in Table 2: in a round bottom flask equipped with a refrigerant and a switchable inlet for nitrogen and vacuum connector were introduced under inert atmosphere 60 mL of pure toluene and 1.7182 g (0.0272 mol) of SBR dry and the resulting mixture was allowed to stir until complete solubilization of the polymer. Indeed, under nitrogen, 1.633 g (0.011 mol) of L-CysEt and 0.0036 g (2.2×10^{-5} mol) of AIBN were added and the solution was heated under stirring at 90 °C for 4 h. The polymer was precipitated by pouring the solution into 1 L of acetone, then purified by re-precipitation and kept at room temperature under vacuum until constant weight. For the runs 2 and 4–6 insoluble polymer fractions were collected and the amount of gel determined by solvent extraction with Kumagawa with toluene for 16 h. The samples were characterized by IR, NMR, GPC and DSC analysis.

2.2.3. Addition of L-CysEt and Ac-L-CysMet to SBR in the melt

The runs were carried out by using the SBR oil extended in a Brabender Plastograph PL2100 Mixer (30 cc) (Table 3): the torque values and temperature data were acquired by Brabender Mixing software WinMix ver.1.0. SBR oil (20 g) was added to the reactor chamber under nitrogen flux at a temperature of 120 °C and a rotational speed of 50 rpm; after stabilization of the torque (about 3 min) the chemical reagents L-CysEt (1 g, 6.7×10^{-3} mol), or Ac-L-CysMet (1.2 g, 6.7×10^{-3} mol), AIBN (0.0022 g, 1.3×10^{-5} mol) or BPO (0.0031 g, 1.3×10^{-5} mol) were added to the molten SBR and the reaction carried out for 15 min. The samples were recovered, about 2 g dissolved in chloroform ($CHCl_3$), and precipitated in methanol in order to remove the low molecular weight products (the decomposition products of the peroxide and the unreacted functionalizing molecules) and then dried until constant weight. The samples were characterized by IR, NMR, and GPC analysis.

2.3. Instrumentations

2.3.1. FT-infrared analysis

Infrared spectra were performed with a Fourier transform spectrometer "Perkin–Elmer FT-IR 1750" on films cast from chloroform solution on a KBr window; or by deposition of a drop of liquid between two KBr windows.

2.3.2. ^1H NMR analysis

Proton magnetic resonance spectra were performed with a spectrometer "Varian Gemini 200 MHz"; all the spectra were obtained in deuterochloroform solution and the chemical shifts were assigned in ppm using tetramethylsilane (TMS) as internal standard.

2.3.3. SEC analysis

The SBR molecular weight was obtained by using the instrument as follows: Jasco PU-1580 equipped with Jasco 830-RI as Refractometer Index and two columns PL gel mixed C 5 m (polymer Laboratories). The analysis were performed onto chloroform diluted solutions (0.1 wt%). The calibration curve was realized with polystyrene standard samples.

2.3.4. GC–MS analysis

Gas chromatography analysis was performed with a Perkin–Elmer 8550 instrument interfaced with a mass spectrography Q-mas 910. The samples were prepared in diethyl ether solution.

2.3.5. Differential scanning calorimetry

DSC analysis was performed with a Perkin–Elmer DSC7 calorimeter in the temperature range from −90 °C to 30 °C at a scanning rate of 20 °C/min. The calibration was carried out using mercury (m.p. −38.4 °C) and indium (m.p. 156.2 °C) standards.

2.3.6. Polarimetric analysis

The optical activity measurements for cysteine derivatives and functionalized polymers were performed with a Digital Polarimeter Jasco DIP-360 in chloroform or methanol solutions.

2.4. Determination of the functionalization degree

The functionalization degree (FD, mol%) defined as the number of L-CysEt grafted molecules per 100 monomeric units of SBR copolymer (referred to styrene + butadiene units) was determined on the basis of a FT-IR calibration curve carried out by employing mixtures between SBR and L-CysEt containing a well-known amount of L-CysEt.

Four different chloroform solutions between SBR (2 g) and determined amount of L-CysEt 0.0477, 0.1415, 0.2384, 0.5215 g, respectively (1, 3, 5, 11 mol with respect to 100 monomeric units of SBR), were prepared in a flask, stirred and heated at 50 °C for 4 h. Five FT-IR spectra of each mixture were recorded on cast films and the area of the 1740 cm^{-1} (A1 due to the grafted carbonyl groups stretching of L-CysEt) and 1826 cm^{-1} bands (A2 aromatic overtone) was calculated (Fig. 2).

The corresponding average ratios A1/A2 were reported in a graph versus the FD values determined on the basis of the mixture compositions. The curve obtained was used to quantitatively determine the FD: for the functionalized samples the C=O stretching area A1 (centred at 1734 cm^{-1}) and the area of the overtone band of the aromatic ring A2 (at 1826 cm^{-1}) were calculated and the ratio A1/A2 was correlated to the FD values through the calibration curve.

3. Results and discussion

The radical addition of L-CysEt to low molecular weight monoalkenes, such as 1-dodecene and the *cis* and *trans* isomeric mixture of 7-tetradecene (Table 1), was carried out by using an equimolar ratio between double bonds and thiol groups and 2 mol% of initiator with respect to the cysteine derivative. The NMR and GC–MS analyses of the purified product confirmed even for this particular thiol the higher reactivity towards vinyl groups with respect to the internal double bonds (no addition product was isolated in the case of 7-tetradecene). The structure of the thioether derivative suggested that the reaction proceeded following "anti-Markovnikov" regiochemistry as expected on the basis of previous studies [18,22,35].

The yield of reaction was relatively low when compared to thioglycolic acid or ethyl mercaptoacetate used in our previous work [35] with the same olefin substrate. The formation of cycles through intramolecular hydrogen bond involving the –SH group (Fig. 3) reported for cysteine [36] probably make the thiol group less available to react with primary radicals derived from AIBN and negatively affects the addition to the double bonds. A similar negative effect may arise from the formation of cystine in the presence of oxygen traces [37] or from the formation of the thiolate due to the deprotonation of –SH groups by the amino groups [38].

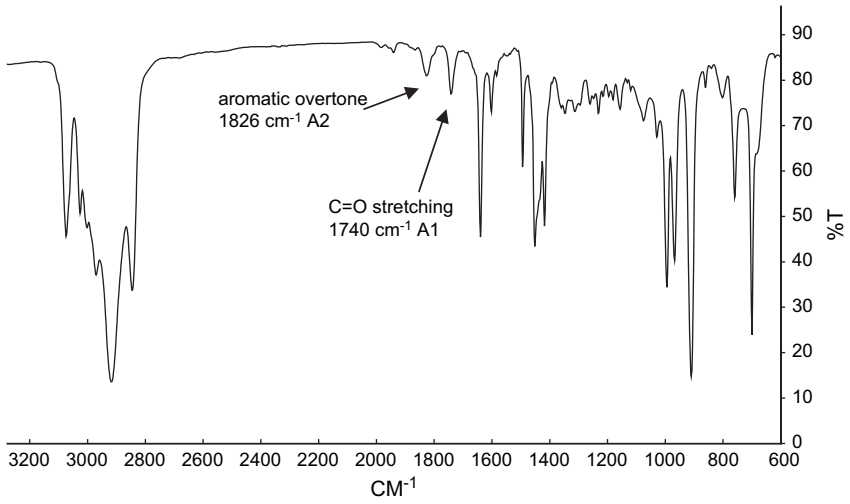

Fig. 2. FT-IR spectrum of the mixture between SBR and L-CysEt (3 mol% obtained by mixing 0.35 g of L-CysEt per 5 g of SBR).

Table 1
Addition reaction of L-CysEt to 1-dodecene and 7-tetradecene

Run	Solvent	Olefin	Addition product	Yield[a] (mol%)
1[b]	Toluene	$CH_3-(CH_2)_9-CH=CH_2$	$CH_3-(CH_2)_{11}-S-CH_2-CH(NH_2)-COOEt$	19
2[c]	None	$CH_3-(CH_2)_9-CH=CH_2$	$CH_3-(CH_2)_{11}-S-CH_2-CH(NH_2)-COOEt$	25
3[b]	Toluene	$CH_3-(CH_2)_5-CH=CH-(CH_2)_5-CH_3$ mixture of *cis* and *trans*	None	0

[a] Calculated with respect to the olefin.
[b] Reaction conditions: $T = 90$ °C, time 4 h, CysEt/olefin 1/1 mol/mol, AIBN = 2 mol% with respect to the CysEt.
[c] Reaction performed without solvent.

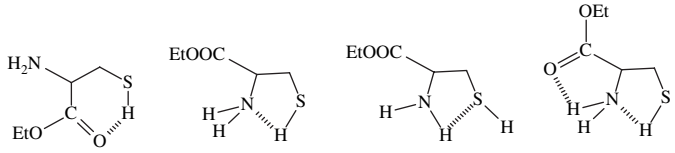

Fig. 3. Possible intramolecular hydrogen bonding of L-CysEt involving −SH group.

Higher molar ratios (between 50 and 100) of L-CysEt to the polymer double bonds than with thioglycolic acid and ethyl mercaptoacetate [35] were used for the reaction with the SBR copolymer (SBR dry), carried out in toluene by using again AIBN as free-radical initiator (Table 2).

The occurrence of radical addition, and thus the functionalization of the SBR copolymer, was confirmed by FT-IR spectroscopy after purification of samples (by re-precipitation in acetone) to remove the low molecular weight unreacted chemicals. An absorption band attributable to the stretching C=O of the grafted L-CysEt was detected at 1734 cm^{-1} (Fig. 4), the intensity of which was related to the functionalization degree (FD) on the basis of the previously obtained calibration curve (see Section 2).

The presence of pendant cysteine derivatives was confirmed by the comparative ^1H NMR analysis of un-functionalized and functionalized SBR samples which were highlighted in the latter one by the presence of weak signals at 4.2, 3.6 and 0.9 ppm, attributable to the protons $>CH-$, $-COOCH_2CH_3$ and $-COOCH_2CH_3$ of the grafted cysteine residues while the protons of the methylene $-CH_2-S-CH_2-$ at about 2.4–2.6 ppm are hidden by strong signals of aliphatic polymer protons (Fig. 5).

The FD values varied from 0.34 to 2.21 mol% depending on the feed composition with particular reference to the AIBN/L-CysEt and L-CysEt/SBR molar ratios. Indeed in all experiments a large excess of L-CysEt was used in respect to the available double bonds (from 50 to 100 mol%) and in particular to the vinyl double bonds which are the only reactive. The FD, even if the data collected were not optimized in a systematic way, showed an increase with the AIBN content by decreasing the L-CysEt/AIBN molar ratio (runs 2 and 4–6). This latter is also fundamental to avoid crosslinking which is higher than 50 wt% for L-CysEt/AIBN lower than 100 (runs 4–6). The FD value even with 3 mol% of AIBN is only 2.2 mol% (run 6) thus indicating that only 20% of vinyl double bonds were reacted.

By using a smaller amount of initiator (0.2 mol% with respect to L-CysEt, runs 1 and 2) samples characterized by a slightly higher $\overline{M}_w$ (as observed from GPC data) were produced without crosslinked polymer.

Table 2
Addition of L-CysEt to SBR in toluene

Run[a]	AIBN (mol%)		L-CysEt/AIBN (mol/mol)	FD, mol% (wt%)	Insoluble fraction (wt%)	$\overline{M}_n$ (10^3 D)	$\overline{M}_w$ (10^3 D)	T_g (°C)
	To SBR	To L-CysEt						
SBR	–	–	–	–	0	415	601	−21.2
1[b]	0.08	0.20	500	0.34 (0.78)	0	454	1142	n.d.
2[d]	0.16	0.20	500	0.53 (1.22)	0	376	1078	−20.5
3[b]	0.80	2.00	50	1.30 (3.00)	100	–[c]	–[c]	n.d.
4[d]	0.80	1.00	100	1.26 (2.91)[e]	53	–[c]	–[c]	n.d.
5[d]	1.60	2.00	50	1.87 (4.32)[e]	70	–[c]	–[c]	n.d.
6[d]	3.00	3.10	27	2.21 (5.10)[e]	80	–[c]	–[c]	−19.7

n.d. = not determined.
[a] Reaction conditions: $T = 90$ °C, $t = 4$ h.
[b] L-CysEt = 40 mol% to SBR (monomeric units) which corresponds to 50 mol% to the double bonds.
[c] Not determined due to the presence of insoluble polymer fraction.
[d] L-CysEt = 80 mol% to SBR (monomeric units) which corresponds to 100 mol% to the double bonds.
[e] FD determined for soluble fraction.

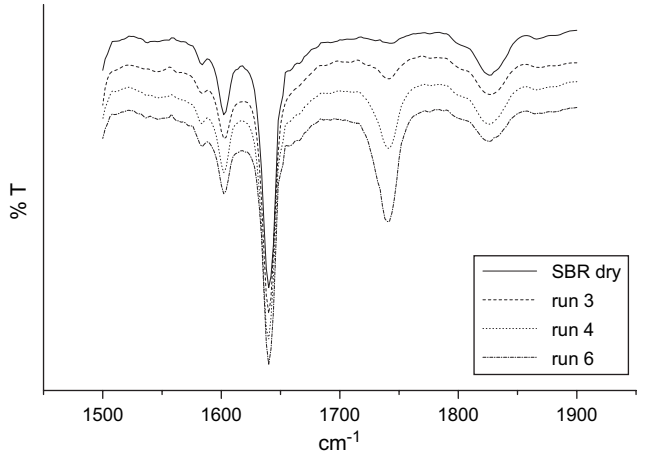

Fig. 4. FT-IR spectra of runs 3–6 compared to the SBR sample (enlargement of carbonyl stretching range).

The T_g of the resulting functionalized samples substantially unchanged with a little increase (of about 1.5 °C) which can be attributed both to the presence of the inserted steric bulky functional groups and of some crosslinking/branching.

The addition reaction of L-CysEt to SBR in the bulk was performed in a Brabender mixer by using the same SBR sample but with added aromatic oil as plasticizing agent (35 wt%, see Section 2) to favour the mixing of reagents (polymer, cysteine derivatives and initiator), to lower the mechanical stress during the processing, and to simulate the industrial conditions and materials. L-Cysteine ethyl ester (L-CysEt) and *N*-acetyl-L-cysteine methyl ester (Ac-L-CysMet) were used in a remarkably smaller molar concentration (3.3 mol% to SBR and 4.2 mol% to the amount of the double bonds, Table 3) to realize more sustainable conditions. Also, AIBN or BPO was used in a very low amount (0.007 mol% with respect to SBR and 0.2 mol% with respect to cysteine derivative) to avoid crosslinking.

The conversion of the monomer was consolidated at about 30–33% with respect to the feed for both cysteine derivatives. Moreover by using a low concentration of initiator (0.007 mol% with respect to SBR) no remarkable variations of molecular weight of the polymer were observed except for the run carried out with the peroxide. In this case the primary radicals reacted promptly and preferentially with polymer through H-abstraction (probably of allylic H) thus favouring the reactions involving macromolecular chains like coupling and crosslinking [39,40] (Scheme 1, reaction 2), whereas the 2-cyano-2-propyl radicals derived from AIBN are characterized by a lower tendency to abstract H from macromolecular chains [41] (Scheme 1, reaction 1).

The FD values were appreciable and similar with those generally observed for the radical-mediated modification of polyolefins with maleic anhydride derivatives in the melt, (i.e. about 1 mol% [33,34]). This FD corresponds to approximately 30–35 pendant L-CysEt or Ac-L-CysMet residues for SBR macromolecule which should grant compatibility with polyamides and polyamino acids. The functionalized samples show detectable optical rotation in chloroform solution further confirming the occurrence of the radical grafting of the amino acid onto backbone of the SBR. By considering the concentration of cysteine residues in the polymers (about 2 wt% for both the samples) the $[\alpha]_D^{25}$ values were higher than that expected from the monomer as reported for photochemical addition of *N*-acetyl-L-cysteine to low molecular weight chemicals (bilirubin) [42] and to polyesters bearing pendant vinyl ether groups [43]. This is due to the different mobility of chiral atom and to the different chemical surroundings owing to the grafting [44]. The radical addition reaction of L-cysteine derivatives to unsaturated polymers can then be considered a simple synthetic route to obtain optically-active hydrocarbon based polymers.

4. Conclusions

SBR copolymers bearing amino acid derivative as pendant groups were synthesized by free-radical addition of L-cysteine ethyl ester to vinyl double bonds initiated by AIBN; this reaction allowed to obtain in a one-step grafting of ester and amino groups to the hydrocarbon backbone. The grafting was confirmed and quantitatively evaluated by IR and NMR analysis. The results obtained showed complete selectivity towards

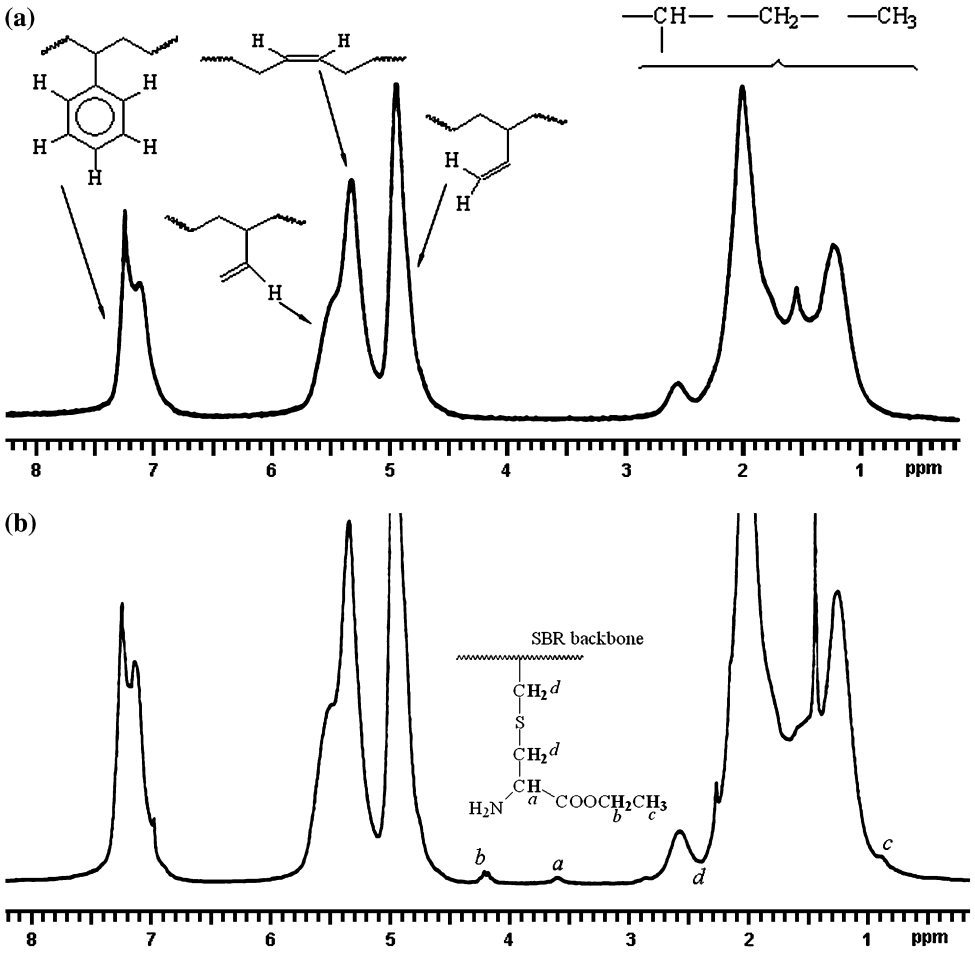

Fig. 5. ^{1}H NMR of SBR samples: (a) un-functionalized and (b) functionalized (run 2).

Table 3
Addition of cysteine derivatives to SBR (oil extended) in the melt

Run[a]	AIBN (mol%)		L-CysEt/initiator (mol/mol)	FD, mol% (wt%)	Insoluble fraction (wt%)	$\overline{M}_n$ (10^3 D)	$\overline{M}_w$ (10^3 D)	$[\alpha]_D^{25}$ [b]
	To SBR	To L-CysEt						
SBR oil	–	–	–	–	0	248	559	–
7	0.007	0.2	470	1.0 (2.3)	0	210	470	−2.1
8	0.007	0.2	470	0.7 (1.6)	100	–[c]	–[c]	–[c]
9[d]	0.007	0.2	470	1.2 (1.7)[e]	0	n.d.	n.d.	−2.4

n.d. = not determined.
[a] Reaction conditions: $T = 120$ °C, $t = 15$ min, rpm = 50; cysteine derivative = 3.3 mol% to SBR and 4.2 mol% to the amount of the double bonds; half-life time at $T = 120$ °C, $t_{1/2}$ AIBN = 50 s, $t_{1/2}$ BPO = 5.5 min.
[b] In chloroform at 25 °C.
[c] Not determined due to the presence of insoluble polymer fraction.
[d] Run carried out with *N*-acetyl-L-cysteine methyl ester (Ac-L-CysMet).
[e] Determined by using the calibration curve obtained for L-CysEt.

vinyl double bonds. L-Cysteine ethyl ester resulted less reactive than thioglycolic acid and ethyl mercaptoacetate previously used in similar process carried out onto SBR and gave functionalization degree about three times lower under various conditions. Conditions were determined under which cross-linking can be avoided. The process was also carried out by performing the reaction in the bulk at high temperature (120 °C), and thanks to better and improved dispersion of the low molecular weight reagents in the polymer that allowed to obtain functionalized polymer with good yield (the conversion of the monomer was 33%), appreciable FD values (about 1 mol%), without remarkable molecular weight changes in spite of the low L-Cys derivative content. Furthermore the chiro-optical properties of modified-SBR confirmed the presence of optically-active residues attached to the backbone thus indicating that by this procedure it is possible to obtain optically-active hydrocarbon polymers due to the grafted functional groups with a prevalent chiral configuration.

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