Alder ene functionalization of polyisobutene oligomer and styrene-butadiene-styrene triblock copolymer

Andrea Pucci[a,b,*], Chiara Barsocchi[a], Riccardo Rausa[c], Luigi D'Elia[c], Francesco Ciardelli[a,d]

[a]*Department of Chemistry and Industrial Chemistry, University of Pisa, Via Risorgimento 35, 56126 Pisa, Italy*
[b]*INSTM, Pisa research unit, Via Risorgimento 35, 56126 Pisa, Italy*
[c]*EniTecnologie SpA, Via F, Maritano 26, 20097 San Donato Milanese, Italy*
[d]*INFM PolyLab, Largo Pontecorvo 1, 56127 Pisa, Italy*

Abstract

The Alder ene functionalization reaction of double bonds containing macromolecules such as polyisobutene oligomer (PIB) and a styrene-butadiene-styrene triblock copolymer (SBS) samples with maleic anhydride (MAH) or diethyl maleate (DEM) as enophiles is described. The analysis of the products by means of different techniques assesses the addition of the polar molecules to the reactive vinylidene units of the polymer with functional degrees (FD) depending on the type of enophile and polymer reactivity. The role of the reaction conditions and the use as Lewis acids as catalysts are discussed in terms of their influence on the addition reaction extent and on the polymer molecular weight.
© 2004 Elsevier Ltd. All rights reserved.

Keywords: PIB oligomer; SBS triblock copolymer; Alder ene functionalization

1. Introduction

In the last years, the Alder ene reactive modification of vinylidene terminated polyolefins has been thoroughly investigated because of its suitability for polymer functionalization in the melt phase [1–4]. Particularly, polyisobutene (PIB) [5–9] and polybutadiene (PB) [10] have been efficiently functionalized in the melt with maleic anhydride (MAH).

The Alder ene reaction involves the interaction between an alkene, having an allylic hydrogen (an ene), and a compound containing an insaturation (enophile), to form a new bond with migration of the ene bond and 1,5-hydrogen

---

shift [11]. Traditionally, the Alder ene reaction has been thought to proceed through a concerted mechanism involving six electrons transition state, similarly to the much better known Diels–Alder reaction [12]. Differently from this last, the reaction between the ene and enophile requires more dramatic conditions, such as highly electron-deficient enophile and elevated temperature. Temperature higher than 150 °C, long residence times and MAH as enophile must generally be used for Alder ene polymer modifications [1]. Since the enophile is electron deficient, Lewis acid is effective in accelerating the Alder ene reaction. Thus, catalytic amount of stannous and ruthenium chlorides in the presence of an inhibiting radical-induced grafting agent, have been shown to be very efficient in the functionalization of olefin terminated polypropylene [3]. In connection with these findings, highly reactive low molecular weight PIBs with terminal double bonds prepared by BASF are very reactive in the Alder ene functionalization [13,14].

The vinylidenic double bonds of PIB oligomers reacts with MAH above 150 °C to give the succinic anhydride PIB derivative (PIBSA) and generate another exo group able to react with an excess of enophile according to Scheme 1.
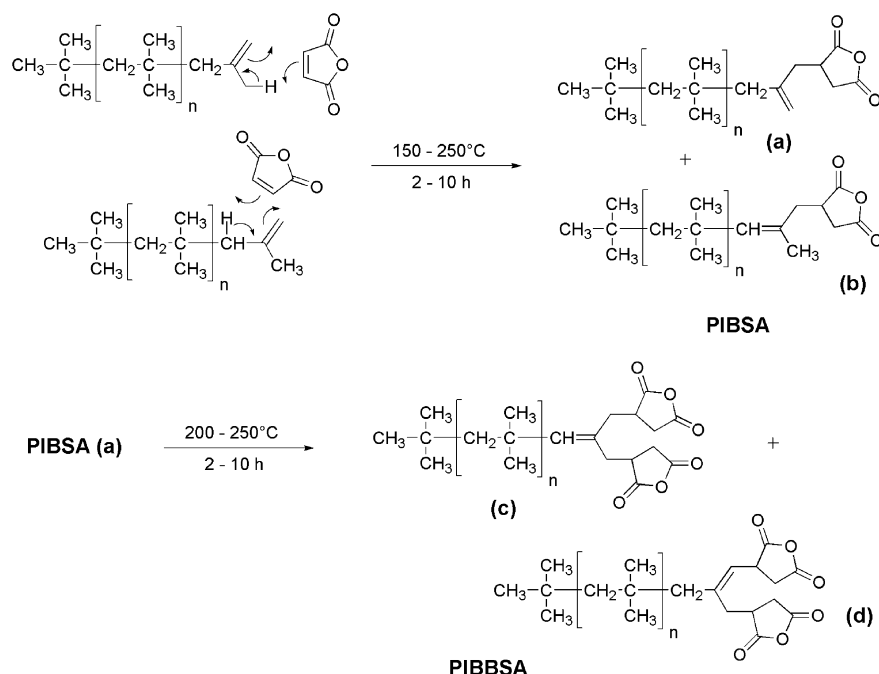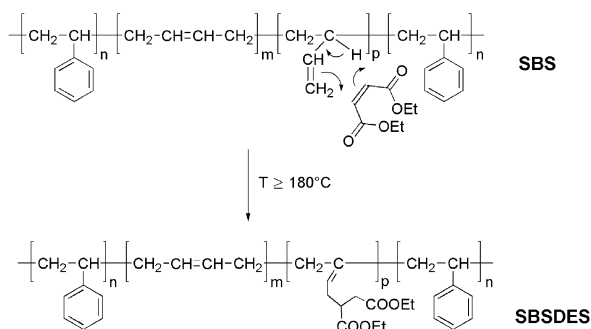
Scheme 1. Alder ene reaction between PIB and MAH.

Two PIBSA derivatives ((a) and (b)) may be obtained, the former with higher yield owing to the less steric hindrance. In the presence of an excess of MAH, the PIBSA (a) may undergo another Alder ene functionalization producing the bis-succinic anhydride derivative PIBBSA.

The styrene-butadiene random copolymer (SBR) and the poly(styrene-*b*-butadiene-*b*-styrene) (styrene-butadiene-styrene triblock copolymer, SBS) may be functionalized by enophiles through the Alder ene mechanism involving preferentially the vinyl side chains of the 1,2-butadiene units as for PB [10,15] and EPDM [1,16]. The Alder ene functionalization of SBS with MAH or diethyl maleate (DEM) as enophiles (Scheme 2) can allow the preparation of modified polyolefins containing different amounts of polar groups [17] without using free radical initiators. This allows to appreciably limit the formation of crosslinked macromolecular chains.

On the other hand, since the reaction requires high temperature and residence time special attention have to be addressed and the stable free radical (2,2,6,6-tetramethyl-1-piperidinyloxy, TEMPO) is used to prevent thermally promoted radical side reactions [2,3].

In the present work, the Alder ene functionalization of highly reactive PIB oligomers ($\bar{M}_n = 1300$) with MAH and/or diethyl maleate (DEM) as enophiles has been studied with the aim of producing polar groups containing hydrocarbon chains with good functionalization degree (FD). The chemical structure of modified PIBs and the effectiveness of the functionalization processes have been evaluated by using Fourier transform infrared (FTIR), proton nuclear magnetic resonance (^{1}H-NMR) and potentiometric titrations according to standard procedures.

At the same time, the Alder ene functionalization of a SBS triblock copolymer has been performed in the melt using DEM as enophile, and methods for enhancing the grafting degree and limiting the crosslinking reactions have been proposed. The modified polymer has been analyzed by FTIR and ^{1}H NMR spectroscopies to evaluate the FD and differential scanning calorimetry (DSC) to detect thermal transitions.

The collected data have provided information on the possibility to introduce polar functionalities in the polymer backbone without using free radical initiators and allowed to get a better understanding of the role of Lewis acids based catalysts during the functionalization process.

2. Experimental part

2.1. Materials

Highly reactive polyisobutene (PIB) Glissopal 1300 was

Scheme 2. Alder ene reaction between linear SBS triblock copolymers and DEM.

supplied by BASF Italia S.p.A. and was employed without further purification. This polymer contains 83% by mol of α-olefin units, 8% of β-olefin and 2.5% of tetrasubstituted olefins and is characterized by $\bar{M}_n = 1300$, $\bar{M}_w/\bar{M}_n = 1.6$ and less than 1 mg/kg of chlorine content.

The SBS linear triblock copolymer (Calprene 501) was provided by Softer S.p.A. (Forlì, Italy) and was employed without further purification. The polymer is characterized by a butadiene/styrene ratio of 69/31 by weight, an average molecular weight of blocks of 9300-41400-9300, a content of the vinyl units in the butadiene block of 10 wt % and a density of 0.94 g/cm^3.

Maleic anhydride (MAH; briquettes, Aldrich) was purified by recrystallization from benzene (Carlo Erba, Italy). Diethyl maleate (DEM; Aldrich) was distilled under reduced pressure (45 °C at 0.2 mmHg). (2,2,6,6-tetra-methyl-1-piperidinyloxy, free radical) TEMPO (Aldrich), SnCl$_2 \cdot$2H$_2$O (Aldrich), RuCl$_3 \cdot$nH$_2$O (Aldrich), N,N-dimethylformamide (J.T. Baker), 1-dodecanol (Aldrich), p-toluenesulfonic acid monohydrate (Aldrich), KOH (Carlo Erba, Italy), 2-propanol (Riedel-de Haën®), phenolphthalein (1% by vol hydroalcoholic solution; Carlo Erba, Italy), chloroform (CHCl$_3$; Carlo Erba, Italy) and n-heptane (Carlo Erba, Italy) were used without purification.

2.2. PIB functionalization reaction

In a general procedure, 100 g (0.077 mol) of PIB and the appropriate amount of enophile is placed in a 250 mL glass cylindrical reactor, equipped with a mechanical stirrer and a reflux condenser, swept by nitrogen flux and heated at a temperature higher than 180 °C. After 21 h of stirring (250 revolutions per minute (rpm)), the temperature was lowered to 180 °C and the unreacted enophile stripped off under vacuum (0.2 mmHg). After cooling to room temperature the crude product was dissolved in n-heptane, filtered and, after solvent evaporation, dried at reduced pressure (0.2 mmHg). In the case of Lewis acid catalyzed functionalization, 0.8% mol eq. of SnCl$_2 \cdot$2H$_2$O was added to the reaction mixture.

The reaction conversion degrees were evaluated after elution over silica gel of weighted amounts of the dried polymer dissolved in n-heptane. The eluted phases, containing just the unreacted PIB, were vacuum evaporated, dried at under pressure (0.2 mmHg) and weighted.

For samples functionalized with MAH, the functionalization degree (FD), defined in all cases as the molar number of grafted enophile groups per mole of reacted polymer, was determined by potentiometric titration (combined glass electrode, Metrohm AG), following the standard procedure ASTM D 664: a weighted amount of functionalized PIB was dissolved in 125 mL of a solvents mixture composed by 50% of toluene, 0.5% of water and 49.5% of 2-propanol in volume, and titrated with KOH solutions in 2-propanol, standardized with p-toluenesulfonic acid dissolved in 2-propanol and phenolphthalein as indicator. The total acid number (TAN) was calculated by dividing the milligrams of

KOH required to neutralize all acidic constituents per gram of reacted polymer, this last obtained from the grams of PIBSA employed in the analysis corrected by the conversion degree, to account for unreacted PIB present in the reaction mixture at the end of the functionalization process.

The functionalization degree (FD), was calculated as the mol of grafted succinic anhydride (SA) per mole of reacted polymer, adopting a modified formula derived from US 4,952,328, patent by Lubrizol Corporation. Being

$$FD = \frac{mol\ SA}{mol\ reacted\ PIB} \tag{1}$$

$$mol\ SA = \frac{g\ PIBSA \times TAN}{56100} \tag{2}$$

$$mol\ reacted\ PIB = \frac{g\ PIBSA - g\ SA}{1300}$$

$$= \frac{g\ PIBSA}{1300} \times \left(1 - TAN \times \frac{98}{56100}\right) \tag{3}$$

FD may be calculated by using Eq. (4):

$$FD = \frac{1300 \times TAN}{56100 - TAN \times 98} \tag{4}$$

When DEM is the only functionalizing monomer, the FD was determined by ^{1}H-NMR (Varian Gemini 200 MHz spectrometer at 20 ± 0.1 °C) analysis on CDCl$_3$ (internal standard; 99.6 + atom % D, Aldrich) functionalized PIB solution (5 10 wt%), comparing the area of the signals of diethyl-succinic groups grafted to the polymer (centred at 4.1 ppm –O–CH_2–CH$_3$) with respect to the area of methyl groups of the reacted polymer (centred at 1.0 ppm).

The FD was also determined with FTIR spectroscopy (PerkinElmer™ Spectrum One) on films obtained by the deposition of a chloroform solution onto a KBr window, by using a calibration curve, necessary to convert the intensity data into concentrations, determined by recording spectra of PIB/polydiethylfumarate (PDEF) mixtures prepared by simple dissolution of PIB and PDEF (prepared by free radical polymerization by using azobisisobutyronitrile as initiator) in prefixed amounts in chloroform [18]. The experimental points were then fitted by a linear regression (correlation coefficient $r^2 = 0.997$) performed by using Origin 7.5, software by OriginLab® Corporation.

PIB and functionalized polymer samples dissolved in CHCl$_3$ (0.5 wt%) were analyzed by gel permeation chromatography (GPC; PL-GPC210) at 25 °C. Refraction index Jasco 830-RI, two PLgel 5 μm MIXED-C columns (Polymer Laboratories) connected in series and a Jasco PU 1580 pump were used. Monodisperse poly(styrene) samples were used as calibration standards.

2.3. SBS functionalization reaction

In a general procedure, about 20 g of polymer was

introduced in the mixer under a nitrogen atmosphere at 200 °C; after 3 min, a mixture of DEM and TEMPO was added to the melt. The reaction was carried out for 18 min at a speed of rotor rotation of 50 revolutions per min (rpm) and then stopped. The recovered polymer was purified by dissolution in $CHCl_3$ and precipitation in methanol. The dissolution-precipitation cycle was repeated twice. The purified product was then dried at reduced pressure (0.2 mmHg), weighted and characterized.

In the case of Lewis acids catalyzed functionalizations, $SnCl_2 \cdot 2H_2O$ and $RuCl_3 \cdot nH_2O$ were previously dissolved respectively in 20 μL of DMF and 1-dodecanol, and added to the reaction mixture.

The FD was determined by means of FTIR spectroscopy (PerkinElmer™ Spectrum One) on films obtained by the deposition of a chloroform solution onto a KBr window, by using a calibration curve determined by recording spectra of SBS/polydiethylfumarate (PDEF) mixtures prepared by simple dissolution of SBS and PDEF in prefixed amounts in chloroform [18]. The experimental points were then fitted by a linear regression (correlation coefficient $r^2 = 0.997$) performed by using Origin 7.5, software by OriginLab® Corporation.

The differential scanning calorimetry (DSC) analyses were performed under nitrogen flux (80 mL/min) with a Mettler-Toledo/DSC 822^e equipped with a cooling system. The calibration was performed with Zinc and Indium. Heating and cooling thermograms were carried out at a standard rate of 20 °C/min.

SBS and functionalized polymer samples dissolved in $CHCl_3$ (0.5 wt%) were analyzed by gel permeation chromatography (GPC; PL-GPC210) at 25 °C. Refraction index Jasco 830-RI, XPLgel 20 μm MIXED-A columns (Polymer Laboratories) and a Jasco PU 1580 pump were used. Monodisperse poly(styrene) samples were used as calibration standards.

3. Results and discussion

3.1. PIB functionalization

The PIB functionalization was carried out in all cases with an excess of reactive monomer (molar ratio ≥ 1.5) and a catalytic amount of Lewis acid in order to promote the grafting of two enophile molecules to each PIB chain (Table 1).

The reactions were followed by FTIR spectroscopy, monitoring the disappearance of the vinylidene peak of PIB centred at 890 cm^{-1} as depicted in Fig. 1 [7].

3.1.1. PIB functionalization with MAH

At the end of the functionalization process, the unreacted enophile was removed by stripping the crude product at reduced pressure, and the modified polymer, purified through dissolution in *n*-heptane followed by filtration,
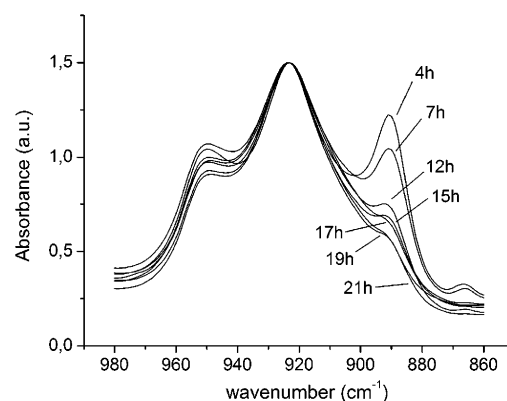

Fig. 1. Evolution of the vinylidene FTIR absorption during the Alder ene functionalization process.

was recovered after vacuum solvent evaporation. The very low amount of tar formed after PIB functionalization evidenced by the pale colour of the product and the low turbidity of the solution after filtration may indicate the prevention of side chain extension reactions promoted by free radical mechanism.

The FTIR spectra of PIBSA, reported in Fig. 2, shows, apart from the PIB macromolecular chain signals, the presence of the grafted succinic anhydride band due respectively to the symmetric carbonyl stretching at 1855 cm^{-1} and the asymmetric one pointed at 1780 cm^{-1} [7].

The α-olefin mol % content of the highly reactive PIB may be evaluated (Fig. 3b) by comparing the integrals of the exo groups with those of the methyl signals in the aliphatic region around 1 ppm [9,19].

In particular, the disappearance of the exo peaks at about 4.6 and 4.8 ppm confirms the progress of the reaction. Moreover, when the reaction extent reaches high values, the probability of a second enophile grafting on PIB becomes notable and new signals appear in the olefinic region from 5.1 to 5.3 ppm, assigned respectively to (c) and (d) PIBBSA derivatives [8,9]. The NMR characterization beside indicating the effectiveness of the reaction suggest at the same
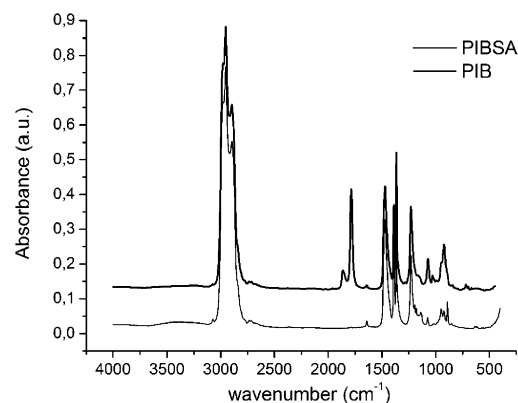

Fig. 2. FTIR spectra of PIB and of the product resulting from the reaction with MAH.

Table 1
Feed composition, conversion, GPC analysis and functionalization degrees of the products in the Alder ene functionalization reactions of PIB

Entry[a]	Enophile (g, mol $\times 10^{-2}$)	α-olefin/ enophile (mol)	RuCl$_3$ (g, mol $\times 10^{-4}$)	SnCl$_2$ (g, mol $\times 10^{-4}$)	Conversion degree[b] (wt.%)	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	FD[c]
PIB	–	–	–	–	–	1300	1.6	–
P1	9.4, 9.6	1/1.5	–	–	70	1300	1.8	1.4[d]
P2	11.3, 11.5	1/1.8	–	–	71	1400	1.8	1.5[d]
P3	11.3, 11.5	1/1.8	0.120, 5.8	–	44	1400	1.8	0.9[d]
P4	11.3, 11.5	1/1.8	–	0.141, 6.2	59	900	2.0	1.2[d]
P5 [g]	16.5, 9.6	1/1.5	–	–	30	1400	1.5	1.5[e];1.6[f]

[a] In all cases, 100 g of PIB was employed and the reaction maintained for 21 h.
[b] Determined through a mass balance after elution over silica gel of weighted amounts of the dried polymer dissolved in *n*-heptane.
[c] defined as the mol number of grafted enophile per mol of reacted PIB.
[d] By means of potentiometric titration.
[e] By means of FTIR.
[f] By means of ^{1}H NMR.
[g] DEM as enophile.

time a substantial prevalence of the Alder ene functionalization mechanism with respect to the free radically promoted process. Actually, in the last case the vinylidene double bonds of PIB would be functionalized without the formation of trisubstituted double bonds (Scheme 1).

The conversion degrees, calculated through a mass balance and the FD, were evaluated as described in the Section 2 (Table 1).

The functionalization reaction of PIB oligomers was performed at a temperature higher than 180 °C for 21 h with an excess of enophile (1:1.5 or 1:1.8 by mol respect to polymer α-olefin units) in order to favour the reaction rate and to get the highest grafting yield. Indeed the Alder ene reaction of MAH with various olefins is second order overall [11] and maleation experiments performed onto end unsaturated polypropylene indicated that high temperature, but below 230 °C, and MAH concentration increase the grafting of SA units [3].

The increasing of MAH feeding from 1:1.5 to 1:1.8 by mol with respect to the α-olefin PIB content (entry P1 and P2) leads to slightly improved conversion (70%) and functionalization degree with FD close to 1.5 mol of SA grafted per mol of reacted polymer.

Low toxic, low expensive and low moisture sensitive stannous and ruthenium chlorides, resulted in this concentration as efficient catalysts in the terminal maleation of PP in the melt [2–4]. Unfortunately, in our case, much lower conversion degree and FD were recorded for catalyzed Lewis acid functionalizations. In particular, very low conversion degree, 44%, and functionalization degree, less than 1, was recorded by using ruthenium chloride as catalyst.

Very probably, evolution of HCl from the catalysts promotes the isomerization of the vinylidene double bonds of PIB to the less reactive β-olefin [3]. The ^{1}H NMR spectra of PIBSA derivative (Fig. 4) obtained in the presence of RuCl$_3$ (entry P3) reveals the increased amount (16% by mol instead of 8%) of endo olefin groups compared with that of

unreacted PIB. However, the most striking evidence of catalyst promoted exo→endo isomerization comes from the β-olefin units (30% by mol) generated after heating PIB at 200 °C for 21 h with just ruthenium chloride in catalytic amount (5×10^{-3} mol equivalents).

This result reveals the inability of the investigated Lewis acids to promote in such conditions the Alder ene functionalization and, on the contrary, the high activity towards the exo→endo isomerization of PIB.

3.1.2. PIB functionalization with DEM

The reactivity of PIB oligomers versus Alder ene reaction was also tested by using liquid diethyl maleate (DEM) (entry P5). Maleate esters are weaker as enophiles but successfully employed in polyolefins radical modification giving good FD values and grafting efficiency, thanks to the solubility in the polymer melt and lower tendency to homopolymerize with respect to MAH [1].

The PIB functionalization conditions were the same as with MAH, and the molar ratio α-olefin/DEM of 1.5, as in entry P1. The grafting of diethyl succinate units (DES) on PIB is confirmed by the carbonyl band centred at 1735 cm^{-1} (Fig. 5a), but a significant amount of unreacted vinylidene groups is detected (890 cm^{-1}, Fig. 5b). Moreover, ^{1}H NMR spectrum of PIBDES shows at 4.1 ppm a multiplet assignable to the attached DES unit (Fig. 5c).

Even though the conversion degree is low (30%), the reacted polymer, PIBDES, showed FD of about 1.6 (Table 1), as for P1 and P2 trials with MAH as enophile. The tendency of DEM to give relatively high functionalization degree in the Alder ene conditions could be ascribed to the improved mixing efficiency of the high boiling point (225 °C) liquid enophile with respect to maleic anhydride.

In addition, the good agreement between the FD values of PIBDES obtained from ^{1}H NMR and IR spectroscopies confirms the effectiveness of the calibration method used in the last characterization procedure.
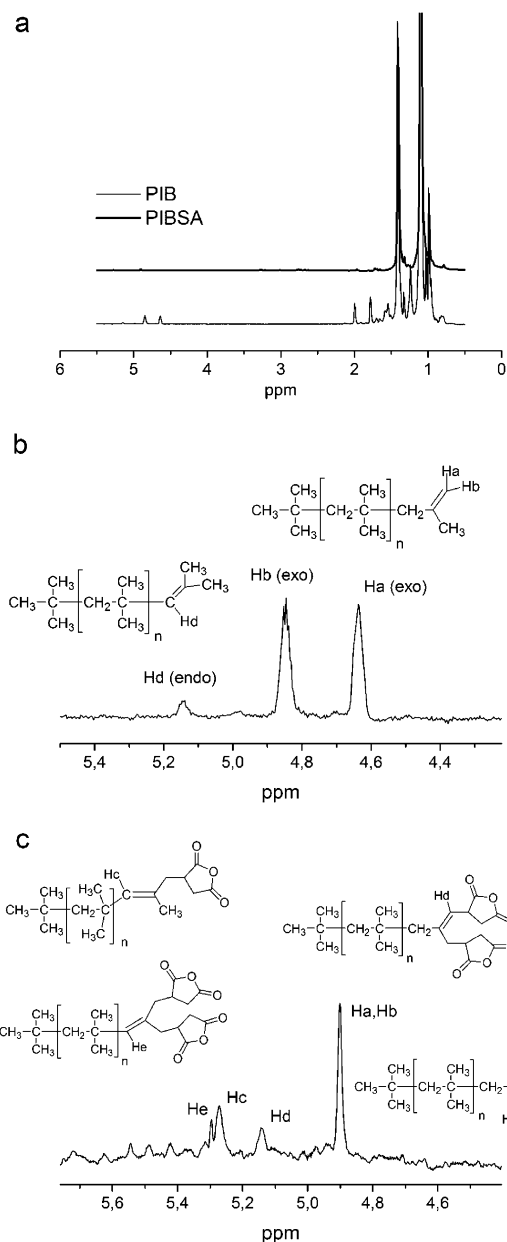
a

b

c

Fig. 3. ^{1}H NMR spectra of PIB and of the product resulting from the reaction with MAH: (a) full range; (b) the enlargement of the olefinic region in the range from 4.4 to 5.6 ppm of the PIB spectrum and (c) that of the PIB derivative.

3.1.3. GPC analysis of the functionalized PIB oligomers

No detectable changes of the PIB molecular weight are observed after functionalization without catalyst or with RuCl₃, whereas for entry P4 some degradation induced by the possible evolution of HCl from the stannous chloride based catalyst was observed (Table 1) [3].

3.2. SBS functionalization

The linear thermoplastic triblock copolymer poly (styrene-*b*-butadiene-*b*-styrene) (SBS) consisting of (^{1}H NMR, Fig. 6) respectively of 18.9 mol% styrene,
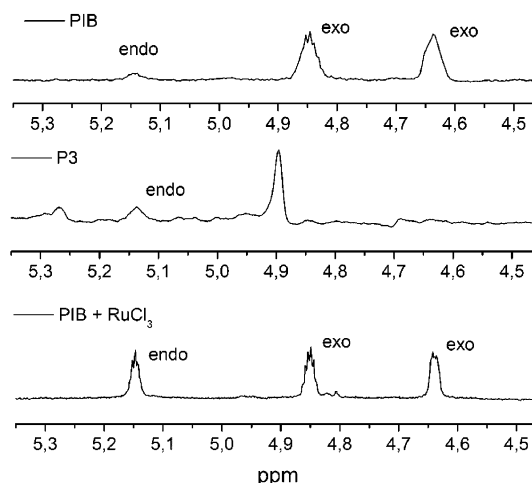

Fig. 4. ^{1}H NMR spectra in the range from 4.4 to 5.6 ppm of PIB (top), of the product resulting from entry P3 (middle), and of the product derived from the PIB thermal treatment in the presence of RuCl₃ (down).

11.8 mol% 1,2-butadiene and 69.3 mol% 1,4-butadiene repeating units [20] was treated in a Brabender type mixer at a constant rotor speed of 50 rpm under nitrogen atmosphere at 200 °C for 18 min of residence time and 0.15 mol% of the stable free radical TEMPO.

In all cases, an equal or higher molar amount of DEM with respect to the 1,2-butadiene reactive repeating units of the polymer was used to promote the Alder ene functionalization. Only DEM was used as the preliminary runs with MAH lead to highly crosslinked materials.

The results of the SBS functionalization carried out by varying DEM concentration and catalyst are reported in Table 2.

3.2.1. GPC analysis of the functionalized polymers

All the SBS samples after Alder ene functionalization with DEM showed an increasing of the weight average molecular weight $\bar{M}_w$ and a decreasing of the $\bar{M}_n$ indicating the contemporary occurrence of degradation and crosslinking reactions. This phenomenon is particularly emphasized for catalyzed reactions using Lewis acid concentration higher than 0.1% by mol.

The reason why crosslinking reactions appear favoured in the presence of the catalysts may be attributed to a complex formation between the vinylidene group of the 1,2-butadiene units of SBS and the Lewis acid leading to an increase in the reactivity of the exo group as reported in literature for RuCl₃ catalyzed Alder ene reactions [4,21]. The higher reactivity of the exo groups promotes the Alder ene reaction of the 1,2-butadiene units of the macromolecule with a reactive enophile as 1,2-butadiene unit of another macromolecular chain. These are less reactive than DEM but in much higher concentration.

Without adding catalysts the tendency to give cross-linked SBS products appears less pronounced particularly

Fig. 6. ^{1}H NMR spectrum of SBS triblock copolymer.

The Alder ene functionalization of SBS triblock copolymers with DEM as enophile lead to functionalized polymers with low FD ranging from 0.1 to 0.3 mol% (0.5–0.8 wt%, defined as the weight of DES units per 100 g of functionalized polymer) even using a twofold molar excess of DEM with respect to 1,2-butadiene units (Table 2).

The use of $SnCl_2$ as Lewis acid catalyst to promote Alder ene functionalization does not positively affect the FD of the processed SBS polymers.

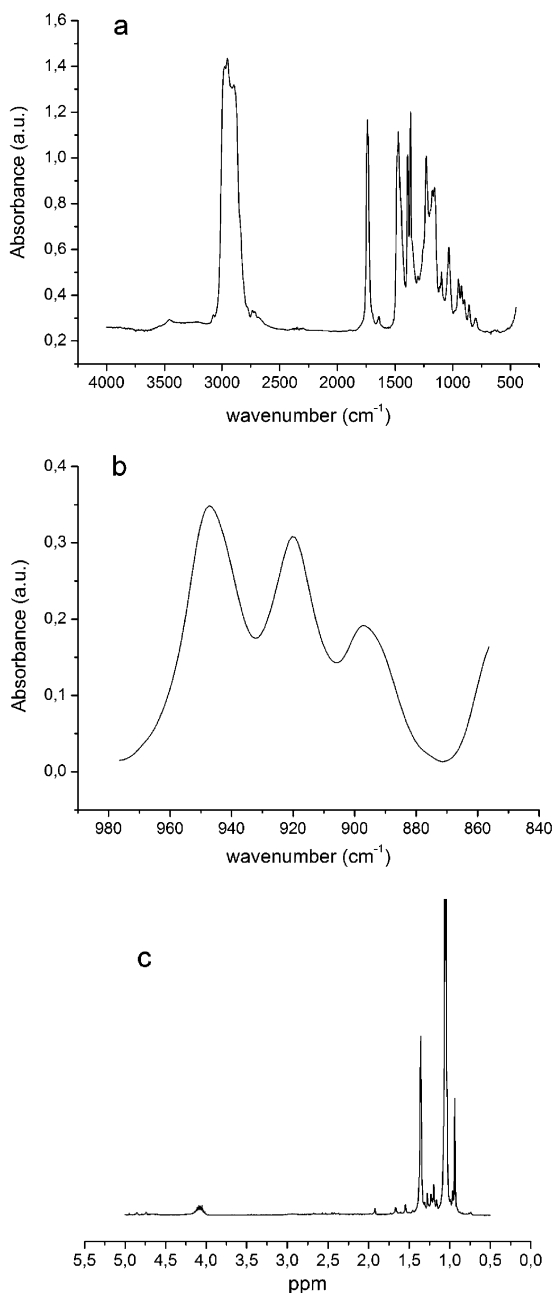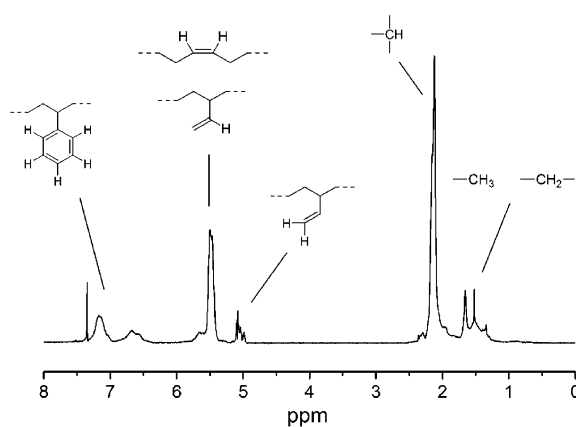On the contrary, $RuCl_3$ promotes at the same time the

Fig. 5. (a) FTIR spectrum of the product resulting from the reaction with DEM (entry P5), and (b) its enlargement in the vinylidene absorption region from 980 to 860 cm^{-1}; (c) ^{1}H NMR spectrum of the product resulting from the reaction with DEM (entry P5).

with increasing the concentration of the enophile which act as a solvent.

3.2.2. Functionalization degree of the reaction products

All the functionalized polymers were analysed by FTIR and ^{1}H NMR spectroscopies in order to check the grafting occurrence and extent. The peak at 1737 cm^{-1} in the FTIR spectrum (Fig. 7a) and the broad band at about 4.2 ppm in the ^{1}H NMR spectrum (Fig. 7b) reveal the insertion of diethyl succinate groups in the polymer backbone.
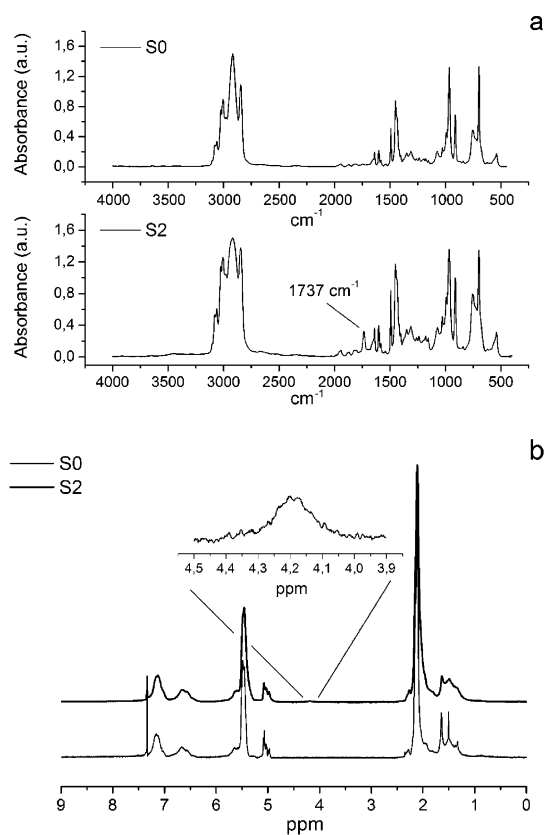

Fig. 7. FTIR (a) and ^{1}H NMR spectra (b) of SBS and of the product resulting from the reaction with DEM.

Table 2
Alder ene functionalization reactions of SBS in the Brabender type mixer

Entry[a]	DEM[b] (%mol eq.)	SnCl$_2$[b] (%mol eq.)	RuCl$_3$[b] (%mol eq.)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	FD[c] (mol%)
S0	–	–	–	127,000	153,000	1.2	–
S1	1	–	–	81,000	202,000	2.5	0.2
S2	1.5	–	–	98,000	205,000	2.1	0.1
S3	2	–	–	107,000	199,000	1.9	0.3
S4	1	0.1	–	–	–	–	0.2
S5	1	0.5	–	105,000	252,000	2.4	0.2
S6	1	1	–	82,000	215,000	2.6	0.1
S7	1,5	0.1	–	110,000	206,000	1.9	0.2
S8	1,5	0.5	–	72,000	209,000	2.9	0.1
S9	1,5	1	–	–	–	–	0.1
S10	1	–	0.1	–	–	–	0.1
S11	1	–	0.5	[d]	[d]	[d]	1.1[d]
S12	1	–	1	[d]	[d]	[d]	0.9[d]
S13	1.5	–	0.1	102,000	184,000	1.8	0.1
S14	1.5	–	0.5	[d]	[d]	[d]	1.2[d]

[a] In all cases, 20 g of SBS was employed.
[b] Calculated respect to 100 mol of 1,2-butadiene repeating units.
[c] Mol of inserted DEM per 100 mol of 1,2-butadiene repeating units.
[d] Crosslinking reactions occurred; the FD was evaluated on the polymer fraction soluble in chloroform.

Alder ene reactions with DEM as evidenced by the FD of S11, S12 and S14 entries chloroform soluble fraction.

The linear SBS thermoplastic triblock copolymer showed a sharp glass transition temperature for the polybutadiene (PB) block at −88 °C ($T_g\alpha$) and another less visible for the polystyrene (PS) block at about 105 °C ($T_g\beta$). The DSC thermograms of the functionalized SBS with DEM appears quite similar with values of the $T_g\alpha$ close to that of the unprocessed polymer, from −86.7 °C for S3 to −87.7 °C for S4 [20].

4. Conclusions

The functionalization reactions performed on highly reactive PIB oligomers in a glass reactor by using maleic anhydride (MAH) as enophile without using free radical initiators gave conversion degree slightly higher than 70% and provided materials with very high functionalization degree, i.e. 1.5 mol of succinic anhydride per mol of reacted polymer.

The use of ruthenium chloride and stannous chloride as Lewis acid catalysts to increase the reaction rate and the grafting extent did not positively affect the functionalization process, due to the promotion of exo→endo isomerization process of the PIB reactive vinylidene units.

On the other hand, the diethyl maleate (DEM) gave low conversion degree due to its minor reactivity as enophile compared to MAH. Nevertheless FD of 1.5–1.6 as for MAH were obtained thanks also to the improved mixing efficiency of the liquid enophile.

No detectable changes of molecular weight and molecular weight distribution were found at the end of the functionalization processes of PIB, except for the stannous chloride catalyzed reaction.

The functionalization reactions of linear SBS triblock copolymers in the melt using a Brabender type mixer and DEM as the enophile provided functionalized materials with FD ranging from 0.1 to 0.3 mol of grafted DES per 100 repeating units of the polymer and limited modifications of the starting molecular weight. The Alder ene insertion on the polymer backbone was favoured by a high concentration of DEM units and appreciably limited crosslinking phenomena.

The use of ruthenium and stannous chloride as Lewis acid catalysts increased markedly the crosslinking reaction between SBS macromolecules especially in the case of ruthenium catalyzed runs that gave processed polymer samples mostly insoluble in the common organic solvents. However, differently from SnCl$_2$, the ruthenium chloride catalyst promoted the Alder ene grafting of soluble chloroform polymer fractions giving FD even higher than 1 mol%.

The results obtained in this work seem to indicate the prevalence of the Alder ene functionalization mechanism as proposed by several authors for the reaction between reactive vinylidene end-substituted polymers and unsaturated monomers under similar conditions. The occurrence of a free radical mechanism potentially promoted by the high process temperature seems to be of minor impact according to products from PIB functionalization and restricted in the case of SBS also for the use of a stable free radical trapping species.

Anyway more detailed investigation has to be performed in the future aimed to clarify the influence of the free radical mechanism on the thermal functionalization of vinylidene terminated polyolefins with unsaturated reactive monomers.

Acknowledgements

References

[1] Moad G. Prog Polym Sci 1999;24:81–142.

[2] Thompson MR, Tzoganakis C, Rempel GL. Polymer 1998;39: 327–34.

[3] Thompson MR, Tzoganakis C, Rempel GL. J Polym Sci: Part A: Polym Chem 1998;36:2371–80.

[4] Thompson MR, Tzoganakis C, Rempel GL. J Appl Polym Sci 1999; 71:503–16.

[5] Aleman-Vazquez LO, Villagomez-Ibarra JR. Fuel 2001;80:965–8.

[6] Deak G, Bartha L, Baladincz J, Auer J. 15th Proceedings of the world petroleum congress 1998. 657–658.

[7] Walch E, Gaymans RJ. Polymer 1994;35:1774–8.

[8] Tessier M, Marechal E. J Polym Sci: Part A: Polym Chem 1988;26: 2785–810.

[9] Tessier M, Marechal E. Eur Polym J 1984;20:269–80.

[10] Luchtenberg J, Ritter H. Macromol Chem Phys 1994;195:1623–32.

[11] Benn FR, Dwyer J, Chappell I. J Chem Soc Perkin Trans II 1977;5: 533–5.

[12] Snider BB, Ron E. J Am Chem Soc 1985;107:8160–4.

[13] Mach H, Rath P. Lubrication Sci 1999;11:175–86.

[14] Mach H, Rath P. Additives in petroleum refinery and petroleum product formulation practice, proceedings, Sopron, Hung., May 21– 23 1997. 52–58.

[15] Xanthos M. In: Xanthos M, editor. Reactive extrusion: principles and practice.

[16] Trivedi BC, Culbertson BM. Maleic anhydride 1982.

[17] Maurano CHF, Portal LL, Baumhardt Neto R, Mauler RS. Polym Bull (Berlin, Germany) 2001;46:491–8.

[18] Passaglia E, Aglietto M, Marrucci M, Ruggeri G. Gazzetta Chimica Italiana 1997;127:91.

[19] Si J, Kennedy JP. J Polym Sci: Part A: Polym Chem 1994;32: 2011–21.

[20] Romani F, Passaglia E, Aglietto M, Ruggeri G. Macromol Chem Phys 1999;200:524–30.

[21] Alderson T, Jenner EL, Lindsey Jr RV. J Am Chem Soc 1965;87: 5638–45.