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Study of Grafting Reactions of Polar Groups onto Polystyrene (PS) by Reactive Mixing

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Summary: Two different bulk modifications have been carried out aimed to the introduction of carboxyl groups into atactic polystyrene (PS) based on the reaction at 180°C with diethylmaleate (DEM) or 4-carboxybenzensulfonyl azide (CBSA) respectively. The former system proceeds with a free radical mechanism giving functionalization around 0.5% by mol but with reduction of molecular weight and T_g increase. On the other side CBSA which grafts by addition to the C-H bond gives appreciable functionalization with rather limited degradation and moderate T_g increase. Detailed analysis of the molecular structure of the functionalized PS was performed to propose possible reaction mechanisms.

Keywords: functionalization; FT-IR; melt processing; polystyrene; thermal properties

Introduction

The introduction of a moderate amount of functional groups onto polystyrene improves its compatibility with polar polymers, such as polycarbonate and polyamides[1] and with different organic or inorganic substrates[2-4]. Contrary to aliphatic polyolefins[5], there are only few papers about free radical functionalization of PS[1,6,7,8]. The process has been carried out by using maleic anhydride (MA) as functional monomer and peroxides as radical initiators in solution or in bulk and the collected products have been analyzed by IR to determine the functionalization degree (FD) and by Size Exclusion Chromatography (SEC) or viscosity measurements to evaluate the changes of molecular weight related to the occurrence of crosslinking and degradation processes. All the authors reported that the conversion of the monomer is very low even if the monomer/polymer ratio is high (at constant monomer/peroxide ratio), for all the peroxide

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concentrations. Gaylord and co-workers[7] observed a very large decrease of the molecular weight by adding peroxide alone to the molten polymer. This effect was partially reduced in the presence of MA which presumably reacted with the internal PS radicals before chain scissions. Kesslmeier and co-authors[8] described the free radicals induced degradation and the grafting of MA as two independent processes; the final chain length distribution was considered the result of the equilibrium reached very rapidly between chain scission and radical recombination. The low conversion of the monomer was attributed to the product decomposition after grafting reaction and as a consequence of the low solubility of the MA in the fluid polymer. The low efficiency of the grafting process has been related to the resonance stabilization of styrilic macroradicals, which hinders the insertion of the monomer[9]. Theoretical studies[10,11] of thermomechanical or UV-irradiation processes brought out the hypothesis that the chain disproportionation and/or β-scission have to be considered equilibrium reactions. These[12] depend on the temperature but mainly on the amount of defects in the primary structure of the polymer.

In previous paper we reported about the easy radical functionalization of polyolefins in the melt by using the ester derivatives of MA with particular reference to the diethyl maleate (DEM)[13-16] and in case of SEBS[17] only the aliphatic block was functionalized.

In this paper we report about attempts to atactic PS functionalization in the fluid state at high temperature. Dicumyl peroxide (DCP) alone or in the presence of diethyl maleate (DEM) was used to study the functionalization and the degradation processes. Also, a different approach has been performed by using the 4-carboxybenzensulfonyl azide (CBSA) as functionalizing agent which acts without involvement of free radicals.

Experimental Part

Materials- Atactic polystyrene (aPS, Repsol) with $\overline{Mn}$=86000 g/mol (SEC) and T_g approximately 88°C (DSC) was used as received. Dicumyl peroxide (Sigma-Aldrich) and 4-carboxybenzensulfonyl azide (Sigma-Aldrich) were used without further purification. Diethyl maleate (Sigma-Aldrich) was used after distillation under reduced pressure (0.33 mmHg, 53°C).

Polystyrene reactions- All the runs were carried out in a Brabender Plastograph PL2100 Mixer (30 cc): the torque values and temperature data were acquired by Brabender Mixing software

WinMix ver.1.0. 20 g of polystyrene was added to the reactor chamber at a temperature of 180°C and a rotational speed of 50 rpm; after stabilization of the Torque the chemical reagents [peroxide (DCP), or peroxide and monomer (DCP and DEM), or the sulfonyl azide (CBSA)] were added to the molten PS and the reaction carried out for 20 min. All the samples were recovered, 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 not reacted functionalizing molecules) and then dried until constant weight.

Characterization- The PS molecular weight were obtained by SEC Jasco PU-1580 with Jasco 830-RI as Refractometer Index of chloroform diluted solutions. The DSC Perkin Elmer DSC7 was used to determine the glass transition temperature (T_g) and Mettler Toledo TGA/STDA851 for thermogravimetric analysis (TGA) (the onset, the temperature at 10% by weight loss and the inflection point). The DSC instrument was calibrated by using Indium (T_m=156.6 °C and ΔH=28.47 J/g) and Zinc (T_m=419.47 °C) and the analysis were performed in the temperature range between 30°C and 200°C with a scanning rate of 20°C/min.

The presence of monomer grafted onto the PS backbone was checked by Fourier Trasform Infrared (FT-IR, Spectrometer Perkin Elmer FT-IR 1760-X) spectra onto film obtained by casting onto KBr windows of $CHCl_3$ diluted solution. Proton magnetic resonance spectra were performed by a spectrometer Varian Gemini 200 MHz in $CDCl_3$ solution.

Result and Discussion

Treatment of PS with DCP

The reactivity of PS in the bulk was checked out by testing the influence of the temperature and of the initiator concentration on the final product properties. The experiments were carried out by using different amounts of DCP, ranging from 0.05% by mol to 1% by mol (table 1) with respect to PS molar units. By size exclusion chromatography (SEC) analysis of the samples a significant decrease of the number average molecular weight ($\overline{Mn}$) was determined (table 1). The degradation of PS in presence of DCP results, presumably, from the formation of styril macroradicals (by H-atom abstraction from the PS macromolecular chains) which give β-scission reactions. After the chain breaking, the primary radicals formed could proceed to depropagation reactions and/or transfer reactions. In overall, this mechanism[10,11], explains the experimental data and the direct relationship between the amount of DCP and the $\overline{Mn}$ decrease.

Table 1: Treatment of Polystyrene with DCP: feed composition, GPC, TGA and DSC results

Sample	DCP % mol	$\overline{Mn}$ g/mol	Id[a)]	$T_{10\%}$[b)] °C	T_g °C
PS	-	86400	1.83	383.7	87.8
PS180°C	-	80500	1.91	395.9	88.3
PSDCP1	0.05	69400	1.84	381.4	86.3
PSDCP2	0.10	58700	1.95	378.2	85.8
PSDCP3	0.30	47100	2.07	366.3	80.3
PSDCP4	0.50	42600	1.97	349.2	77.7
PSDCP5	1.00	35000	1.91	-	65.5

[a)] Index of polydispersity

[b)] $T_{10\%}$: T at which 10% by weight loss is observed

The temperature associated with the 10% by weight of mass loss ($T_{10\%}$), evaluated by thermo-gravimetric analysis (TGA), showed that the thermal stability of the samples analysed was influenced by the peroxide treatment. In fact, the $T_{10\%}$ decreased with the increasing of the DCP amount used, probably due to the presence of double bonds onto the polymer backbone, formed during the material degradation by β-scission and disproportion reactions too[7], which act as weak points (as defects) and affect the polymer thermal stability especially at the beginning of the degradation steps. Also the glass transition temperature (T_g) decreased for PS specimens treated whit DCP as a result of the formation of lower molecular weights macromolecules content that can act as plasticizing agents.

Functionalization reaction with DEM and DCP

The PS functionalized reactions with DEM were carried out in the bulk using several DEM/DCP molar ratios, as reported in table 2. In order to improve the monomer grafting, the DEM amount used was rather high for all the runs, if compared with aliphatic polyolefins functionalization reaction conditions[16,18,19].

The samples were analysed by FT-IR (figure 1), after the un-reacted monomer removal, to weigh up the functionalization degree (FD) of the polymer (number of inserted groups with respect to 100 monomeric units).

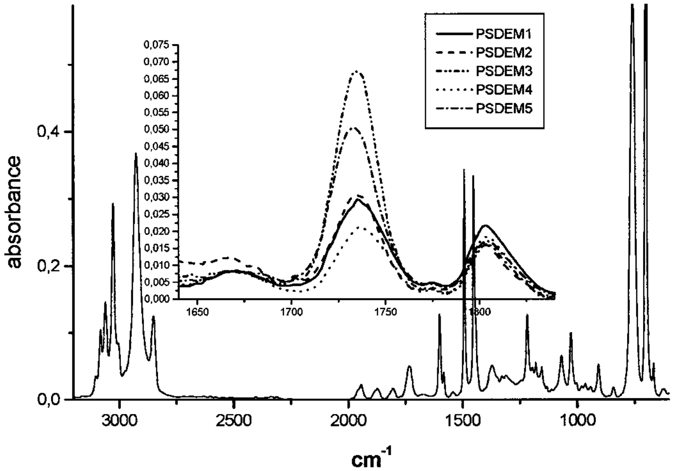


Figure 1: The FT-IR spectrum of the PSDEM5 sample and enlargement of the carbonyl stretching region of all the DEM functionalized samples

From the peak area ratio A1/A2, where A1 is the area of the peak at 1734 cm^{-1} (stretching C=O ester groups of diethyl succinate) and A2 is the area of the peak at 1028 cm^{-1} (bending in the plane of aromatic C-H) (figure 1), the FD was calculated by knowing the integral absorptivity (ε) for the two bands:

$$FD_{(DES)} = \frac{\overline{\varepsilon_{1028}}}{\varepsilon_{DES}} \cdot \frac{\overline{A_{DES}}}{A_{1028}}$$

The molar extinction coefficient for the integral band of the stretching C=O (ε_{DES}) is reported in literature[15], instead the molar extinction coefficient for the band A2 (ε_{1028}) was evaluated by considering the "absolute" FD value for the sample PSDEM3 measured by ^{1}H-NMR spectroscopy by using the signals at 4.2 ppm (associated to the -O-CH$_2$-CH$_3$ protons of the grafted ester groups) and from 6.2 to 7.5 ppm (associated to the aromatic protons of the monomeric unit).

$$\overline{\varepsilon_{DES}} = 1.78\cdot 10^4 \mathrm{l}\cdot \mathrm{mol}^{-1}\cdot \mathrm{cm}^{-2}$$

$$\overline{\varepsilon_{1028}} = FD_{PSDEM3}(^1H - NMR)\cdot \varepsilon_{DES}\cdot \frac{A_{1028}}{A_{DES}} = 4.58\cdot 10^3 \mathrm{l}\cdot \mathrm{mol}^{-1}\cdot \mathrm{cm}^{-2}$$

Table 2: Functionalization of Polystyrene with DEM and DCP: feed composition, GPC and DSC results

Sample	DCP % mol	DEM % mol	DEM/DCP mol/mol	FD % mol	$\overline{Mn}$ g/mol	T_g °C
PS180	-	-	-	-	80500	88.3
PSDEM1	0.15	6.0	40.0	0.12	70500	98.1
PSDEM2	0.30	12.0	40.0	0.16	70900	98.6
PSDEM3	0.60	12.0	20.0	0.40	57200	100.4
PSDEM4	0.30	3.5	11.7	0.10	71800	98.8
PSDEM5	0.80	12.0	15.0	0.43	60200	103.1

The deconvolution of the spectra in the carbonyl stretching region, by a non-linear fitting of the experimental points, was necessary to calculate the area A1 for all the samples, due the overlapping of the diagnostic band at 1734 cm^{-1} and the band at 1749 cm^{-1} associated to the overtone of γ_w of C-H aromatic (figure 2).

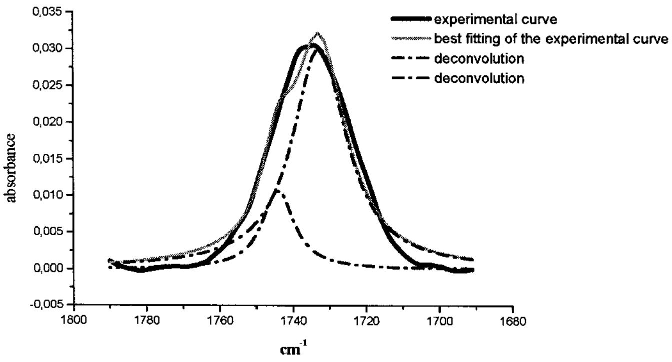
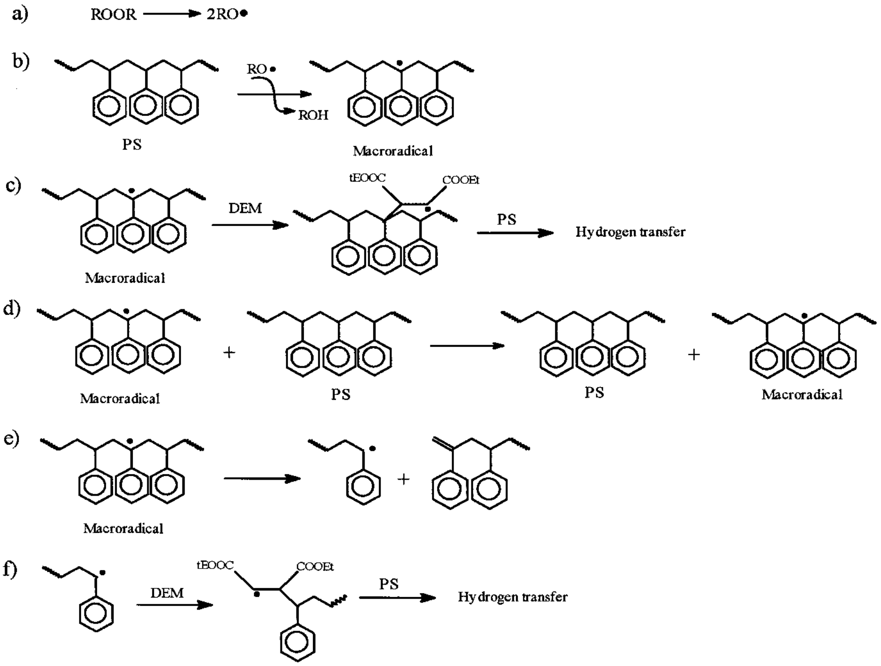


Figure 2: Deconvolution of 1734 cm^{-1} peak (sample PSDEM3)

The FDs values ranged between 0.10 and 0.43 % by mol as showed in table 2 and increased by increasing both DCP and DEM molar amount with DEM/DCP ratio always higher than the minimum value (~11) necessary to avoid side reactions in polyethylene[20]. The $\overline{Mn}$ values of the functionalized PS samples decreased for a monomer/peroxide molar ratio lower than 20. Probably, for a higher concentration of peroxide there is again competition between the functionalization reaction and the degradation processes, even if the presence of the functionalizing monomer prevents this effect (for example PSDEM2 has $\overline{Mn}$=70900 and PSDCP3 has $\overline{Mn}$=47100 and were produced by using the same concentration of DCP in the feed).



Scheme 1: Schematic mechanism of PS grafting with DEM

The free radicals formed through DCP thermal decomposition are able to abstract a hydrogen atom from the macromolecules to give the styril macroradical whose formation is favoured for thermodynamic reasons (scheme 1: b)[11].These macroradicals can react with DEM, leading to the polar group insertion onto the polymer backbone (scheme 1: c), but also can be involved in hydrogen transfer reactions (scheme 1: d) and in β-scission reactions (scheme 1: e) (favoured by DEM/DCP molar ratio lower than 20). In this last case, the degradation reaction generates a ~$CH_2\cdot$ macroradical and a macromolecule with a terminal double bond. Also the formed ~$CH_2\cdot$ macroradical can react with DEM giving macromolecules with a terminal functional group and lower molecular weight (scheme 1: f). The glass transition temperature of the functionalized PS increases markedly with FD. The presence in the polymer backbone of polar groups, at different concentration can be claimed for the increase of T_g as the consequence of the reduced mobility of the chains following interchain interactions of the grafted groups.

Treatment of PS with CBSA

The reaction of sulfonazide with PP gives functionalized polymers which exhibits a larger compatibility with polyamides[21]. The functionalization mechanism involves[22] the formation of nitrenes able to promptly react with $\geq$CH groups.

The presence of –COOH groups in the structure of the 4-carboxybenzenesulfonazide (CBSA), allowed to evaluate FD by FT-IR deconvolution procedure (figure 3) referred to the absorption peak of the carbonyl stretching of the azide (centred at 1700 cm^{-1}) (to subtract the contribution of the overtone γ_w of aromatic C-H centred at 1668 cm^{-1}). FD was determined as the ratio between the area of C=O stretching at 1700 cm^{-1} and of the band at 1028 cm^{-1} due to the bending in the plane of C-H of the aromatic side chains (figure 3, table 3). This ratio increased with the amount of the starting azide in the feed but a limit value of insertion is finally reached.

Apart from the decrease observed in all functionalized CBSA samples and due probably to the thermal and oxidative degradation effect caused by the opening of the chamber at 180°C in order to add the CBSA, the molecular weight of the collected functionalized samples was the same for all CBSA contents. This result confirms that the insertion mechanism does not provide any macroradicals formation. The T_g associated to the functionalized samples was higher than for the pristine polymer and slowly increased for higher functional group content, being probably due to the interaction between polar grafted chains which limits chain mobility.

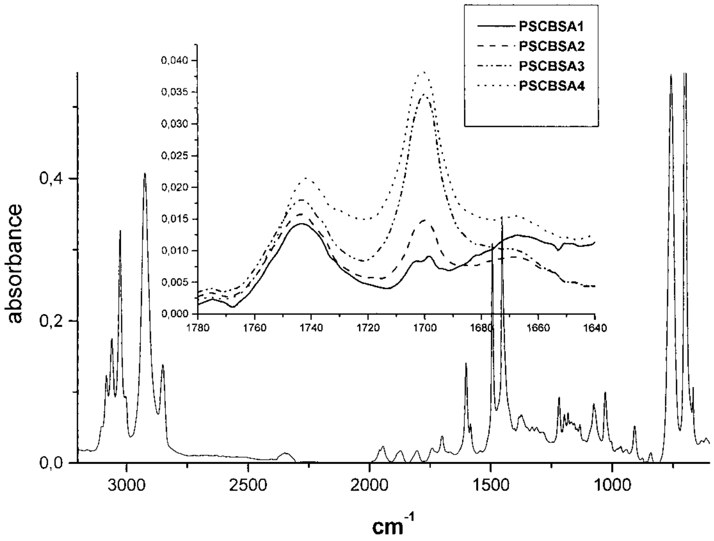


Figure 3: The FT-IR spectrum of the PSCBSA4 sample and enlargement of the carbonyl stretching region of all the CBSA functionalized samples

Table 3: PS functionalized with CBSA: feed composition, GPC and DSC results

Sample	CBSA % mol	A_{1CBSA}/A_{2PS}	$\overline{Mn}$	T_g °C
PS	-	-	80500	88.3
PSCBSA1	0.3	0.04	74500	89.2
PSCBSA2	0.5	0.16	71500	90.0
PSCBSA3	1.0	0.57	71700	90.7
PSCBSA4	1.5	0.58	n.d	93.8

Concluding Remarks

New applications of styrene polymers can remarkably broadened by the introduction (grafting) of a controlled amount of polar groups covalently bound to the chain backbone.

The typical process used for functionalization of ethylene polymers gives relatively lower results in term of FD and a significant degradation. These results can be attributed to the fact that the macro-PS radicals (PS·), formed through H-abstraction exerted by the primary radical has low tendency to react with the maleate (DEM) due to the lower stability of the derived product (scheme 1 reactions b and c) while undergoes facile transfer reaction with another PS unit (scheme 1 reaction d). Because of this rapid dynamic the degradation (scheme 1 reaction e) is less favoured than with polypropylene. Clearly the reaction c (grafting) becomes more probable with respect to reactions d and e when the monomer content in the feed is increased.

On the other side the use of CBSA which proceeds through a nitrene addition to the CH bonds does not give degradation and can then be used to obtain functionalized PS with similar molecular weight characteristic as the starting material. Finally it is of interest to notice that in both cases the grafting of functional groups is flanked by an increase of T_g. This effect is more remarkable in the case of DEM probably due to the closer vicinity of the polar groups to the macromolecule backbone.

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