Effect of Styrene Addition on Polystyrene Molecular Degradation by Lewis Acids

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Received 14 July 2008; accepted 10 May 2009
DOI 10.1002/app.30797

ABSTRACT: The polystyrene molecule can suffer chain scission by beta-cleavage mechanism in the presence of Lewis acids. This is an undesirable secondary reaction, particularly when the Friedel-Crafts alkylation is applied to immiscible polyolefin/polystyrene (PS) blends compatibilization. It competes with the main copolymerization reaction, degrading the PS and impairing the properties of the blend. A simple experimental procedure of styrene (St) addition is proposed to compensate the PS degradation. The effect of St on the chain scission is studied by the PS molecular weight variation and reaction gases evolution. Some hypotheses are worked out to get a basic description of this complex cationic reactive process. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3081–3086, 2009

Key words: polystyrene degradation; chain scission; Lewis acid; cationic mechanism

INTRODUCTION

A promising technique for reactive compatibilization of immiscible polyolefin/polystyrene (PS) blends is the graft copolymerization of hydrocarbon molecules onto PS by Friedel-Crafts (F-C) reactions. These reactions, which occur by cationic mechanisms and are catalyzed by Lewis acids, were carried out either in solution or in molten state.[1–8] Baker and coworkers[4,8] worked on copolymerization via F-C alkylation of PE/PS blends and added styrene (St) to the reaction in molten state. They reported that the St performed as cocatalyst, promoting the macrocarbocation formation and increasing the copolymer yield. In the presence of Lewis acids, the PS can suffer chain scission by beta-cleavage mechanism as reported elsewhere.[3,8–10] This kind of secondary reaction is undesirable, particularly when the F-C process is applied to blend compatibilization. It competes with the main copolymerization reaction, degrading the PS and impairing the properties of the blend.[6,11] Other researchers investigated about the effect of Lewis acids on PS. Pukanszky et al.,[9] carried out the reaction between PS and 1 wt % $AlCl_3$ in melt at 180°C. They reported the occurrence of significant molecular weight reduction from the beginning of the reaction and the formation of unsaturated species during degradation. Nanbu et al.,[10] studied the bulk degradation of PS (0.2 g) with excess of $AlCl_3$ (0.6 g) at 50°C. They found that the molecular weight decreased linearly with the reaction time (4 h), and then the volatile degradation product was identified as benzene. However, no alternatives to minimize the effects of this secondary reaction were proposed. In this work, a simple procedure is proposed to compensate the PS degradation in melt reaction with $AlCl_3$. The effect of the addition of St on chain scission is studied by the PS molecular weight variation and analysis of the reaction gases. Three sets of samples were tested, covering a wide range of $AlCl_3$ concentrations (0.1, 0.3, 0.5, 0.7, 1.0 wt %) and St (0.0, 0.3, 0.6 wt %). Some hypotheses are worked out to get a basic description of this complex reacting process.

EXPERIMENTAL

Materials

Homopolymers

PS Lustrex HH-103 (M_w: 271,000 g/mol, M_n: 136,000 g/mol) was supplied by UNISTAR SA.

Catalysts

The reaction was catalyzed by a system containing anhydrous aluminum chloride ($AlCl_3$; >98% purity from Merck) and St (>99% purity).

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Contract grant sponsors: CONICET (National Research Council of Argentina), MINCyT (Ministry of Science, Technology and Productive Innovation of Argentina), UNS (National University of the South).

Journal of Applied Polymer Science, Vol. 114, 3081–3086 (2009)

Reaction in melt

The reaction was carried out in a batch mixer (Brabender Plastograph W50) at 200°C in nitrogen atmosphere. The mixing procedure was performed at 60 rpm for 24 min, including a PS melting step (~ 2 min) and subsequent incorporation of $AlCl_3$ and St. Three sets of samples were prepared using a wide range of $AlCl_3$ concentrations (0.1, 0.3, 0.5, 0.7, 1.0 wt %) and St (0.0, 0.3, 0.6 wt %). Samples were withdrawn periodically at 5, 10, 15, and 24 min during mixing for characterization. The samples were named as PSR followed by the catalyst content and the St content (i.e., PSR01 00 means PS reacted with 0.1 wt % $AlCl_3$ and 0.0 wt % St).

Characterization

Gel permeation chromatography

Average molecular weights of all samples prepared were obtained in a Waters Scientific Chromatograph model 150-CV. The different samples were dissolved in 1,2,4-trichlorobenzene (0.0125 wt % 2.6-di-*tert*-butyl-*p*-cresol) and then injected at 135°C. Several replications were averaged for each point, assuring an error level lower than the gel permeation chromatography (GPC) accuracy of ±5%.

Fourier transform infrared spectroscopy

A Nicolet 520 instrument was used to obtain the Fourier transform infrared spectroscopy (FTIR) spectra of samples (70-μm film). Possible oxidative degradation was analyzed by the typical carbonyl oxidative absorption peak, at about 1700 cm^{-1}. Furthermore, FTIR spectra were used to find evidence about the reactive processes. The evolving gases from the reaction, collected from the mixer's headspace during blending, were analyzed using a gas cell with CaF_2 windows.

Gas chromatography and mass spectrometry

A gas chromatography and mass spectrometry (GC-MS) equipment model Clarus 500 (PerkinElmer) was used to analyze the reaction gases, which were collected in the same way as in FTIR technique. The analytical column connected to the system was a PE-5MS capillary column (60 m × 0.25 mm ID, 0.25-μm film thickness). In the full-scan mode, electron ionization (EI) mass spectra in the range of 35–200 (m/z) were recorded at electron energy of 70 eV. To identify compounds, the NIST library available in the instrument was used.

RESULTS AND DISCUSSIONS

Chemical aspects

Lewis acids are characterized by a central atom bonded to a number of strongly electronegative atoms or groups (halogens, alkoxides) that yield an incomplete electronic arrangement around such central atom. The best known example is $AlCl_3$ having an incomplete sp^3 electronic shell. This readily accepts any compound with an unbonded electron pair into its vacancy. In this way, in the presence of water impurity, a complex is formed [eq. (1)].[12–15]

$$AlCl_3 + H_2O \longrightarrow [Cl_3AlOH_2] \longrightarrow [Cl_3AlOH]^- + [H^+] \qquad (1)$$

This complex contains two hydrogen atoms bonded to oxygen, which is linked to the aluminum by a dative covalent bond. On the other side, the halogen atoms exert a strong pull on the oxygen electrons. As a result, the hydrogen bonds are extremely weak, giving a powerful acid and a cationic initiator.[12–14]

Literature reported degradation of PS in the presence of $AlCl_3$ at different catalyst concentrations and reaction conditions than those studied in this work.[9,10] These authors are in agreement about the PS molecular weight decrease and the cationic nature of the process, but they differ on the suggested mechanism for this reaction. Pukanszky et al.[9] carried out the reaction by adding 1 wt % $AlCl_3$ to PS, in melt at 180°C, and characterized the resultant solid. However, the volatile products were not considered for analysis.

$$PS + [H^+] \longrightarrow \underset{(A)}{PS^+} + H_2\,(g) \qquad (2a)$$

$$PS + [H^+] \longrightarrow \underset{(A')}{PS^+} + C_6H_6\,(g) \qquad (2b)$$

$$\underset{(A)}{PS^+} \xrightarrow{\text{Beta cleavage}} R{-}\underset{(B)}{CH_2}{-}C(Ar){=}CH_2 + R'{-}\underset{(C)}{CH_2}{-}C(Ar)H^+ \qquad (3)$$

They proposed that in the presence of the complex [eq. (1)], the proton subtracts a hydride by forming a benzyl macrocarbocation [species A, eq. (2a)]. This carbocation induces beta-cleavage [eq. (3)] forming a new macrocarbocation (C) and a lower length molecule (B) with a C=C double bond. This is a chain-breaking process, conducting to molecular weight degradation.[9,13–15]

On the other hand, Nanbu et al.[10] studied the bulk degradation of PS (0.2 g) with excess of $AlCl_3$ (0.6 g) at 50°C. They reported PS molecular weight decrease

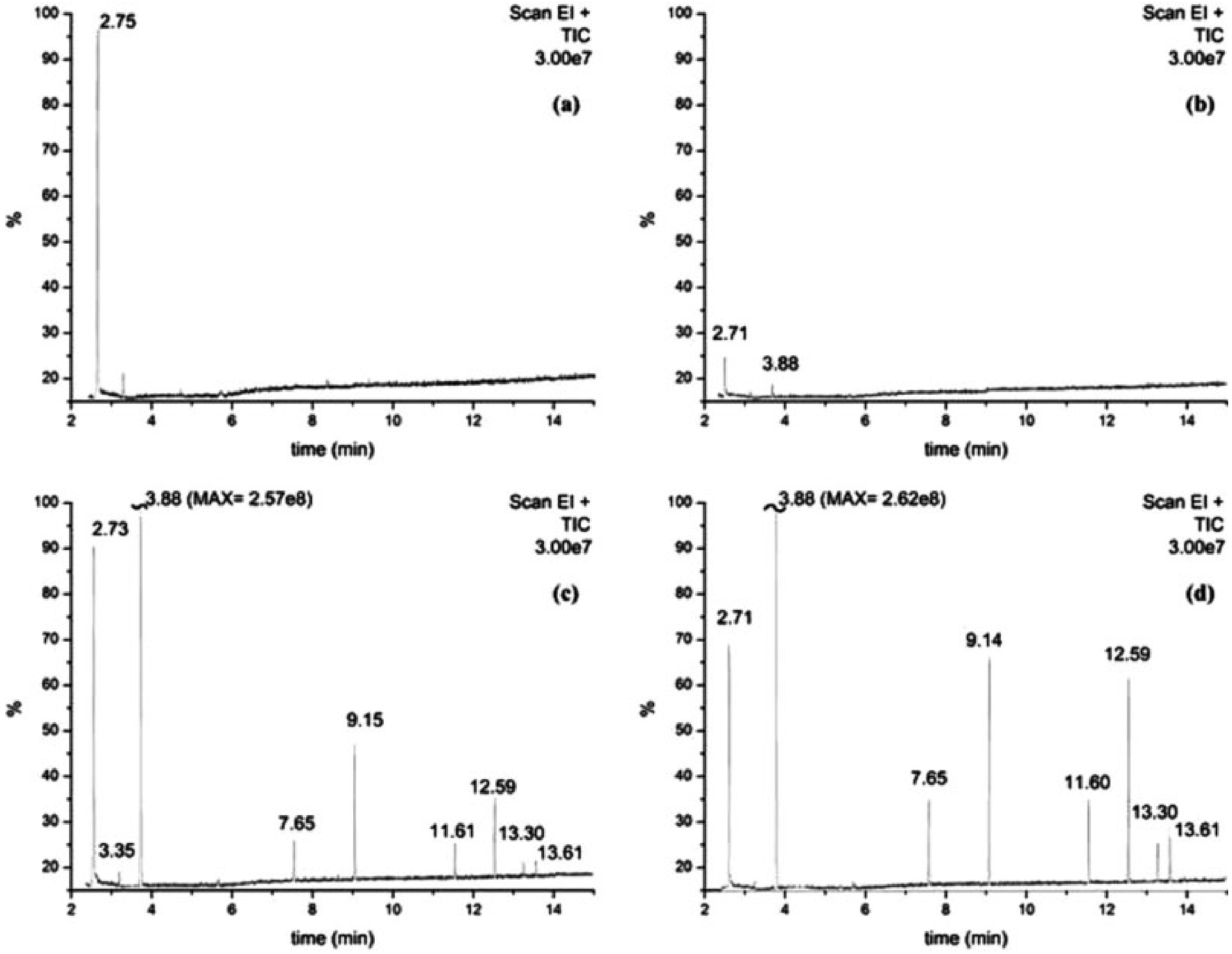

Figure 1 Total ion chromatograms of gases from (a) PSR00 00, (b) PSR01 00, (c) PSR03 00, and (d) PSR07 00.

and identified the volatile degradation product as benzene. They proposed a cationic mechanism with the elimination of phenyl groups by the addition of protons [eq. (2b)], not a hydride subtraction, and consequently beta-scissions leading to species like B and C [eq. (3)]. Also, Audisio et al.[16] reported derivatives from benzene and indane in gases of reaction of PS degradation using silica-alumina as well as zeolites catalysts (200–550°C). They proposed a cationic mechanism with a sequence of benzene elimination, internal rearrangements, intramolecular hydrogen transfer, and finally beta-scissions that lead to the formation of the other volatile products.

In this work, different processing conditions are used when compared with the references discussed earlier. To confirm the cationic nature of this degradation reaction, PS and $AlCl_3$ (0.1–0.7 wt %) were mixed together in molten state (200°C, N_2 atmosphere) for 24 min, and the gases from headspace of the mixer were collected and analyzed by GC-MS and FTIR. Figure 1(a) shows the total ion chromatogram (TIC) corresponding to the gas evolved from molten PS without catalyst addition (PSR00 00). It can be observed that only argon (peak at 2.75 min), a normal impurity of the nitrogen stream, is present. Upon the addition of 0.1 wt % of $AlCl_3$ [Fig. 1(b)], a benzene peak at 3.88 min is clearly visible, and its intensity increases with the catalyst concentration [Fig. 1(b–d)]. Other six derivatives from benzene and indane are observed for 0.3 wt % catalyst addition and they are more evident for 0.7 wt % [Fig. 1(c,d)]. It is worth to notice that St, typical product from thermal PS degradation, was not detected. The MS-identified compounds with respect to their retention times are listed in Table I.

TABLE I
GC-MS Peak Retention Times and the Corresponding Compounds Identified by NIST Library

Retention time (min)	Compound
3.88	Benzene
7.65	Ethylbenzene
9.14	Ethylmethylbenzene
11.61	Indane
12.59	Indane-1-methyl
13.30/13.61	Indane-dimethyl (position isomers)

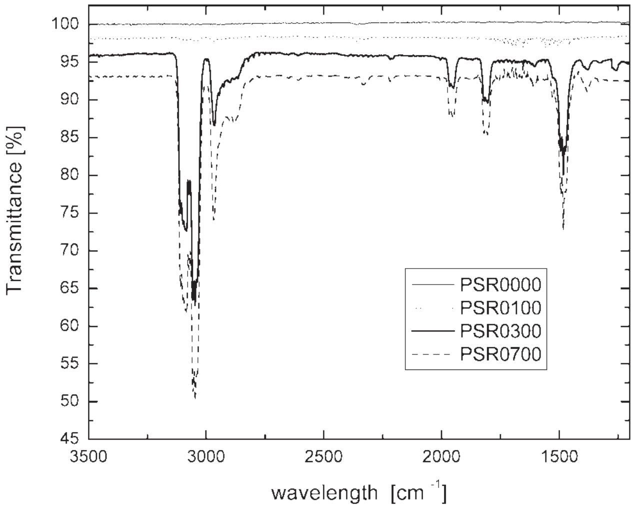

Figure 2 FTIR spectra for gases from PSR00 00, PSR01 00, PSR03 00, and PSR07 00.

To confirm these results, the same gas samples were analyzed by FTIR (Fig. 2). The presence of characteristic peaks for aromatic compounds (3100–3000; 2000–1800; 1500 cm^{-1}) can be observed in all samples except for PSR00 00. Methyl group (2900–2800 cm^{-1}) bands were also identified.

These results from GC-MS and FTIR analysis are in agreement with the work by Audisio et al.[16] We suppose that the excess (300 wt %) of catalyst applied by Nanbu et al.[10] exclusively conducted the reaction to the way of benzene elimination. In contrast, under softer conditions, the formation of more than one volatile product, besides the main component (benzene), seems to be possible.

In addition, retention time chromatograms for PS and PSR00 00 were compared to assess a possible contribution of thermal cracking processes (Fig. 3). As it is observed, molecular weight distribution curves match closely. Hence, the possible chain scission from thermal cracking was discarded. These evidences allow inferring that the mechanism for the PS degradation with $AlCl_3$ is cationic. Therefore, species like B and C [eq. (3)] would be present and this assumption is important to sustain the hypothesis proposed later.

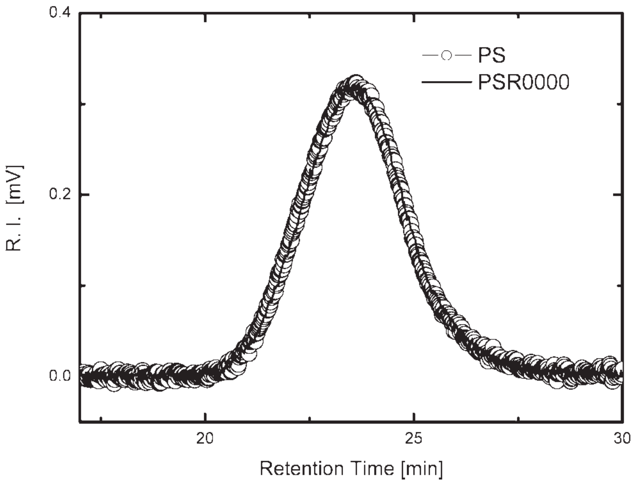

Figure 3 GPC chromatograms for pure PS and PSR00 00.

Molecular weight assessment

To verify the absence of sample oxidation, carbonyl groups originated in acids, aldehydes, or ketones as oxidation products were searched by FTIR spectra (1700 cm^{-1} region). The spectra from the samples resulted identical to the starting PS one, so oxidation could be discarded as a cause of degradation. This was the expected behavior since oxygen was not present during the melt reaction. Molecular weight (MW) of the samples subjected to reaction, withdrawn at different times (5, 10, 15, and 24 min), were determined. The average MWs, M_n and M_w, were plotted as a function of catalyst concentration. The discussion is presented separately for reactions with and without St addition.

Reaction without St

The reactions carried out in the absence of St (Figs. 4 and 5) show that the effect of $AlCl_3$ on the PS molecule caused chain scission at all the concentrations tested, except for 0.1 wt % $AlCl_3$ where the degradation is not significant. The M_w degradation occurs almost linearly with the catalyst concentration (Fig. 4), which decreased to 20,000 g/mol (detection limit) at $AlCl_3$ concentrations $\geq$0.7 wt %.

Figure 5 shows the M_w change with mixing time. For $AlCl_3$ concentrations up to 0.5 wt %, the M_w decreases sharply during the first minutes of reaction, remaining constant afterward. This behavior

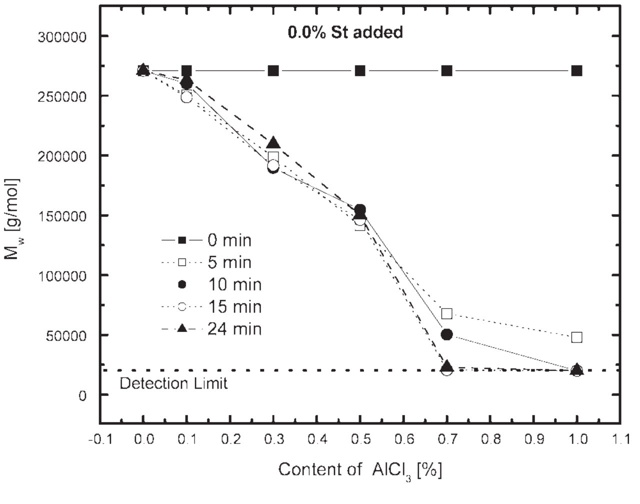

Figure 4 Variation of PS M_w with $AlCl_3$ content for different mixing times without St.

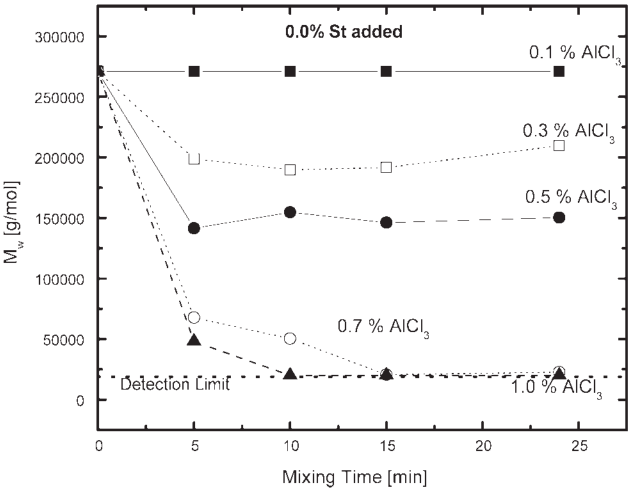

Figure 5 Variation of PS M_w with mixing time for different $AlCl_3$ contents and without St.

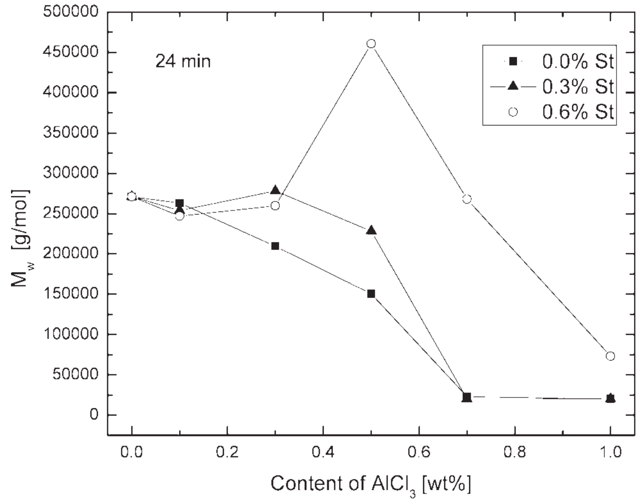

Figure 7 Variation of PS M_w with $AlCl_3$ content for 0.0, 0.3, and 0.6 wt % St added. Data for 24-min mixing time.

suggests that the reaction is completed in about 5 min. However, the homogenization may require longer mixing time for these processing conditions. For this reason, the samples used to determine the MW were taken at 24-min mixing time. It is also observed (Fig. 5) that the higher the $AlCl_3$ concentration, the more PS molecules cleaved, and that MW fall down to GPC detection limit.

Reaction with St addition

The addition of St to the reaction reduces the molecular degradation and even overcomes the starting PS MW. Figures 6 and 7 show the variation of M_n and M_w with catalyst concentration after 24-min mixing time. The M_n falls down almost linearly with the $AlCl_3$ concentration for the three sets of samples. However, a higher slope results from 0.6 wt % St concentration indicating a markedly lower degradation (Fig. 6). This effect is shown in Table II, by comparing the ratios between the M_{n0} (at 0 min) and the M_{n24} (at 24 min) of each sample. For the same $AlCl_3$ concentration, a decrease in M_{n0}/M_{n24} ratio is observed, in particular for 0.6 wt % St and higher $AlCl_3$ contents.

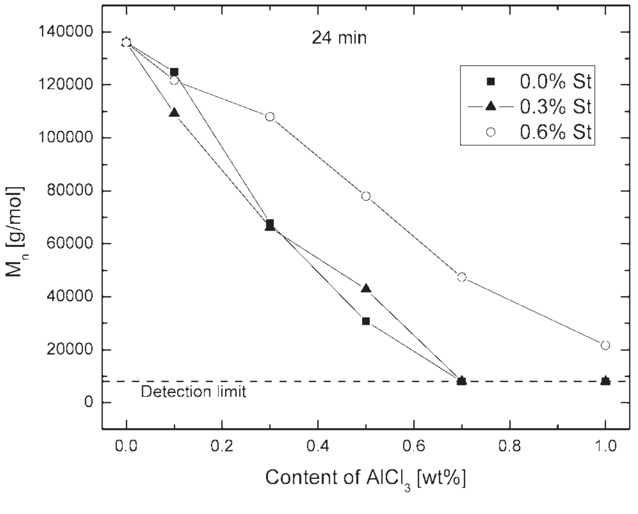

Figure 6 Variation of PS M_n with $AlCl_3$ content for 0.0, 0.3, and 0.6 wt % St added. Data for 24-min mixing time.

The behavior of M_w is rather different. In the absence of St, chain scission increases consistently with the catalyst concentration. However, the addition of St slows down the molecular degradation up to 0.3 wt % $AlCl_3$, and even produces greater M_w by increasing the higher MW fractions (Fig. 7). These results suggest that the presence of St may give rise to one or more reactions leading to MW increase, opposite to beta cleavage and competing with it. Some hypotheses to get a basic description of the reaction process are developed later.

In the first place, the occurrence of crosslinking reactions (as a source of MW increase) can be discarded since neither of the samples presented changes in solubility when subjected to common solvents for PS (THF, toluene, TCB) after reaction. The PS molecules react almost instantaneously with the $AlCl_3$. So, when the St molecules reach the reaction

TABLE II
Chain Scission for the Different St Concentrations Calculated as the Ratio of M_{n0} (at 0 min) to M_{n24} (at 24 min)

	M_{n0}/M_{n24}		
$AlCl_3$ (%)	0.0% St	0.3% St	0.6% St
0.1	1.1	1.2	1.1
0.3	2.0	2.1	1.3
0.5	4.4	3.2	1.7
0.7	17	17	2.9
1.0	17	17	6.3

medium, even if added immediately after, they encounter macrocarbocations and unsaturated species (C=C derived from beta-scission) already formed. The St molecule has a highly reactive C=C bond that, as it is known, can polymerize by temperature action (via free radicals). Moreover, it can add to a macrocarbocation to generate species of higher molecular weight via cationic polymerization and/or copolymerization. The possible contribution of free radical polymerization can be assessed by considering the MW variation at very low $AlCl_3$ concentration (0.1 wt %), where the catalyst effect is negligible. It is clear from Figures 6 and 7 that no increment in MW is observed at such low catalyst concentration, neither for 0.3 nor 0.6 wt % St additions, and therefore, the reaction via free radicals was declined.

It is worth noting that the St molecule is identical to the end link of the B species in [eq. (3)], it presents the same reactive group but attached to a hydrogen atom instead to a group of generic length R. Because of their low molecular weight, the mobility and reactivity of St molecules are comparatively greater than those in the B species. Taking this into account and following the Le Chatelier's principle,[17] some hypotheses can be postulated. In the first place, the presence of St would displace the reaction equilibrium to the left [eq. (3)], leading to molecules with greater MW. Also, the possible formation of graft copolymers should be considered. For example, it was reported that in PS polymerization production, a F-C catalyst is added at the reactor feed to improve the monomer conversion. This catalyst gets activated at high temperatures (about 200°C) converting the residual St to phenethyl carbocations. These carbocations can either initiate a cationic polymerization of St or can alkylate the PS benzene ring allowing their covalent bonding.[18] In this work, the conditions are suitable for F-C catalyst activation, and then a graft copolymer formation where a St molecule becomes attached to a PS benzene ring cannot be discarded. Cationic polymerizations of St were also reported where similar degradations and posterior copolymerizations by benzene addition were performed (Ref. 13, Chapter 8). Finally, it can be inferred that, at the processing conditions used in this work and the St addition made subsequently to the catalyst feed, cationic polymerizations and graft copolymerization reactions are feasible. These reactions could compete with the degradation reactions for the MW increment.

Although the general outcome of St addition is to offset chain scission, it seems that certain St/$AlCl_3$ concentration ratios would favor polymerization and/or copolimerization reactions that result in higher MW than the initial ones. This effect can be observed at points 0.3 St/0.3 $AlCl_3$ and 0.6 St/0.5 $AlCl_3$ in Figure 7. Here, increases in M_w of 10 and 64 wt %, respectively, are noted when compared with the starting PS. As it was mentioned earlier, the mechanism of these complex reactions is far from being known in detail. Nevertheless, the original chain scission can be altered by the addition of St to minimize the PS molecular degradation.

CONCLUSIONS

This work shows experimental evidence of the PS degradation due to $AlCl_3$ and the effect of St addition. The cationic nature of this degradation process was corroborated by analyzing volatile products, the results being in agreement with those supported by other authors. Moreover, it can be observed that the chain-scission process was compensated by the presence of St, and even greater MW than the starting PS was obtained. A simple explanation was proposed based on a possible competence between chain scission and polymerization and/or copolymerization reactions. The balance between macrocarbocations and unsaturated species concentrations would regulate this competence. This reactive process appears as a simple and effective tool to minimize molecular degradation in applications where the PS chain scission is undesirable.

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