

# Effects of Functional Groups on the Thermal Properties of Modified Polystyrene

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**ABSTRACT:** Polystyrene is, after polyolefins, the most widespread polymer in both industry and everyday life, successfully replacing some raw natural materials. In this study, the chemical modification of polystyrenes of different molecular weights was performed with various functional group modifiers (epichlorohydrin, maleic anhydride, and acetic anhydride) in one stage and in the medium of the cationic catalyst  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  according to previous studies. The concentration of the functional groups bonded to the aromatic ring of the polymer as a result of the chemical modification of polystyrenes of different mole-

cular weights depended on the molecular weight of the polymer, and more functional groups were bonded to lower molecular weight polystyrene. The effects of the functional groups bonded to the structure of the polymer on the thermal properties of modified polystyrene were investigated. The polystyrene that was modified by maleic anhydride was more stable against thermal destruction at high temperatures. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2549–2553, 2007

**Key words:** modification; polystyrene; thermal properties

## INTRODUCTION

New polymeric materials with complex properties have recently become of great practical importance to polymer chemistry and plastic technology, and they can be synthesized through the polymerization of monomers or chemical modification. In the last decade, there has been great interest in the chemical modification of traditional polymers with the aim of enhancing their chemical properties and making them useful for special applications. In recent years, the synthesis of polyfunctionalized polymers by chemical modification to increase their resistance against heat and their application areas have been developed continuously. Several studies on modifications of polymers have been reported.<sup>1–7</sup>

Thermal analysis is an important analytical method for understanding the structure–property relationships and thermal stability of composite materials. There have been several publications on the thermal properties of styrene polymers.<sup>8–13</sup>

The thermal stabilities of polystyrene (PS), poly(*p*-chloromethyl) styrene, and their corresponding derivatives were investigated by Lisa et al.<sup>8</sup> As a result of the influence of the chemical structure on the ther-

mal stability, it was determined that the chloromethylation reaction led to a significant decrease in the thermal stability of the PS polymers.

The thermal stability of a styrene/maleic acid copolymer was studied by Switała-Zeliazkow.<sup>10,11</sup> The heating of the styrene/maleic acid copolymer to 250°C caused an increase in its glass temperature. The thermal stabilities of styrene copolymers with two stereoisomers of 1,2-ethylene dicarboxylic acids were strongly dependent on the concentration of the acid units.

As the literature shows, polyfunctionalized polymers are an important subject in polymer chemistry. Therefore, in this study, we aimed to obtain modified PSs with various functional groups and to investigate their thermal properties.

## EXPERIMENTAL

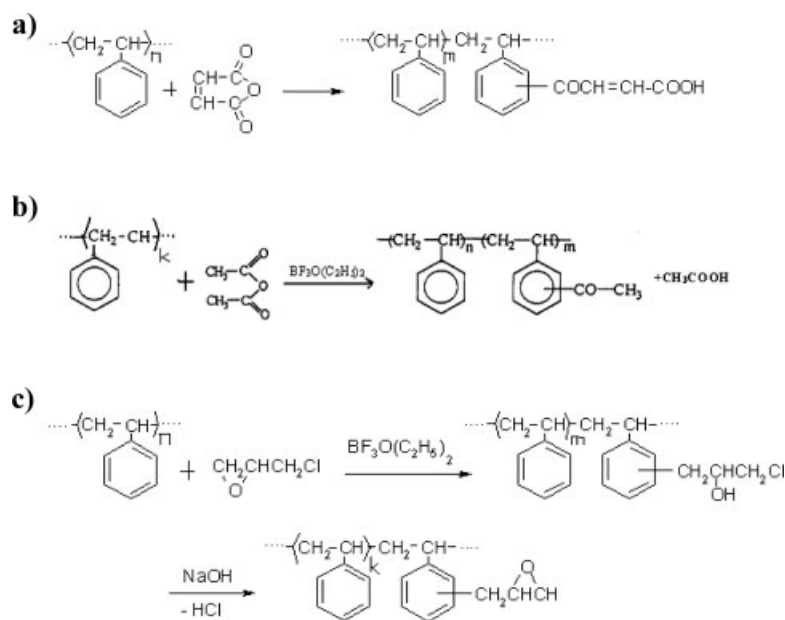
PS samples of different molecular weights [number-average molecular weight ( $M_n$ ) =  $350 \times 10^3$  or  $500 \times 10^3$ ], epichlorohydrin (ECH), maleic anhydride (MA), acetic anhydride (AA), 1,2-dichloroethane as a solvent, and the cationic catalyst  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  were purchased from Merck (Darmstadt, Germany).

## Synthesis of polyfunctionalized PS

A reactor composed of a mixer, a cooler, and a thermometer was used in the experiments. The modifier (0.0125 mol; 25% of the polymer amount) was added

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**Figure 1** Modification reactions of PS with (a) MA, (b) AA, and (c) ECH.

to a solution of 0.05 mol of PS in 60 mL of 1,2-dichloroethane through mixing. After the modifier was completely dissolved, 0.0125 mol of  $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$  was added drop by drop, and the reaction was ended in 2 h at  $30^\circ\text{C}$ . Modified PS was obtained without the formation of any byproduct. The mixture was poured into a beaker, and the modified PS was precipitated with methanol, dried in a vacuum oven at  $50\text{--}60^\circ\text{C}$  for 1 h, and weighed.<sup>5</sup>

The dehydrochlorination of PS, modified with ECH to obtain PS with epoxy groups, was also performed. To this end, modified PS was dissolved in toluene, 20% NaOH was added, and they were mixed for 3 h at  $70^\circ\text{C}$ . Then, the mixture was washed by water until all NaOH was removed, precipitated with methanol, and dried at  $50\text{--}60^\circ\text{C}$  for 1 h.

## Measurements and analyses

### Determination of the acid number

The number of functional groups bonded to the structure of modified PS was determined by func-

tional group analysis. To determine the number of carboxyl ( $-\text{COOH}$ ) groups in PS, the polymer sample was boiled under refluxing with excessive 0.1N KOH, and then the remaining KOH was titrated with a 0.1N hydrochloric acid (HCl) solution:

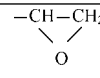
$$\text{Acid number (AN)} \text{ (mg of KOH/g of the polymer)} = 56.1(V_1N_1 - V_2N_2)/m$$

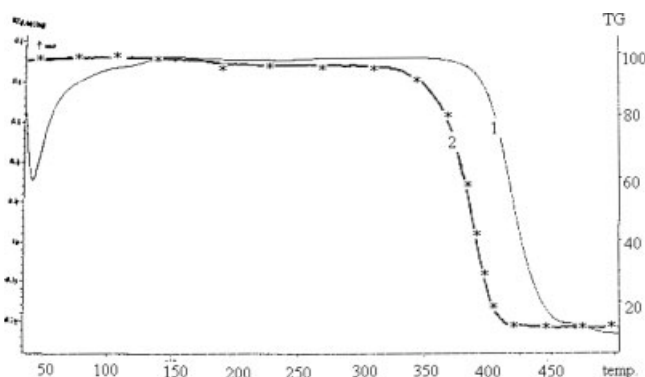
where  $V_1$  is the volume of the added 0.1N KOH (mL),  $N_1$  is the normality of the KOH solution,  $V_2$  is the volume of wasted 0.1N HCl (mL),  $N_2$  is the normality of the HCl solution, and  $m$  is the amount of the sample (g).

### Determination of the acetyl ( $-\text{CO}-\text{CH}_3$ ) groups

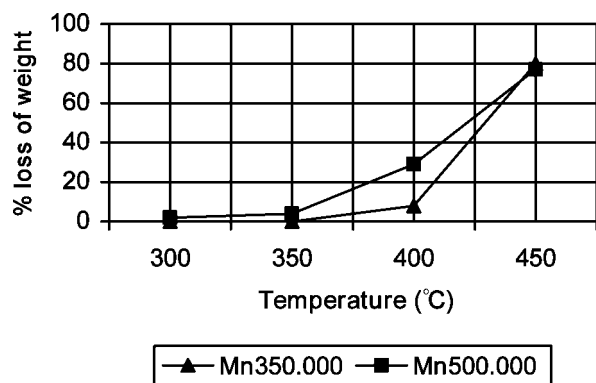
The concentration of the acetyl group, connected to the structure of PS, was calculated by the titration of

**TABLE I**  
Effects of the Molecular Weight of PS on the Number of Functional Groups in Modified PS

$M_n$ for PS ( $\times 10^3$ )	$-\text{COOH}$ (mg of KOH/g)	$-\text{CO}-\text{CH}_3$ (mol %)	$-\text{CH}-\text{CH}_2$  (mol %)
350	34.27	9.8	7.9
500	29.48	4.9	3.6



**Figure 2** TGA curves of PS modified with MA: (1)  $M_n = 350 \times 10^3$  and (2)  $M_n = 500 \times 10^3$ .



**Figure 3** Weight loss of PS modified with MA according to TGA.

acetic acid with 0.1N KOH, which occurred after the chemical modification of PS with AA with  $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$  as a catalyst:

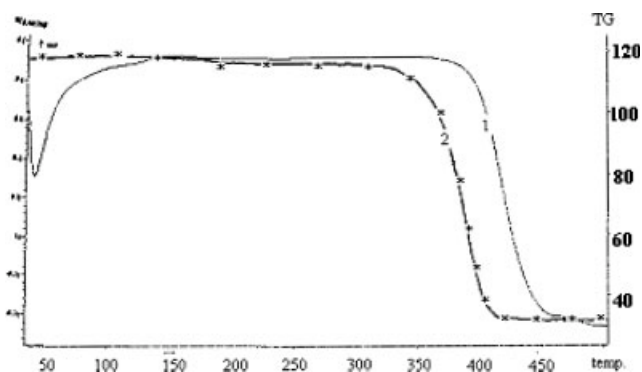
$$\text{AA (mol/L)} = (\Delta V \times T_{\text{KOH}} \times 1000) / 56.1 \times 2$$

where  $\Delta V$  is the volume of 0.1N KOH used for the titration of acetic acid in a 1-mL sample (mL),  $T_{\text{KOH}}$  is the amount of KOH in a 1-mL 0.1N KOH solution (0.005208 g), and 56.1 is the molecular weight of KOH (g).

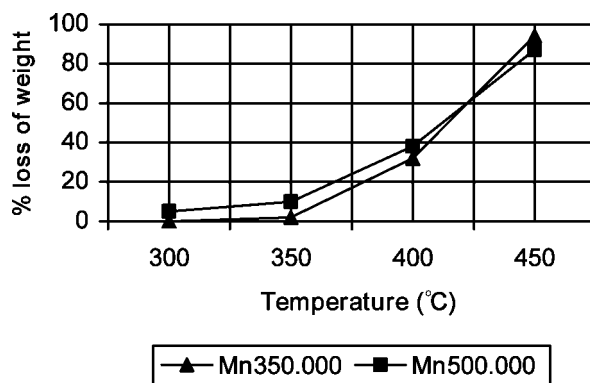
#### Determination of the epoxy groups

To determine the percentage of epoxide groups bonded to PS, 0.5 g of modified PS was placed in a 250-mL flask, and a 25-mL solvent mixture (60 mL of acetone and 1.5 mL of concentrated HCl) was added to it. It was mixed for 2 h at room temperature. The epoxy groups in the sample were cleaved with excessive HCl, and then the remaining HCl was titrated with 0.1N KOH. The epoxy group was calculated with the following equation:

$$\text{Epoxy groups (\%)} = (V_1 - V_2) \times 0.0043 \times F \times 100/m$$



**Figure 4** TGA curves of PS modified with AA: (1)  $M_n = 350 \times 10^3$  and (2)  $M_n = 500 \times 10^3$ .



**Figure 5** Weight loss of PS modified with AA according to TGA.

where  $V_1$  is the volume of 0.1N KOH used for the titration of the control (mL),  $V_2$  is the volume of 0.1N KOH used for the titration of the sample (mL),  $F$  is a titration factor for the 0.1N KOH solution,  $m$  is the amount of the sample analyzed (g), and 0.0043 is the number of epoxy groups corresponding to 1 mL of 0.1N KOH.

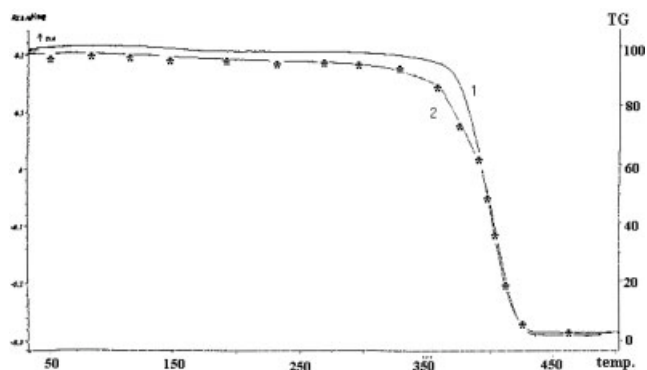
#### Thermal analysis

The thermal analysis experiments were performed with a Netzsch Geratebau GmbH thermogravimetric analyzer (Selb/Bavaria, Germany). The samples were heated under a nitrogen atmosphere from 250 to 450°C at a heating rate of 10°C/min.

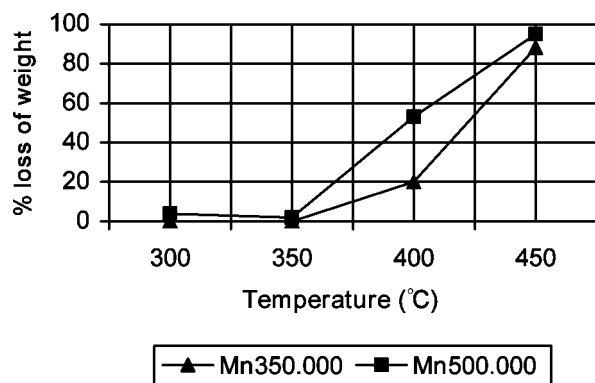
## RESULTS

The bonding of functional groups to the aromatic ring of the polymer with the  $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$  catalyst is shown in Figure 1.

The number of functional groups bonded to the aromatic ring of the polymer as a result of the chemi-



**Figure 6** TGA curves of PS modified with ECH: (1)  $M_n = 350 \times 10^3$  and (2)  $M_n = 500 \times 10^3$ .



**Figure 7** Weight loss of PS with epoxy groups according to TGA.

cal modification of PS samples of different molecular weight depends on the molecular weight of the polymer, so more functional groups are bonded to lower molecular weight PS (Table I).

PS ( $M_n = 350 \times 10^3$ ) modified with MA has a low weight loss because more  $\text{CO}-\text{CH}=\text{CH}-\text{COOH}$  groups (34.27 mg of KOH/g) are bonded to the aromatic ring. The weight loss at 400°C is 8%. The maximum decomposition is 80% at 450°C (Figs. 2 and 3).

The thermal analysis results for PS modified with AA are shown in Figures 4 and 5. The low-molecular-weight modified PS is more stable against thermal destruction and has weight losses of 2% at 350°C and 32% at 400°C.

Figures 6 and 7 shows that PS with epoxy groups is more stable against thermal destruction than unmodified PS.

According to our research, PS samples modified by various modifiers with cationic catalysts have more stability against thermal destruction than unmodified PS; this depends on the structure and

amount of the active polyfunctional groups bonded to the aromatic ring.

When we inspect the effect of the molecular weight on the destruction, we find that low-molecular-weight PS has more functional groups and more stability for all modifiers (Table II). The best results were obtained with MA and followed this order:  $-\text{CO}-\text{CH}=\text{CH}-\text{COOH} > -\text{COCH}_3 > -\text{CH}=\text{CH}_2$ .

As shown in Table II, unmodified PS has a 95% weight loss at 400°C, but PS modified with MA has an 8% weight loss at the same temperature.

We can explain this result as follow: a high temperature cracks the  $-\text{COOH}$  groups of the polymer, and the obtained  $-\text{CH}=\text{CH}_2$  groups crossbond and increase the stability of the polymer against thermal destruction (Fig. 8).

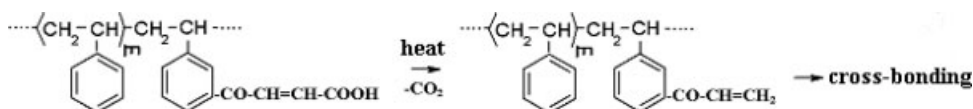
## CONCLUSIONS

Modified PS samples of various molecular weights were synthesized by chemical modification in the medium of the catalyst  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  with the modifiers MA, AA, and ECH. The functional groups bonded to the structure of the polymer had effects on the thermal properties of modified PS. PS modified by various modifiers had more stability against thermal destruction than unmodified PS; this depended on the structure and amount of the active polyfunctional groups bonded to the aromatic ring. PS samples with lower molecular weights were more resistant against thermal destruction.

It was determined that the PS modified with MA was more stable against thermal destruction at high temperatures.

**TABLE II**  
Effects of the Functional Groups on Thermal Destruction for Most Functional-Group-Bonded Modified PSs ( $M_n = 350 \times 10^3$ )

Functional group	Amount of the functional group	Loss of weight (%)			
		300°C	350°C	400°C	450°C
$-\text{CH}_2-\text{CH}=\text{CH}-\text{COOH}$	36.22 mg of KOH/g	0	0	8	80
$-\text{COCH}_3$ mole (%)	9.8 mol %	0	2	32	94
$-\text{CH}=\text{CH}_2$	7.9 mol %	0	0	20	88
Unmodified PS	—	50	76	95	100



**Figure 8** Thermal changes to the structure of PS modified with MA.

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