

Side-Chain Functionalization of Polystyrene with Maleic Anhydride in the Presence of Lewis Acids

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SYNOPSIS

Polystyrenes with different molecular weights were chemically modified with maleic anhydride by use of certain cationic catalysts of Lewis acid type ($\text{BF}_3 \cdot \text{OEt}_2$, AlCl_3 , TiCl_4 , ZnCl_2 , FeCl_3 , and SnCl_4) in chloroform. The effects of molecular weight of polystyrene, as well as type of Lewis acid used, on properties and structure of products were investigated. The interrelation between the molecular weight of polystyrene and content of carboxyl groups in the products was made. A direct relationship between the activity of catalyst used and the number of carboxyl groups was found. For characterization of side-chain functionalized polystyrene, fractional precipitation was applied which yielded carboxyl groups in all fractions. The carboxyl group concentrations were found to be the highest in the case of $\text{BF}_3 \cdot \text{OEt}_2$. Modified polystyrene samples containing $-\text{CO}-\text{CH}=\text{CH}-\text{COOH}$ fragments in side chains are easily crosslinked at 140–150°C and by UV irradiation as proved by IR, DTA, and TGA analyses. Functionalized polymers obtained are characterized by their high thermostability, adhesion, and photosensitivity. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The reaction of maleic anhydride with commercial polymers such as polyethylene,^{1,2} polypropylene,³ ethylene-propylene copolymer,⁴ polystyrene,⁵ and styrene-(ethylene-butylene)-styrene block copolymer⁶ in the presence of peroxide catalysts were investigated extensively. In most of these studies, the possibility of the addition of anhydride units on the polymer backbone accompanied mainly by crosslinking and degradation of macromolecules has also been demonstrated.

On the other hand, modifications on the side

chain of the macromolecule is also possible and has been frequently employed. For example, introduction of carboxyl groups in phenyl rings of polystyrene^{7–9} can be easily carried out by (a) cleavage of benzoylated or chlorobenzoylated polystyrene and by (b) oxidation of commercial formyl resin and chlormethylated polystyrene.⁹ Modification of side chains (phenyl rings) can be achieved with carbonyl-containing compounds by use of cationic catalysts which has not been studied with enough detail, although acylation of benzene with maleic anhydride (as a model system) was demonstrated by Pummer.¹⁰ Pummer used AlCl_3 in this studies. A Fiedel-Crafts reaction of polystyrene with phosgene was the subject of another study.¹¹ It was also shown that the same modification can be accomplished by use of a number of different reagents, like epichlorohydrin, various organic anhydrides, and en- and dien-hydrocarbons in the presence of Lewis acids.^{12–14} By use of these modified polystyrenes, it

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was shown that new coating systems with improved heat resistance, anticorrosive, and impact properties can be obtained.¹⁵⁻¹⁷

Thus, functionalization of polystyrene can be carried out either via the polymer backbone in the case of radical catalysts or through the side chain of macromolecules (phenyl rings) using cationic catalysts. The present work was undertaken to study the side-chain modification of polystyrene with maleic anhydride in the presence of various Lewis acids. The main objective of the study was to reveal the effect of the molecular weight of polystyrene and the type of Lewis acid used as a cationic catalyst on the structure and properties of the resulting functionalized polystyrenes.

EXPERIMENTAL

Materials

Polystyrene (PS) used was of emulsion ($M_n = 5.0 \cdot 10^5$) and/or of bulk type ($M_n = 2.5 \cdot 10^5$). Maleic anhydride (MA) used was purified by recrystallization from benzene followed by sublimation in vacuum; mp 52.8°C. The Lewis acids such as $\text{BF}_3 \cdot \text{OEt}_2$, AlCl_3 , TiCl_4 , ZnCl_2 , FeCl_3 , and SnCl_4 were commercial products and all were distilled under nitrogen atmosphere, diluted with chloroform, and sealed in glass ampules.

Modification

For modification of PS, 5.2 g (0.05 mol) of PS and 40 mL of chloroform were mixed and stirred in a flask at 20°C for 2 h to which 0.98 g (0.01 mol) of MA (corresponding to 20 mol % MA with respect to PS) was added and all were stirred for another hour. Above this solution, at the same temperature, the catalyst ($\text{BF}_3 \cdot \text{OEt}_2$) was added dropwise and all were stirred for 2 more h. Modified PS was precipitated by methanol from the reaction mixture, filtered, and dried under vacuum at 40°C for 5 h. Yield is 6.0 g (97.5%). The synthesized polymer had the following characteristics: T_g (by DSC analysis) 145°C; $[\eta]$ in toluene at 25°C 0.75 dL/g; acid number (AN) 136 mg KOH/g; thermostability (by TGA analysis) 350°C; adhesion of coating (by the "lattice notch" method) 98%; and photosensitivity 87 cm²/J. IR spectra (film), cm⁻¹: 2750, 1760, 1725, 1555, and 1410 ($\nu_{\text{C=O}}$), 1610, 900, 840, 730, and 705 (phenyl group), and 1635 ($\nu_{\text{C=C}}$), 2900–3150 (ν_{CH} and ν_{CH_2}).

The reaction above was repeated at a series of temperatures (between 0 and 30°C) and at different compositions of a feed PS:MA:catalyst mixture in mol % (90–60:10–40:10–40) and the optimum reaction condition was found to be as follows: 20°C, PS/MA = 4, and MA/catalyst = 1. Other Lewis acids (AlCl_3 , TiCl_4 , ZnCl_2 , FeCl_3 , and SnCl_4) were employed at the same optimum reaction conditions obtained for $\text{BF}_3 \cdot \text{OEt}_2$.

Measurements

The IR spectra of polymer films were recorded by use of a UNICAM SP 1025 spectrometer. Intrinsic viscosities of the whole modified polymer and its fractions were determined by an Ubbelohde viscometer in toluene at 25°C. Fractions of functionalized PS were obtained by the conventional fractional precipitation method in the benzene (solvent)–methanol (precipitant) system, in which 1% solutions of polymers were used. Molecular weights of whole derivatized PS and fractions were calculated by use of intrinsic viscosities.¹⁸

Photosensitivities of thin polymer coatings formed on a glass surface were determined by change of their optical densities in UV irradiation. The Osram-Ultra Vitalax E 27 moderate-pressure UV lamp (300 W) served as a source of irradiation.

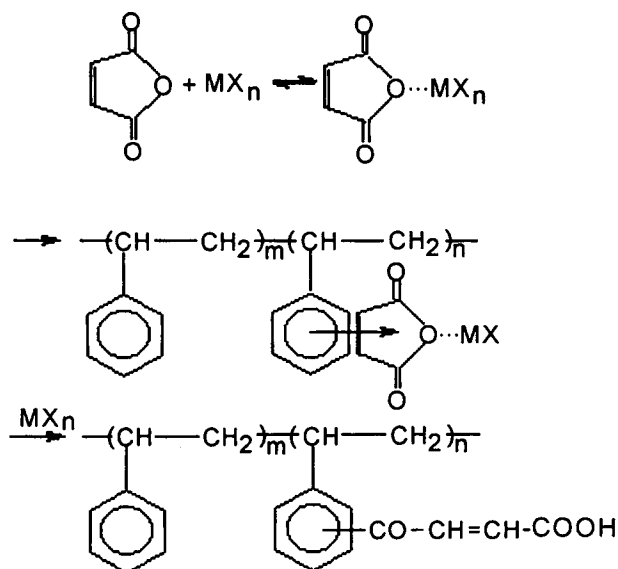
Thermal Analysis

Thermogravimetry (TGA) and differential/thermal analysis (DTA) experiments were carried out by use of a Paulik-Erday derivatograph system. The thermal stability of modified PS has been arbitrarily defined by the initial weight loss observed with increase in temperature at a 10°C/min heating rate in an air atmosphere. DSC analysis were realized by use of a DuPont TA 2000 at a heating rate of 10°C/min under a nitrogen atmosphere.

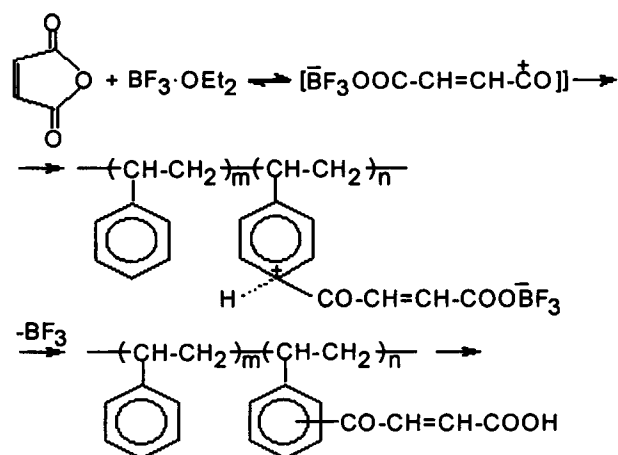
RESULTS AND DISCUSSION

Side-chain Acylation

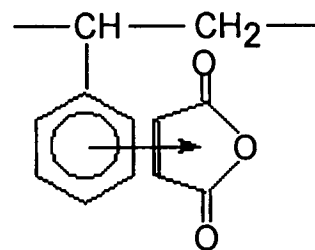
First of all, it should be taken into consideration that benzene is easily acylated with MA in the presence of AlCl_3 .¹⁰ This fact can serve as a model system for studies of PS–MA–Lewis acid systems. Results obtained allow one to present the general scheme for the side-chain modification of PS in the presence of Lewis acid in the following way:



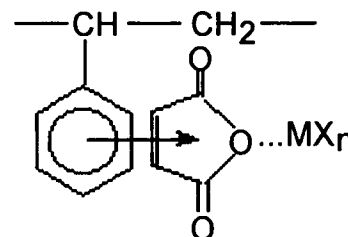
In the case of the use of $BF_3 \cdot OEt_2$ as the catalyst, the reaction scheme can be suggested as follows:



As one can see, the scheme consists of several stages: (1) complex formation of MA with Lewis acid (MX_n), (2) addition of the $MA \cdots MX_n$ complex to the phenyl ring of PS, and (3) break of the hydrogen atom from the *p*- or *o*-position of phenyl ring and its addition to maleate fragment. In this scheme, complex formation plays a very significant role in the acylation reaction. On the other hand, it can also be suggested that in the acylation reaction the charge-transfer complex between MA and phenyl ring of PS



or between complexed MA and PS



also can take place, which helps facilitate the acylation reaction. Complex formation between MA and aromatic carbohydrogens such as benzene and toluene was noticed in earlier studies.¹⁹

Table I Results of Characterization of Modified PS Prepared by Using Various Catalysts; Condition: PS/MA = 2.33; MA/Catalyst = 1, 20°C, 2 h

Catalyst	Initial PS with $M_n = 2.5 \cdot 10^5$				Initial PS with $M_n = 5.0 \cdot 10^5$			
	AN (mgKOH/g)	—COOH (Mol %)	$a_{(m:n)}$	$[\eta]$ (dL/g)	$M_n \cdot 10^{-5}$	—COOH (Mol %)	$a_{(m:n)}$	$M_n \cdot 10^{-5}$
$BF_3 \cdot OEt_2$	136	20.0	5 : 1	0.75	1.91	10.2	9 : 1	3.7
$AlCl_3$	132	16.6	6 : 1	0.51	0.96	8.7	11 : 1	3.1
$TiCl_4$	140	20.8	5 : 1	0.48	0.91	—	—	—
$SnCl_4$	106	14.3	7 : 1	0.53	1.16	4.4	22 : 1	4.05
$ZnCl_2$	64	7.7	13 : 1	0.54	1.17	3.4	30 : 1	3.61
$FeCl_3$	39	4.5	22 : 1	0.55	1.21	2.5	41 : 1	3.82

^a Ratio of contents of virgin PS (*m*) and acylated PS (*n*) units in macromolecules.

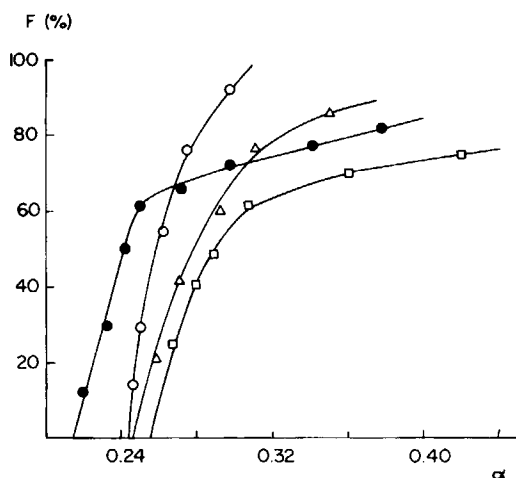


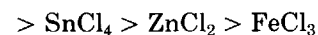
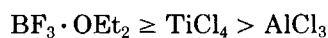
Figure 1 Curves of precipitation for functionalized PS prepared in the presence of (—○—) $\text{BF}_3 \cdot \text{OEt}_2$, (—●—) TiCl_4 , (—△—) SnCl_4 , and (—□—) FeCl_3 . F , the content of fractions (%), and α , the ratio of solvent (benzene)/precipitant (methanol).

The following experimental results can serve as proof of the proceeding of the acylation reaction in the direction shown in the scheme above:

The results of analysis for carboxyl group contents, intrinsic viscosities, molecular weights of functionalized PSs and the ratio of virgin and acylated PS fragments ($m : n$) are presented in Table I. From Table I, it is clear that modification of PS by MA occurred in all cationic catalyst media—however, at different levels. The highest carboxyl group concentration is found to occur with $\text{BF}_3 \cdot \text{OEt}_2$ and TiCl_4 . But in the case of TiCl_4 , acylated PS has a relatively low value of viscosity, which indicates that acylation is accompanied by

degradation of the main chain. The results of chemical analysis show that carboxyl group concentration increased from 4.5 to 20.8 mol % in the case of PS with $M_n = 2.5 \cdot 10^5$ and from 2.5 to 10.2 mol % for PS with $M_n = 5.0 \cdot 10^5$. In the comparison of the molecular weights of modified PS, the highest molecular weight was obtained when the $\text{BF}_3 \cdot \text{OEt}_2$ catalyst was used.

The degree of acylation of PS depends both on the type of catalyst used and on the molecular weight of the initial virgin PS. As seen from the data of Table I, virgin PS with a higher molecular weight is acylated to a smaller degree in the equal conditions of modification. From Table I, the activities of Lewis acids in the reactions studied are as follows:



Curves of precipitation (Fig. 1) of modified PS prepared in the presence of various Lewis acids also prove that $\text{BF}_3 \cdot \text{OEt}_2$ is the most convenient catalyst for the reaction studied.

In Table II, intrinsic viscosities and carboxyl contents of different fractions of modified PS obtained using different catalysts are presented. As evidenced from these data, all PS samples used were acylated. As viscosity of fractions decreases, the carboxyl contents in the products increase. The highest degree of acylation for all fractions is observed when $\text{BF}_3 \cdot \text{OEt}_2$ is used as the catalyst.

The existence of carboxyl groups in the structure of modified PS was also confirmed by IR studies (Fig. 2). The IR spectra of acylated PS have characteristic bands at 1760, 1725, 1555, and 1410 cm^{-1}

Table II Effect of Lewis Acid on the Intrinsic Viscosity and Degree of Acylation for the Various Fractions of Modified Block PS

Catalyst	Fractions									
	I		II		III		IV		V	
	$[\eta]^a$	—COOH ^b	$[\eta]$	—COOH	$[\eta]$	—COOH	$[\eta]$	—COOH	$[\eta]$	—COOH
$\text{BF}_3 \cdot \text{OEt}_2$	0.93	2.12	0.64	2.77	0.51	3.12	0.50	8.70	0.40	17.82
AlCl_3	1.08	2.38	0.86	5.26	0.55	9.10	0.32	12.52	0.27	16.15
TiCl_4	1.63	1.37	1.15	2.27	0.86	3.33	0.44	8.71	0.30	14.32
SnCl_4	1.30	1.85	0.83	3.12	0.47	7.14	0.35	10.26	0.27	15.15
ZnCl_2	1.27	1.64	1.04	2.27	0.77	4.54	0.50	7.14	0.40	7.71
FeCl_3	1.33	1.26	0.92	2.12	0.61	2.77	0.34	4.02	0.26	5.55

^a $[\eta]$ in toluene at 25°C (dL/g).

^b COOH is content of carboxyl group in the modified PS (mol %).

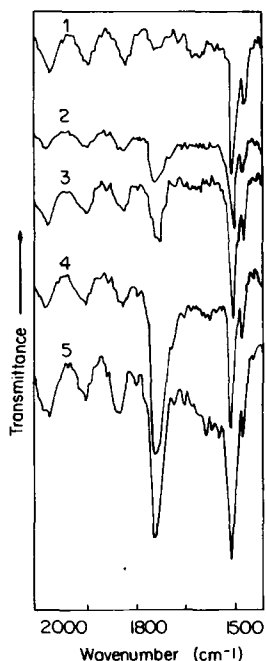


Figure 2 IR spectra of (1) virgin PS and (2-5) acylated PS synthesized by using of various catalysts: (2) FeCl_3 ; (3) SnCl_4 ; (4) TiCl_4 ; (5) $\text{BF}_3 \cdot \text{OEt}_2$.

corresponding to $\nu_{\text{C}=\text{O}}$ of acyl fragments in the side chain which are absent in the spectra of virgin PS. These bands are more intensive in the acylated PS prepared in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ (spectra 5) and TiCl_4 (spectra 4).

Crosslinking

From the data of DTA and TGA analysis, illustrated in Figure 3, it is evidenced that the visible exo-peaks in the range of 140–150°C appear in the DTA curves [Fig. 3(a)], which can be taken as evidence of the crosslinking reaction of acylated macromolecules at the expense of side-chain fragments. On the other hand, from the TGA curves [Fig. 3(b)], it is observed that there is a small weight loss (4–5%) at 110–140°C for modified PS, after which all TGA curves are straightened up to 275°C. The observed weight loss probably is related to the decarboxylation reaction of unsaturated acyl groups with the formation of vinylketon groups in the side chain, which, further, took place easily in the crosslinking reaction:

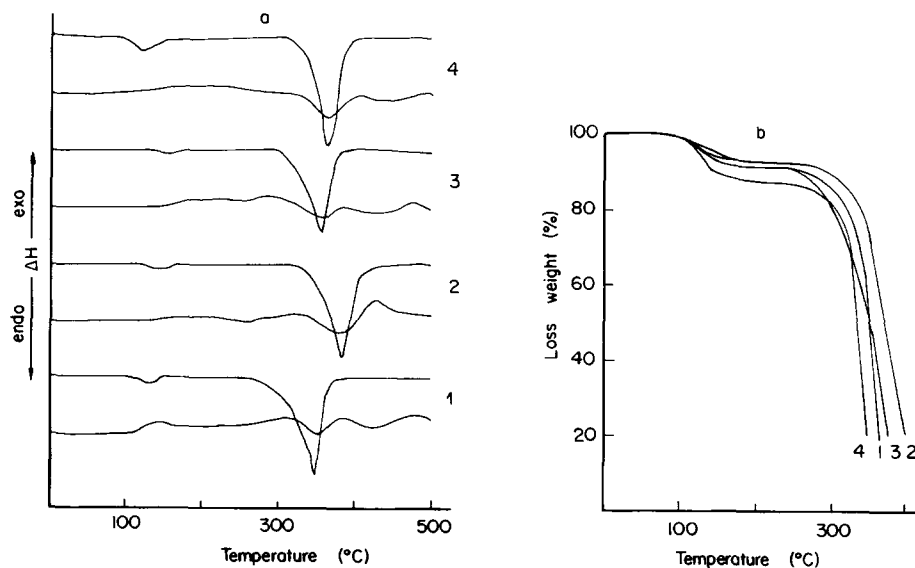
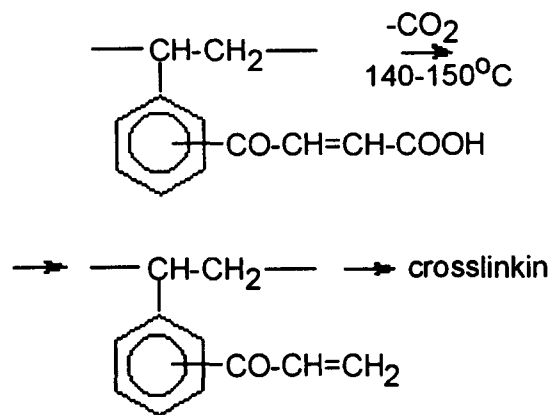


Figure 3 (a) DTA and TG and (b) TGA curves of modified PS in the presence of (1) $\text{BF}_3 \cdot \text{OEt}_2$, (2) FeCl_3 , (3) AlCl_3 , and (4) SnCl_4 . Heating rate 10°C/min in air.

The possibility of the proceeding of the first reaction during of thermotreatment of modified PS is also confirmed by the observed weight loss in the TGA curves [Fig. 3(b)] at the beginning stage. On the other hand, crosslinking of macromolecules is confirmed by exo-peaks of DTA curves [Fig. 3(a)] and also by the rather high thermostability of the studied polymer analogs observed. The temperature of decomposition for these polymers is 310–335°C. The characteristics of DTA and TGA curves also depend on the nature of the catalyst used in the synthesis of the functionalized PS characteristic by the content of carboxyl groups in the side chain (Table I).

The results of the IR studies illustrated in Figure 4 for modified PS films thermotreated at 75 and

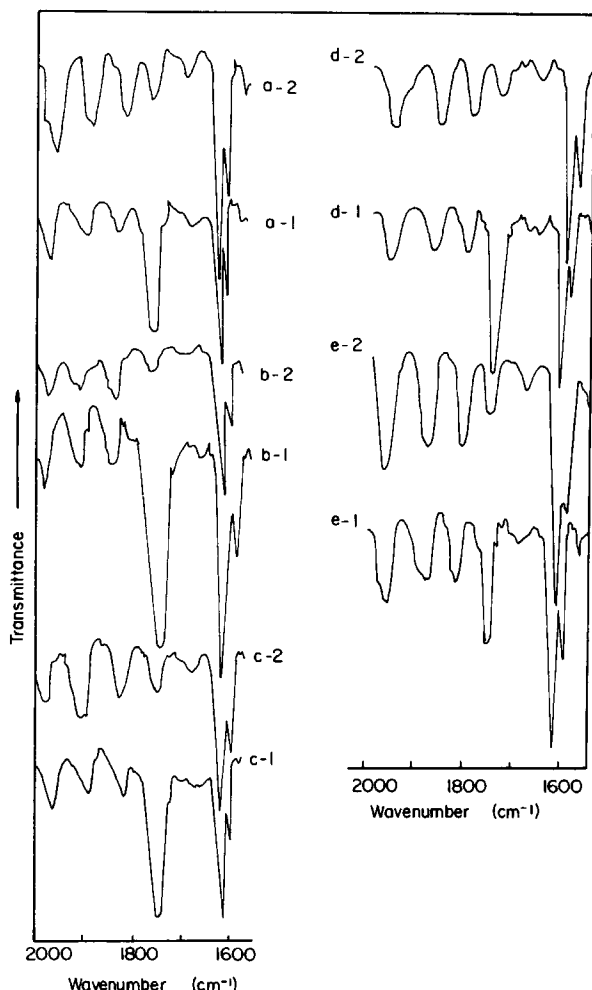


Figure 4 IR spectra of acylated PS films after thermotreatment (1) at 75°C during 45 min and (2) at 150°C during 30 min. Catalysts: (a) $\text{BF}_3 \cdot \text{OEt}_2$; (b) TiCl_4 ; (c) SnCl_4 ; (d) ZnCl_2 ; (e) FeCl_3 .

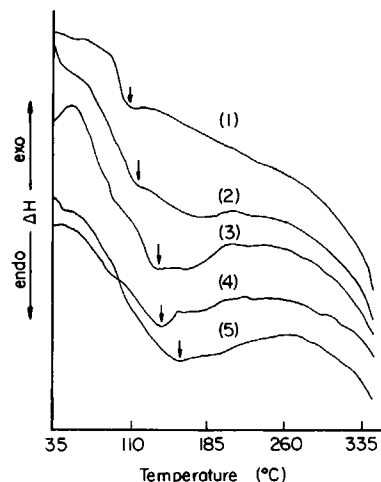


Figure 5 DSC scans of (1) PS ($M_n = 2.5 \cdot 10^5$) and its acylated derivatives with following contents of carboxyl group: (2) 4.5, (3) 14.3, (4) 16.6, and (5) 20.0 mol %, prepared by using FeCl_3 , SnCl_4 , AlCl_3 , and $\text{BF}_3 \cdot \text{OEt}_2$, respectively.

150°C during 45 and 30 min, respectively, can also confirm the proceeding of the crosslinking reaction. Figure 4 shows the dependence of the intensities of carbonyl bands (1760 and 1725 cm^{-1}) on the condition of thermotreatment. It is seen that the thermotreatment at 75°C does not affect the intensity of the carbonyl bands, while the thermotreatment at 150°C significantly decreases the intensity of these bands. This fact can be explained by the decarboxylation reaction of side-chain unsaturated acyl groups and their further crosslinking.

Figure 5 shows the scans of virgin and modified PS synthesized by using various Lewis acids. The position of each transition is designated by arrows. These transitions, which are observed to occur above room temperature, are probably caused by the melting of the hard segment of the macromolecules. Increase of graft/carboxyl fragments in the macromolecules leads to the displacement of the T_g to a higher field. For PS (virgin) with $M_n = 2.5 \cdot 10^5$, $T_g = 108^\circ\text{C}$, while for its modified derivatives, T_g changes from 116 to 145°C , depending on the degree of acylation. The observed exo-effects in the field of 150–280°C, which are absent in the DSC curves of virgin PS, indicated the proceeding of the chemical reactions of acylated macromolecules.

Composition–Property Relationships

As has been expected, introduction of polar and highly reactive unsaturated acyl groups in the PS

Table III Thermostability, Adhesion, and Photosensitivity of Functionalized PS Prepared in the Presence of Various Lewis Acids

Lewis Acid	AN (mgKOH/g)	Adhesion (%)	Photosensitivity (cm ² /J)	T _g (°C)	Loss of Weight (%) at (°C)		
					200	250	300
BF ₃ ·OEt ₂	136	98	87	145	7.0	9.0	12.0
AlCl ₃	132	92	75	131	9.0	10.5	18.5
SnCl ₄	106	90	68	128	12.5	13.5	17.0
FeCl ₃	39	85	16	116	7.5	8.0	11.0
PS (virgin)	—	2–3	—	108	38	44	50

^a Adhesion of polymer coatings (thickness 60–70 μk) formed on the glass surface is obtained by the “lattice notch” method.

introduced significant improvement of some very important properties. The thermal characteristics, adhesion, and photosensitivity of modified PS with different compositions are presented in Table III. Modified PS, using BF₃·OEt₂ as the catalyst, had better properties in comparison with virgin PS and other modified polymers. The high thermostability and photosensitivity of modified PS in comparison with virgin PS is explained by the crosslinked structure of macromolecules formed during the processes of thermo- and phototreatment. High adhesion and sensitivity to UV-irradiation of these polymer coatings allow one to use them as a base for the preparation of polymer resists of negative type.

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