

# Preparation of Modified Polystyrene with Maleic Anhydride in the Presence of Different Solvents

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**ABSTRACT:** Polystyrenes (PS's) with different molecular weights were chemically modified with maleic anhydride (MA) with of benzoyl peroxide as an initiator or with a cationic catalyst such as  $\text{FeCl}_3$  in chloroform. The effect of the solvents (i.e.; chloroform, benzene, toluene, xylene, and tetrahydrofuran), PS and MA concentration, molecular weight of PS, and type of catalyst used in the chemical modification was studied. The rate of the reaction was different with different solvents because of chain transfer to the solvent. The IR spectra of the modified polystyrene (MPS) existing at the

end of the chemical modification were taken to show the presence of a carboxyl group fixed to the aromatic ring of PS. The kinetics of the reaction of MPS with MA were also studied. MPS samples containing  $-\text{CO}-\text{CH}=\text{CH}-\text{COOH}$  fragments inside chains were crosslinked, as proven by differential thermal analysis. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 4099–4104, 2008

**Key words:** addition polymerization; modification; polystyrene

## INTRODUCTION

The synthesis of new polymeric materials can be carried out by either the polymerization of new monomers or the chemical modification of polymers with an appropriate technique.<sup>1,2</sup> With the chemical modification, substances that have big molecular weights react chemically, like the small ones, and new kinds of polymers can be synthesized. Chemical modification has great importance because of the impossibility of polymerization of the modified polymers with proper monomers. The use of polymer materials, especially polymers with polyfunctional groups, has increased because of the demand of modern techniques with chemical modification.

Aside from its wide use in industrial applications, polystyrene (PS) is also used for the production of plastic materials, which are used instead of metals in technology. The acylation reaction of PS with organic anhydrides is very important for the synthesis of polyfunctional PS.<sup>3,4</sup>

When maleic anhydride (MA) is used in the process of polymerization, the acylation reaction occurs on both sides of MA, either from the olefinic bond or the anhydride group. Therefore, to fully understand the acylation reaction mechanism

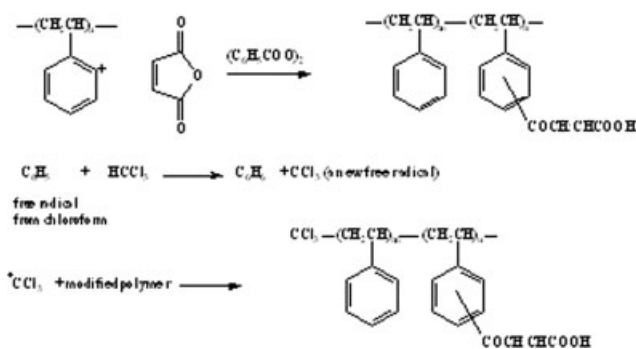
of PS with MA, toluene and ethylbenzene have been investigated as model compounds under similar conditions. The structure of the acylation reaction product of ethylbenzene with MA has been determined by chromatographic, spectral, and chemical analysis. The results show that the reaction occurs by the opening of the anhydride groups and anchoring of the phenyl ring of PS. The acylation reaction of PS with MA in the presence of benzoyl peroxide (BPO) can be represented as shown in Scheme 1.<sup>5–7</sup>

The physicomechanical, thermal, and adhesion properties of synthesized polyfunctional PS depend on the nature of the functional groups in the aromatic ring. These properties improve in the new PS produced with chemical modification.<sup>6–8</sup> In this study, the chemical modification kinetics of PS's with various molecular weights were studied. By the use of these modified polystyrenes (MPS's), it was shown that new coating systems with improved heat resistance, anticorrosive, and impact properties could be obtained.<sup>11–13</sup>

Thus, the functionalization of PS can be carried out either via the polymer backbone in the case of radical catalysts or through the side chains of macromolecules (phenyl rings) with cationic catalysts. The main objective of this study was to reveal the properties of the solvents.

The effect of the reaction rate, the effect of the molecular weight, the effects of PS and MA concentrations on the reaction rate, and the effect of the type of catalyst on the chemical modification were studied.

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**Scheme 1** Modification reaction with chloroform as the solvent.

## EXPERIMENTAL

### Materials

#### Monomers

MA was produced by Merck-Schuchardt (Munich, Germany) and was purified by recrystallization.

The first PS [ $PS_a$ : weight-average molecular weight ( $M_w$ ) = 209,713, number-average molecular weight ( $M_n$ ) = 122,983] used in the experiments was obtained from BASF-Germany (Ludwigshafen, Germany). The second PS ( $PS_b$ :  $M_w$  = 79,666,  $M_n$  = 39,049) was prepared in the laboratory.

#### Other reagents

Chloroform, toluene, xylene, tetrahydrofuran (THF) methyl alcohol, ethanol, potassium hydroxide; these reagents were chosen because of their common laboratory use and availability. MA, BPO were purchased from Merck-Schuchardt (Munich, Germany) and were used without further purification.  $FeCl_3$  was a commercial product.

### Kinetics of the chemical modification of PS

A closed system fixed to a thermostat was used for the reaction. After PS and MA were dissolved in chloroform, the reaction was initiated by the addition of 1 wt % BPO with respect to MA as an initiator. Starting at time zero and repeating over regular intervals, 1-mL samples were withdrawn from the reaction mixture. The volumetric method was then used for each sample to determine the amount of carboxyl group fixed to MPS. A known amount of sample dissolved in or-

ganic solvent was titrated with a solution of potassium hydroxide with a known concentration and with phenolphthalein as a color indicator. The acid number was used to quantify the amount of acid present. The quantity of MA was calculated from the amount of added titrant, which was a 0.1N KOH solution. This procedure was repeated to determine the effect of the solvent on the modification reaction of PS and MA. The initial reaction rates ( $v_o$ 's) and the reaction rate constants ( $k$ 's) were calculated for each experimental study.

### Analysis of the MPS

MPS obtained was precipitated with a large amount of pure methyl alcohol, filtered, and dried *in vacuo*. Afterward, MPS was dissolved in chloroform, and a few drops of the solution were placed on a KBr disc and allowed to dry, after which the IR spectrum was obtained with Fourier transform infrared spectroscopy with an ATI Mattson spectrometer (Madison, WI). The wavelength numbers obtained from the IR spectra were  $1725\text{ cm}^{-1}$  (C=O),  $1610\text{ cm}^{-1}$  (phenyl group), and  $1635\text{ cm}^{-1}$  (C=C).

### Thermal analysis

Differential thermal analysis (DTA) experiments were carried out with a Shimadzu DT-50 instrument (Shimadzu, Japan).

## RESULTS AND DISCUSSION

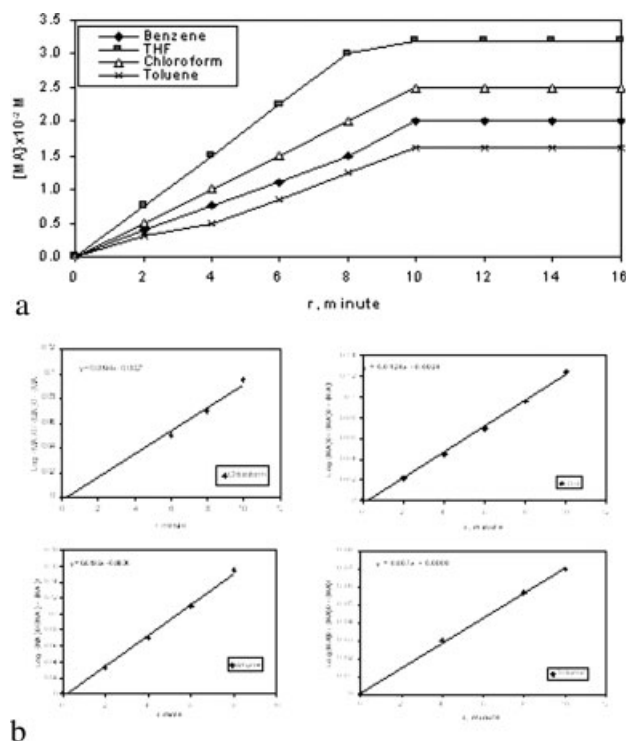
In our study, some physical parameters of the modification reaction of PS with MA were investigated in the presence of a BPO initiator. At first, the activity of the initiator was examined for the modification reaction of PS. The number of bonded groups to the aromatic ring as a result of the chemical modification of PS was higher in the presence of the initiator. Also, the modification reaction was first order because a linear curve was obtained when the reaction rate versus the concentrations of PS, MA, and BPO was plotted.

### Kinetic procedure

In this study,  $v_o$  values were calculated depending on the alteration of MA concentration. For each set

**TABLE I**  
 $v_o$  and  $k$  Values of the Modification Reaction of PS and MA in Different Solvents

	THF	Chloroform	Toluene	Xylene	Benzene
$v_o$ (M/min)	$2.5 \times 10^{-3}$	$2 \times 10^{-3}$	$1.5 \times 10^{-3}$	$2.5 \times 10^{-3}$	$3.75 \times 10^{-3}$
$k$ ( $M^{-1} \text{ min}^{-1}$ )	$12.4 \times 10^{-3}$	$9.4 \times 10^{-3}$	$7 \times 10^{-3}$	$12.4 \times 10^{-3}$	$19.3 \times 10^{-3}$

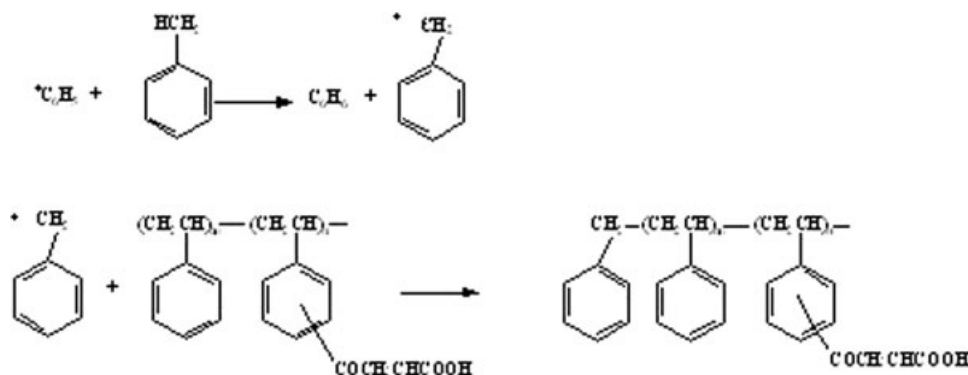


**Figure 1** (a) Effects of different solvents on the modification reaction of PS and MA carried out with PS<sub>a</sub> ([PS]<sub>a</sub> = 0.25M, [MA] = 0.12M, volume = 10 mL, [BOP] = 1 wt %). (b) Variation of time against log ([MA]<sub>0</sub>/[MA]<sub>0</sub> - [MA]<sub>t</sub>). r = t = reaction time/min.

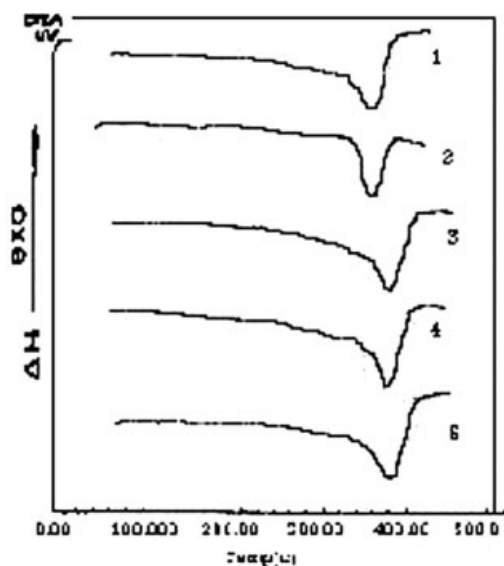
of experiments, the MA concentration versus  $v_0$  was drawn. So, it was found that the  $v_0$ 's of the reactions were the slopes of the curves obtained from the graph.<sup>6,9,10</sup>

$$-\frac{d[MA]}{dt} = v_0 \quad (1)$$

$k$  values, according to the reaction conditions, were reduced to the pseudo first order, and when they were calculated, the following equations were used:



**Scheme 2** Modification reaction with toluene as the solvent.



**Figure 2** DTA of PS with MA in the presence of (1) chloroform, (2) toluene, (3) THF, (4) xylene, and (6) benzene as solvents.  $\Delta H$  is heat exothermal.

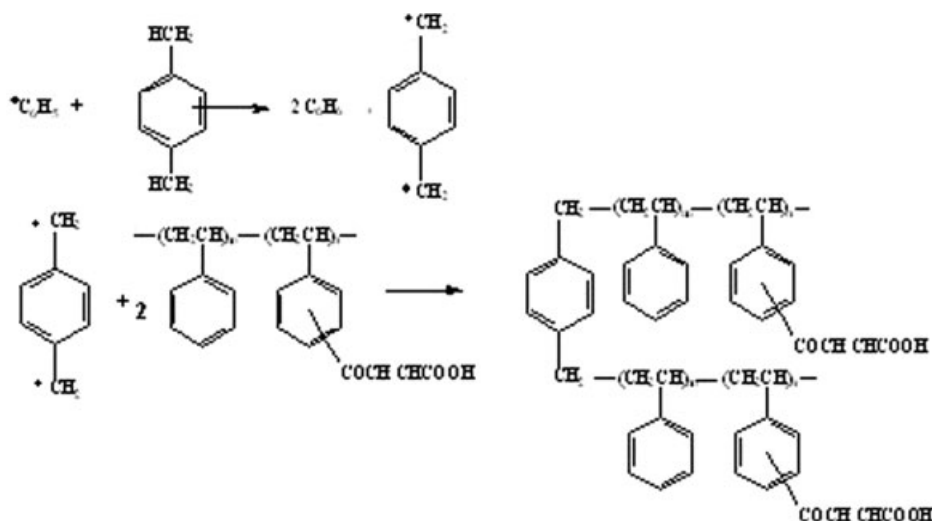
$$k_1 t = \ln \frac{[MA]_0}{[MA]_0 - [MA]_t} \quad (2)$$

$$kt = \frac{1}{[MA]_0 - [PS]_0} \ln \frac{[PS]_0 ([MA]_0 - [MA]_t)}{[MA]_0 - ([PS]_0 - [PS]_t)} \quad (3)$$

where  $k_1$  is the pseudo-first-order rate constant,  $k$  is the reaction rate constant,  $[MA]_0$  is the initial MA concentration,  $[MA]_t$  is the MA concentration at time  $t$ ,  $[PS]_0$  is the initial PS concentration, and  $[PS]_t$  is the PS concentration at time  $t$  (Table I).

$$v_0 = -\frac{d[MA]}{dt}$$

is the rate of decrease of the MA concentration with respect to time. It is clear that this rate changed with changing solvent because the chain transfer to the solvent was different according to the type of solvent.



Scheme 3 Modification reaction with xylene as the solvent.

The rate constant of change of MA concentration with respect to time ( $k_t$ ) was calculated as follows:

$$k_t = \ln \frac{[MA]_0}{[MA]_0 - [MA]_t}$$

It was clear that  $k_t$  changed highly depending on the kind of solvent. It was greatest in the case of benzene. This change in rate constant was due to the presence of chain transfer to the solvent [Fig. 1(a)].

The DTA curves showed the change in temperature versus the intensity of UV light for the polymers in the presence of different solvents. For toluene and xylene, the temperatures of disintegration of the polymer were highest, that is, 421.6 and 420.6°C, respectively. For benzene and chloroform, the temperatures of disintegration of the polymer were 416 and 415°C, respectively. When THF was used as the solvent, the temperature of disintegration of the polymer was 413.6°C.

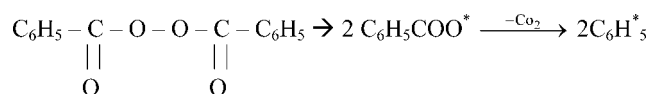
This change in the temperature of disintegration of the polymer with respect to different solvents was due to the presence of chain transfer to the solvent. Because of this chain transfer to the solvent, the polymer became more stable in toluene and xylene and less stable in benzene, chloroform, and THF.

From the data of DTA, as illustrated in Figure 2, it was evident that the visible exopeaks in the range of  $-175^\circ\text{C}$  appeared in the DTA curves, which could be taken as evidence of the crosslinking reaction.

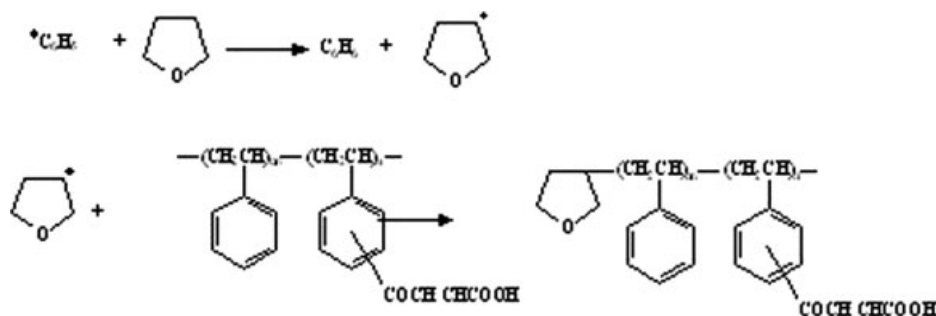
#### Effect of the solvents on the reaction rate

It was clear from the rate of the reaction in the presence of different solvents that there was a difference in the rate of the reaction when different solvents were used (i.e., chloroform, toluene, xylene, THF, and benzene). For benzene, there was no chain transfer to the solvent, and the rate of the reaction was considerably high. For chloroform, toluene, xylene, and THF (see Schemes 1–4), there is a great possibility that chain transfer to the solvent took place.<sup>14</sup>

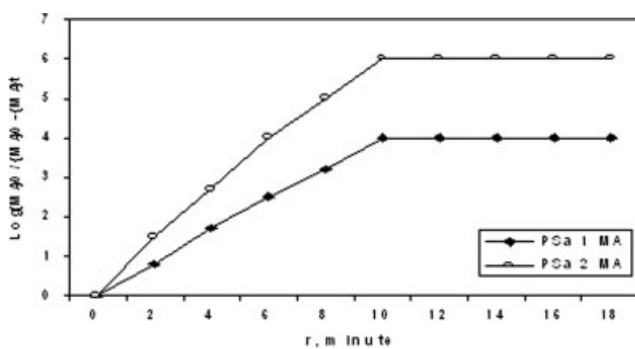
For chloroform



For xylene, if the reaction proceeded for a long time, crosslinking occurred between the upper and lower carboxyl groups of MA, and hence, it would



Scheme 4 Modification reaction with THF as the solvent.

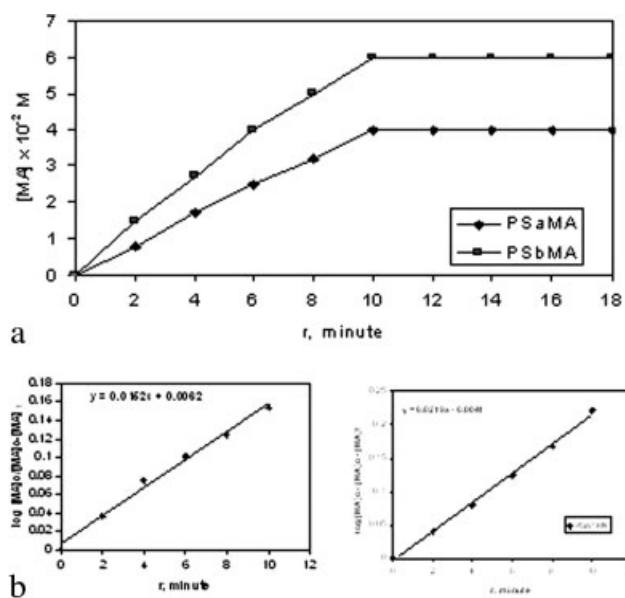


**Figure 3** Effects of the PS and MA concentrations on the modification reactions carried out with PS<sub>a</sub> ([PS<sub>a1</sub>] = 0.25M, [PS<sub>a2</sub>] = 0.5M, [MA] = 0.21M, volume = 10 mL, [BOP] = 1 wt % with respect to MA).  $r = t =$  reaction time/min.

**TABLE II**  
 $v_0$  and  $k$  Values of the Modification Reaction of PS and MA at Different Concentrations

	PS <sub>a1</sub> /MA	PS <sub>a2</sub> /MA
$v_0$ (M/min)	$0.373 \times 10^{-2}$	$0.5 \times 10^{-2}$
$k$ (M <sup>-1</sup> min <sup>-1</sup> )	$2.19 \times 10^{-2}$	$3 \times 10^{-2}$

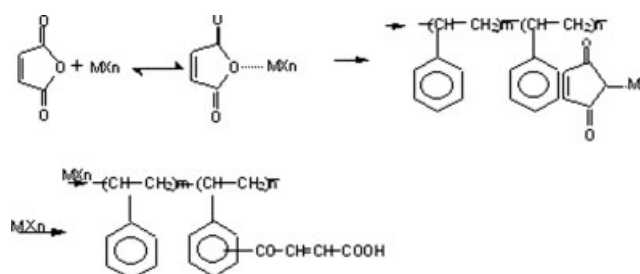
have been difficult to dissolve the polymer in the proper solvents. Also, the polymer would have been difficult to disintegrate by heat at higher temperatures.



**Figure 4** (a) Effects of the molecular weight of PS on the modification reaction carried out with PS<sub>a</sub> ([PS<sub>a1</sub>] = 0.25M, [PS<sub>b</sub>] = 0.25M, [MA] = 0.12M, volume = 10 mL, [BOP] = 1 wt % with respect to MA). (b) Variation of time against  $\log ([MA]_0/[MA]_0 - [MA]_t)$ .  $r = t =$  reaction time/min.

**TABLE III**  
 $v_0$  and  $k$  Values of the Modification Reaction of PS and MA with Different Molecular Weights

	PS <sub>a1</sub> /MA	PS <sub>b</sub> /MA
$v_0$ (M/min)	$0.373 \times 10^{-2}$	$0.75 \times 10^{-2}$
$k$ (M <sup>-1</sup> min <sup>-1</sup> )	$2.19 \times 10^{-2}$	$3.93 \times 10^{-2}$



**Scheme 5** Effect of the type of catalyst on the reaction ratio.

For THF, the chain-transfer reaction shown in Scheme 4 may have taken place.

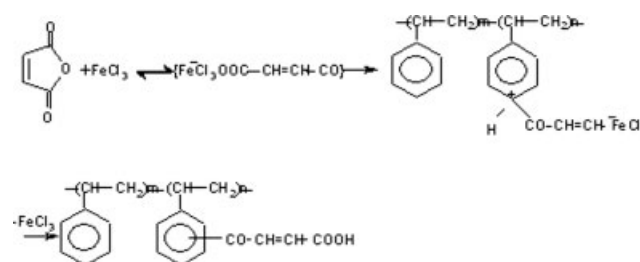
These reactions for chain transfer to the solvents explain the reason for the different values of the rates of reaction when different solvents were used during the modified polymerization of PS with MA.

**Effects of the PS and MA concentrations on the reaction rate**

During the chemical modification reaction of PS with MA, the effects of MA and PS concentrations on the reaction rate were investigated, and the graphs in Figure 3 were obtained. From these graphs,  $v_0$  were found for each study, and afterward, the rate constants were calculated; the  $v_0$  and  $k$  values obtained for PS<sub>a</sub> are shown in Table II. It was indicated that the polymerization proceeded too quickly at high monomer concentrations.

**Chemical modification kinetics of PS's with various molecular weights**

During the chemical modification reaction of PS with MA, the effects of the molecular weight of PS



**Scheme 6** Effect of the type of catalyst on the reaction ratio.

on the reaction rate were investigated, and the graphs in Figure 4 were obtained. From these graphs,  $v_o$ 's were found for each study, and afterward, the rate constants were calculated; the  $v_o$  and  $k$  values obtained for  $PS_a$  with  $M_w = 209,713$  and  $PS_b$  with  $M_w = 79,666$  are shown combined in Table III; virgin PS with a higher molecular weight reacted to a greater degree in equal conditions of modification.

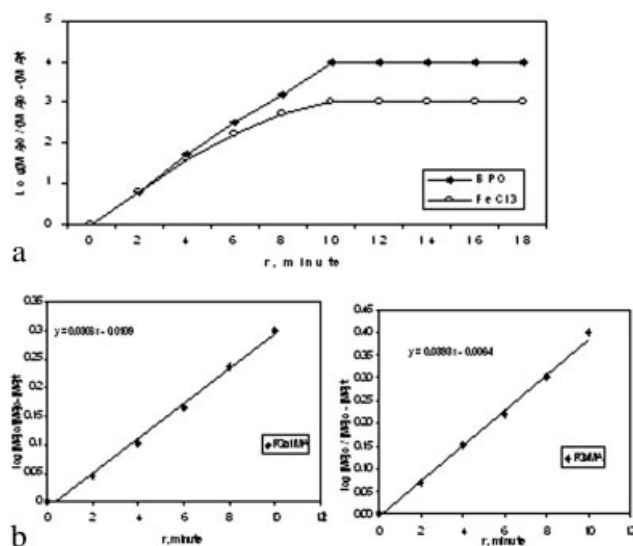
### Effect of the type of catalyst on the reaction ratio (Schemes 5 and 6)

The general scheme for the side-chain modification of PS in the presence of a cationic catalyst occurred in the following steps:<sup>6,15</sup>

1. Complex formation of MA with  $FeCl_3$  ( $MX_n$ ).
2. Addition of the  $MA \dots MX_n$  complex to the phenyl ring of PS.
3. Break of the hydrogen atom from the para or ortho position of the phenyl ring and its addition to the maleate fragment.

In this reaction, the charge-transfer complex between MA and the phenyl ring of PS or between the complexed MA and PS could take place. Complex formation between MA and aromatic carbohydrogens such as benzene and toluene was noticed in earlier studies.

The curves of Figure 5(a) of MPS prepared in the presence of various catalysts prove that the BPO catalyst was a convenient catalyst for the reaction studied. The slope of each curve in this figure shows the rate of the reaction. In the comparison of the molecular weights of MPS, the highest molecular weight



**Figure 5** (a) Effects of the nature of the catalyst on the modification reaction carried out with  $PS_a$  ( $[PS_a] = 0.25M$ ,  $[MA] = 0.12M$ ,  $[BOP] = 1$  wt % with respect to MA,  $[FeCl_3] = 0.1M$ ). (b) Variation of time against  $\log \frac{[MA]_0}{[MA]_t}$ .  $r = t =$  reaction time/min.

**TABLE IV**  
 **$v_o$  and  $k$  Values of the Modification Reaction of PS and MA with Different Catalysts**

	$PS_a1/MA$	$PS_a1/MA$
$v_o$ (M/min)	$0.373 \times 10^{-2}$	$0.45 \times 10^{-2}$
$k$ ( $M^{-1} \text{ min}^{-1}$ )	$2.19 \times 10^{-2}$	$3.93 \times 10^{-2}$

Reaction conditions: 1 wt % BOP with respect to MA and 0.1M  $FeCl_3$ .

was obtained when the BPO catalyst was used (Table IV).

### CONCLUSIONS

With BPO, a modified polymer was prepared from the chemical reaction of PS with MA, and when the kinetic parameters of this modification reaction were determined, it was observed that when PS reacted with MA in the presence of different solvents, the rate of the reaction was different for different solvents because of chain transfer to the solvent. For benzene, the rate of the reaction was higher. For toluene, the rate of the reaction was the slowest.

It was determined the PS and MA concentrations had an effect by increasing the modification reaction rate. The effects of the molecular weight and the nature of the catalyst on the chemical modification were also studied.

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