

Effects of Different Molecular Weights of Polystyrene on the Acylation Reaction and on the Reaction Kinetics

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ABSTRACT: In this study, chemical modification reactions of polystyrenes with different molecular weights with maleic and acetic anhydrides in the presence of a catalyst [$\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$] were examined. The number of polyfunctional groups bound to the polymer structure changed according to the molecular weight of the polymer, and more functional groups were bound to lower molecular weight polystyrenes. The bound functional groups and their amounts were determined with spectral and chemical analysis methods. The effects of the molecular weights of the polystyrenes on the chemical modification kinetics with ma-

leic and acetic anhydrides in the presence of $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ were examined. The kinetic parameters of the reaction and its activation energy were calculated. The higher the molecular weight of polystyrene was, the lower its rate of modification was and the greater its activation energy was; the lower the molecular weight of polystyrene was, the higher its rate of modification was and the lower its activation energy was. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 253–259, 2005

Key words: polystyrene; acylation reaction; reaction kinetic

INTRODUCTION

During recent years, polymer chemists have increasingly focused on the need to maximize efficacy because of the widespread use of polymers in high physicochemical materials and the interest in improving their performance, adhesion, and photosensitivity. Polymer chemistry has been the subject of studies concerning synthesis and applications.^{1–4}

In previous works, we investigated the chemical modification of polystyrene (PS) with maleic anhydride (MA), acetic anhydride (AA), epichlorohydrin, butadiene, and isoprene in the presence of cationic catalysis. The products were resistant to heat, impact, and various substrates and could be used as polymeric plate materials.^{5–11}

Polymer chemistry has been the subject of studies concerning synthesis and applications. The synthesis of new polymeric materials with complex properties has recently become of great practical importance to polymer chemistry and plastic technology. Generally, new polymeric materials can be synthesized through the polymerization of monomers or the chemical modification of polymers appropriate to polymer technol-

ogy. The acylation reaction is very important for producing new polymeric materials from PS polyfunctional groups in industry.

Today, PS, which is as widely used in industrial applications as polyolefins and poly(vinyl chloride)s, is also used for the production of plastic materials, which are used instead of metals in technological applications. Acylation reactions in polymer chemistry, especially for producing new polymeric materials from PS, are very important.

In this study, we examined chemical modification reactions of PS samples with different molecular weights. A high-molecular-weight emulsion of PS was fractionated according to its molecular weight with the dissolution–precipitation method to provide the maximum number of functional group to bind to the structure of the polymer.

The molecular weights of polymers are not constant like those of monomers; instead, polymers are mixtures of polymers with different molecular weights. For this reason, a precipitator was added to a solution of an emulsion of PS (molecular weight = 500,000) in benzene; the mixture was then separated into fractions according to the molecular weights. The molecular weights of these fractions were determined, and PS fractions with molecular weights of 300,000, 200,000, and 100,000 were obtained.

The chemical modification reactions of these PS fractions of determined molecular weights with MA and AA in the presence of a catalyst [$\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$] under optimum reaction conditions for high-molecu-

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lar-weight PS ($M_n = 500,000$) were examined. The amounts of the polyfunctional groups bound to the structure of the polymer were determined according to the molecular weights.

EXPERIMENTAL

Materials

An emulsion of PS, with a molecular weight of 500,000, was fractionated according to the molecular weights, and PS samples with different molecular weights were used.

MA was purified by recrystallization from benzene; this was followed by sublimation *in vacuo* (mp = 52.8°C).

AA was distilled after drying over Na_2SO_4 (mp = 140°C, density (d_4^{20}) = 1.0820, refractive index (n_D^{20}) = 1.3904).

$\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ was used as a cationic catalyst.

Fractionation

One of the most practical methods of fractionating high-molecular-weight polymers according to their molecular weights is fractionation by through the addition of a precipitator to a polymer solution.

For this reason, we selected benzene as a solvent and methanol as a precipitator for PS. After the selection of the solvent–precipitator system, we prepared a 1% solution of high-molecular-weight PS in benzene; it was emptied into a 1-L, three-necked flask with a bottom tap, and the precipitator (methanol) was added dropwise through a dropping funnel until the formation of turbidity. When turbidity formed, the addition of the precipitator was ended. Then, we waited until the formation of two phases, and the bottom phase (first fraction) was separated. This first fraction was the high-molecular-weight fraction of the polymer.

After this, the precipitator was again added dropwise to the transparent solution in the upper phase until the formation of turbidity, and the separation of the other phases was accomplished in the same way. The fractions were separated in descending order of the polymer fraction molecular weights. Thus, this procedure was continued until precipitation was not observed in the separated fractions. After fractionation, each fraction was dried and weighed, and its amount and molecular weight were determined.

Determination of the molecular weights

The molecular weights of the synthesized PS fractions were determined via the viscosimetric method with an Oswald viscosimeter at a constant temperature (25°C).

The molecular weights were calculated according to the Mark–Houwink equation:

$$[\eta] = KM^\alpha$$

The rate constant K and constant α of PS in toluene at 25°C were 1.70×10^{-4} and 0.69, respectively.

After these calculations, PS fractions with molecular weight of 300,000, 200,000, and 100,000 were selected from the molecular fractionation of high-molecular-weight PS ($M_a = 500,000$), and they were used in this study.

Chemical modification

The chemical modification of PS obtained by the emulsion method ($M_a = 500,000$) with MA in the presence of a cationic catalyst was first accomplished by us, and the chemical modification of other PS samples with different molecular weights with organic anhydrides was also carried out according to the same procedure.

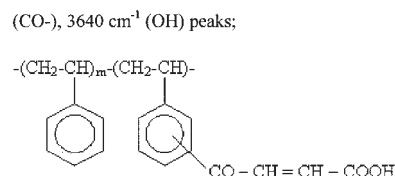
MA (1.0 g, 0.01 mol; 20% with respect to the polymer) was added to a solution of 5 g of PS in 100 mL of dichloroethane, and then the mixture was mixed for 1 h. In a 1:1 ratio with respect to MA, 1.42 g (0.01 mol) of the $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ catalyst was added, and the mixture was mixed for 1 h until the reaction was completely finished. Modified PS was precipitated by methanol from the reaction mixture, filtered, and dried *in vacuo* at 50°C for 5 h. The acid number (AN) was 136 mg of KOH/g.

The chemical modifications of other PS samples with MA and AA in the presence of the catalyst $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ were examined with the same procedure, and the optimum reaction conditions were determined for each modification reaction.

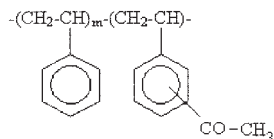
Measurements and analysis

The IR spectra of the modified polymer films were recorded with a UNICAM SP 1025 spectrometer.

In the IR spectra of PS fractions modified with MA, we observed peaks at 1620, 1635 (C=C), 1732 (CO—), and 3640 cm^{-1} (OH):



In the IR spectra of PS fractions modified with AA, we observed peaks at 1740 and 1743 cm^{-1} (CO—):



Chemical analysis

Determination of AN (COOH)

The concentration of the functional groups, which were connected to the modified PS obtained with the aforementioned method, was determined through an analysis by the functional group method.

The polymer (1 g), modified with MA, was dissolved with 20 mL of benzene in a globular flask, and an ethanol solution of 20 mL of 0.1N KOH was added. Then, the mixture was boiled under a reflux condenser in a water bath. After it was cooled, the surplus of KOH was titrated with 0.1N HCl. The concentration of carboxyl groups bound to PS was calculated from the wasted amount of KOH with the following formula:

AN (mg of KOH/g of polymer)

$$= 56.1 \times (V_1N_1 - V_2N_2)m$$

where V_1 is the volume of added 0.1N KOH (mL), N_1 is the normality of the KOH solution, V_2 is the volume of wasted 0.1N HCl, N_2 is the normality of the HCl solution, and m is the amount of the sample (g). AN (56 mg equiv of KOH/g of polymer) was calculated in this way too.

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

The concentration of the $-\text{CO}-\text{CH}_3$ group, connected to the structure of PS, was calculated through the titration of acetic acid, which occurred after the chemical modification reaction of PS with AA in the $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ catalyst medium, with 0.1N KOH.

Modification kinetics

The kinetics of the acylation reaction of PS samples with different molecular weights with MA and AA in the presence of the catalyst $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ in chloroform solutions at a constant temperature in a closed system with a magnetic mixer under a dry nitrogen atmosphere were investigated. The rate of the acylation reaction (r_0), K , and activation energy (E) were observed.

PS (1.5 g), 0.75 g of MA, and 40 mL of chloroform were added to the reactor, which was put in a thermostat. They were dissolved in a medium of dry nitrogen via mixing, and 0.0225 g (0.02 mL) of the $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ catalyst was added to the mixed reaction solution; a 1-mL sample was taken every 3 min. To

TABLE I
Effect of the Molecular Weight of the Polymer on the Amount of the Functional Group of Modified PS with MA (1) and with AA (2)

Polystyrene ($M_n \times 10^3$)	—COOH (1)		—CO—CH ₃ (2) (mol %)
	mg of KOH/g	mg equiv of KOH/g	
500	136	2.43	8.1
300	157	2.80	9.2
200	193	12.5	12.5
100	215	13.6	13.6

stop the activation of the catalyst, two to three drops of water were added, and carboxyl groups connected to the aromatic ring of PS were titrated with 0.1N KOH in the presence of phenolphthalein. The wasted amount of MA, which reacted during the acylation of PS, was calculated as follows:

$$\text{MA (mol/l)} = (\Delta V T_{\text{KOH}} \times 1000) / 56.1$$

where ΔV is the wasted amount of 0.1N KOH (mL) for the titration of carboxyl groups connected to PS in a 1-mL sample, T_{KOH} is the amount of KOH in 1 mL of a KOH solution (0.005208 g), and 56.1 is the weight of 1 mol of KOH.

r_0 (mol/L s) was calculated from a graph of various amounts of MA (mol/L) added to the reaction versus time.

From the rate of the reactions at a constant temperature, K was calculated. For this reason, at different temperatures, the rates of the reaction were observed, and the activation energy of the reaction [E_0 (cal)] was estimated by the graph method from the relation between the rate constant ($-\log K$) and the temperature:

$$E_0 = 4.57 t g \alpha (\text{ccal/mol})$$

where $t g \alpha$ is tangent α .

RESULTS AND DISCUSSION

Chemical modification reactions of PS fractions, with molecular weights of 300×10^3 , 200×10^3 , and 100×10^3 , which were obtained from the separation of a high-molecular-weight emulsion of PS ($M_n = 500,000$) into its fractions, with MA and AA in the presence of the catalyst $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ under different conditions were examined. The optimum reaction conditions 5:1 (mol/mol) PS/anhydride, 1:1 (mol/mol) anhydride/catalyst, and 50°C. The results are shown in Table I.

As shown in Table I, when the molecular weight of PS (MA = 100,000–500,000) decreased under the same reaction conditions as a result of modification with MA, the concentration of $-\text{CO}-\text{CH}=\text{CH}-\text{COOH}$

TABLE II
Chemical Modification Kinetics of the Molecular Weight of the Polymer Versus the Concentration of Functional Groups of PS ($M_n = 500,000$) with MA

	[PS] ₀ (mol/L)	[MA] ₀ (mol/L)	[BF ₃ O(C ₂ H ₅) ₂] ₀ (mol/L)	T (K)	$r_0 \times 10^5$ (mol/Ls)
1	0.173	0.364	0.025	298	8.0
2	0.343	0.364	0.025	298	15.8
3	0.508	0.364	0.025	298	26.6
4	0.343	0.184	0.025	298	10.5
5	0.343	0.541	0.025	298	22.0
6	0.343	0.712	0.025	298	30.0
7	0.343	0.364	0.005	298	4.5
8	0.343	0.364	0.015	298	11.6
9	0.343	0.364	0.050	298	41.0
10	0.343	0.364	0.025	323	21.6
11	0.343	0.364	0.025	343	28.3

$K \times 10^4$ (L mol ⁻¹ s ⁻¹)						E
298°C	323°C	343°C	[PS] ₀	[MA] ₀	[BF ₃ O(C ₂ H ₅) ₂] ₀	(kJ/mol)
12.7	17.1	22.7	1	1	1	11.3

functional groups connected to the structure of the polymer increased.

AN of the modified polymer increased from 136 (2.43 mg equiv of KOH) to 215 mg of KOH/g of polymer (3.84 mg equiv of KOH).

The same results were observed for the acylation of PS samples with different molecular weights with AA in the presence of the BF₃ · O(C₂H₅)₂ catalyst. More —CO—CH₃ groups were connected to the aromatic ring of PS with a low molecular weight.

Thus, as a result of the chemical modification of PS samples of different molecular weights with MA and AA, we determined that the concentration of functional groups connected to the aromatic ring of the polymer depended on the molecular weight of the polymer. For this reason, more functional groups were connected to the lower molecular weight polymer. The investigation of the chemical modification kinetics, the calculation of the reaction rate and *E*, and the determination of the finishing time of the modification of PS samples with different molecular weights are important for developing the technology of chemical modification and determining the useful area of polyfunctional PS and the practical usage of polymeric coverage, which is planned for the future.

The effects of the different molecular weights of PS, the initial concentrations of the materials and catalyst, and the nature of the modifier used in the reaction were investigated.

For this reason; the kinetics of the reaction were investigated under the following conditions: temperature = 298–243 K, [PS]₀ = 0.173–0.05 mol/L, [MA]₀ = [AA]₀ = 0.184–0.712 mol/L, and [BF₃ · O(C₂H₅)₂]₀ = 0.005–0.05 mol/L.

Obtained under the same reaction conditions, the results of the modification reaction kinetics of PS samples with different molecular weights and MA and AA in the presence of the BF₃ · O(C₂H₅)₂ catalyst are shown in Tables II and III and Figures 1 and 2.

As shown in Table II and Figure 1, in the acylation reaction of PS (MA = 500 × 10³) with MA (temperature = 298 K, [BF₃ · O(C₂H₅)₂]₀ = 0.025 mol/L, [MA]₀ = 0.364 mol/L) with the initial PS concentration increasing from 0.173 to 0.508 mol/L, *r*₀ increased from 8.0 × 10⁻⁵ to 26.6 × 10⁻⁵ mol/L (i.e., nearly 3 or 4 times). It was happened because, in the acylation reaction, the concentration of MA connected to PS increased from 2.0 × 10⁻² to 6.2 mol/L in 12 min. The importance of the effect of the concentrations of MA and the catalyst on the reaction rate was determined, and the optimum conditions were as follows: temperature = 298 K, [PS]₀ = 0.343 mol/L, [BF₃ · O(C₂H₅)₂]₀ = 0.025 mol/L, and [MA]₀ = 0.364 mol/L (attention was paid to the amounts of MA and the catalyst wasted for the reaction).

*r*₀ changed between 4.5 × 10⁻⁵ and 41.0 × 10⁻⁵ mol/L s according to the kinetic conditions of the acylation reaction. *K* changed between 12.7 and 22.7 × 10⁻⁴ L/mol s according to the reaction temperature. *E* of the acylation reaction of high-molecular-weight PS with MA was 11.3 kJ/mol.

Under the same kinetic reaction conditions of acylated PS with a high molecular weight (*M_n* = 50 × 10⁴), the kinetics of the acylation reaction of lower molecular weight PS (*M_n* = 30 × 10⁴) with MA in the presence of BF₃ · O(C₂H₅)₂ were examined, and the results are presented in Table III and Figure 2.

As shown in Table III and Figure 2, the effect of the molecular weight of the polymer on the kinetic param-

TABLE III
Chemical Modification Reaction Kinetics of PS ($M_n = 300,000$) with MA in the BF₃ · O(C₂H₅)₂ Catalyst Medium

	[PS] ₀ (mol/L)	[MA] ₀ (mol/L)	[BF ₃ O(C ₂ H ₅) ₂] ₀ (mol/L)	T (K)	$r_0 \times 10^5$ (mol/Ls)
1	0.125	0.250	0.012	298	12.2
2	0.200	0.250	0.012	298	16.6
3	0.250	0.250	0.012	298	30.2
4	0.333	0.250	0.012	298	31.1
5	0.250	0.125	0.012	298	12.2
6	0.250	0.187	0.012	298	22.7
7	0.250	0.375	0.012	298	31.1
8	0.250	0.500	0.012	298	46.1
9	0.250	0.250	0.006	298	4.4
10	0.250	0.250	0.009	298	16.7
11	0.250	0.250	0.018	298	31.6
12	0.250	0.250	0.012	308	32.2
13	0.250	0.250	0.012	318	35.3

$K \times 10^4$ (L mol ⁻¹ s ⁻¹)						E
298 K	323 K	343 K	[PS] ₀	[MA] ₀	[BF ₃ O(C ₂ H ₅) ₂] ₀	(kJ/mol)
14.09	15.23	16.67	1.06	0.99	0.75	9.71

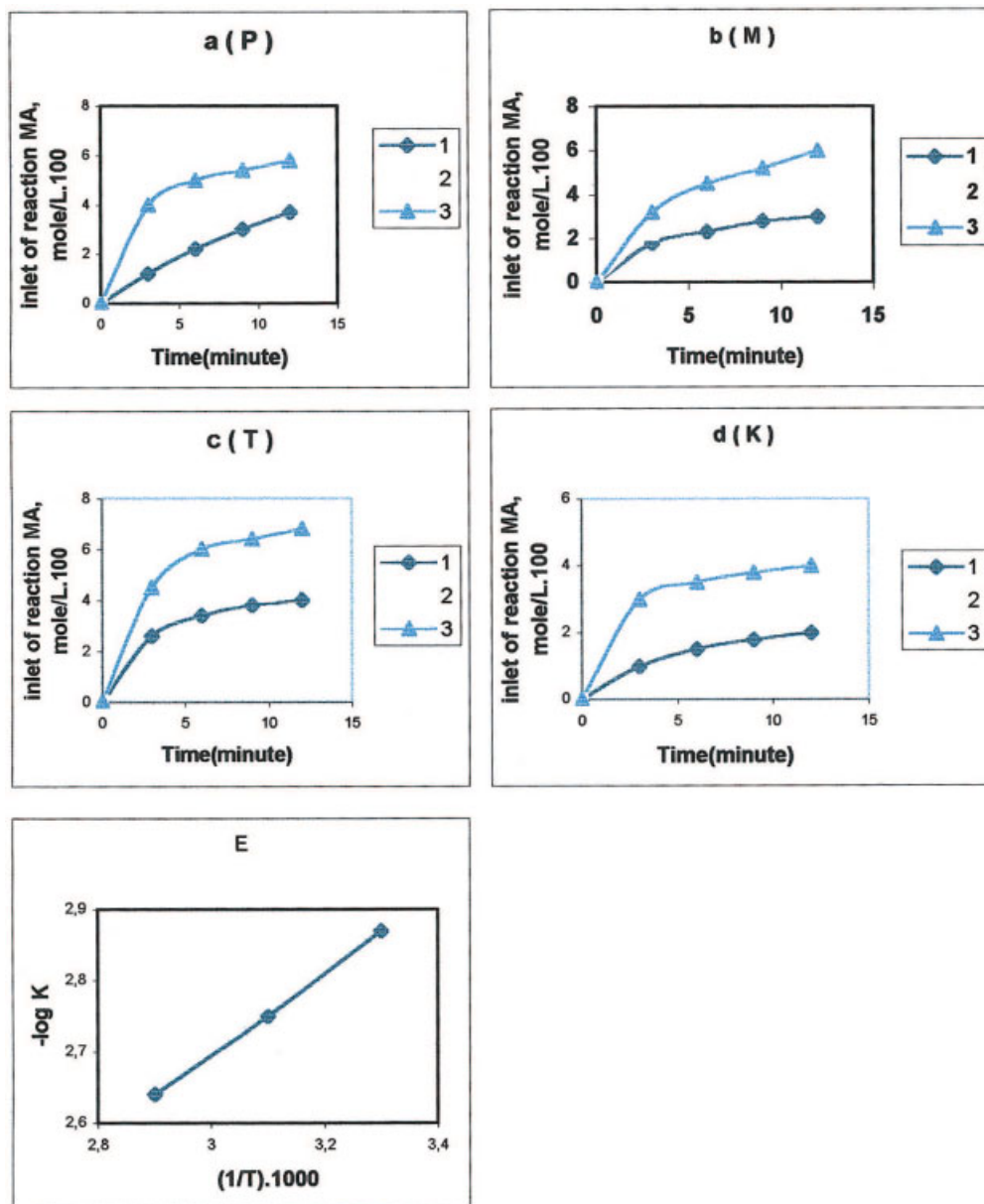


Figure 1 (a–d) Acylation kinetics of PS ($M_n = 50 \times 10^4$) with MA: (a) temperature = 298 K, $[\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2]_0 = 0.025$ mol/L, $[\text{MA}]_0 = 0.364$ mol/L, and $[\text{PS}]_0 = (1) 0.173, (2) 0.343,$ or $(3) 0.508$ mol/L; (b) temperature = 298 K, $[\text{PS}]_0 = 0.364$ mol/L, $[\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2]_0 = 0.025$ mol/L, and $[\text{MA}]_0 = (1) 0.184, (2) 0.541,$ or $(3) 0.712$ mol/L; (c) $[\text{PS}]_0 = 0.343$ mol/L, $[\text{MA}]_0 = 0.364$ mol/L, $[\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2]_0 = 0.025$ mol/L, and temperature = (1) 298, (2) 323, or (3) 343 K; and (d) temperature = 298 K, $[\text{PS}]_0 = 0.364$ mol/L, $[\text{MA}]_0 = 0.364$ mol/L, and $[\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2]_0 = (1) 0.005, (2) 0.015,$ or $(3) 0.025$ mol/L. (e) A graph of $-\log K$ versus $1/T \times 10^3$ ($T =$ temperature).

eters of the acylation reaction of PS with a low molecular weight was greater.

Therefore, with the molecular weight of PS decreasing from 50×10^4 to 30×10^4 , under the same reaction conditions, r_0 increased from 4.4×10^{-5} to 46.1×10^{-5} mol/L s, and E was lower (9.71 kJ/mol). These results show that the lower the PS molecular weight was, the higher the rate was of the chemical modification reaction and the lower the energy was for expending.

The same results were obtained for the kinetic parameters of the acylation reaction of PS samples with

different molecular weights with AA in the presence of the catalyst $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$. The results of the investigation of the acylation reaction kinetics of PS with AA in the presence of cationic catalysts are given in Tables IV and V.

As shown in Table IV, r_0 of PS ($M_n = 50 \times 10^4$) with AA varied between 0.35×10^{-5} and 3.1×10^{-5} mol/L s, and E was 17.15 kJ/mol.

As shown in Table V, r_0 of PS ($M_n = 30 \times 10^4$) with AA varied between 0.63×10^{-5} and 6.20×10^{-5} mol/L s, and E was 12.56 kJ/mol.

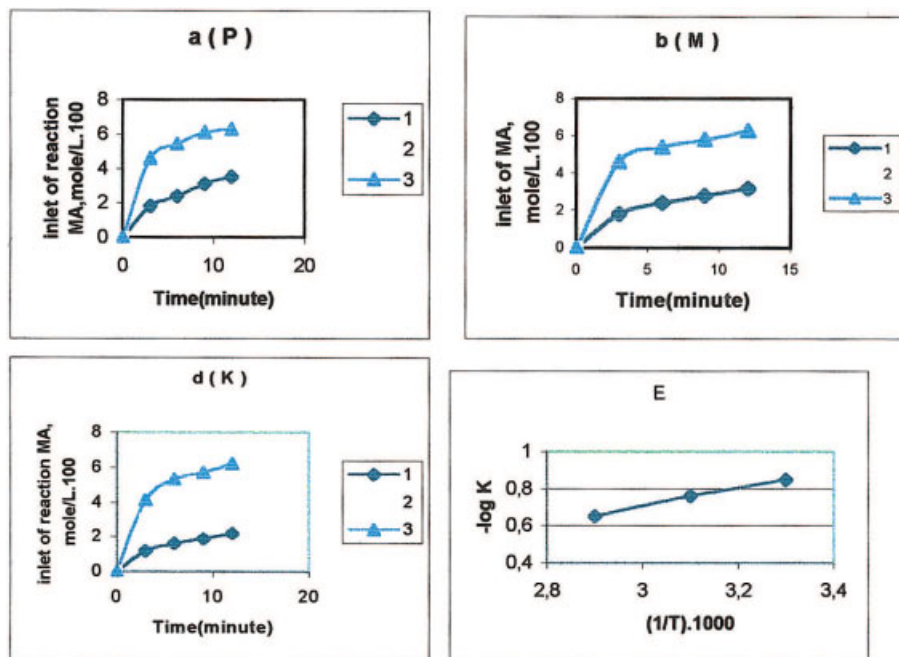


Figure 2 (a–d) Acylation kinetics of PS ($M_n = 30 \times 10^4$) with MA: (a) temperature = 298 K, $[\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2]_0 = 0.025$ mol/L, $[\text{MA}]_0 = 0.364$ mol/L, and $[\text{PS}]_0 = (1) 0.173, (2) 0.343,$ or $(3) 0.508$ mol/L; (b) temperature = 298 K, $[\text{PS}]_0 = 0.364$ mol/L, $[\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2]_0 = 0.025$ mol/L, and $[\text{MA}]_0 = (1) 0.184, (2) 0.541,$ or $(3) 0.712$ mol/L; (c) $[\text{PS}]_0 = 0.343$ mol/L, $[\text{MA}]_0 = 0.364$ mol/L, $[\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2]_0 = 0.025$ mol/L, and temperature = (1) 298, (2) 323, or (3) 343 K; and (d) temperature = 298 K, $[\text{PS}]_0 = 0.364$ mol/L, $[\text{MA}]_0 = 0.364$ mol/L, $[\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2]_0 = (1) 0.005, (2) 0.015,$ or $(3) 0.025$ mol/L. (e) A graph of $-\log K$ versus $1/T \times 10^3$ ($T =$ temperature).

It was determined that the lower the PS molecular weight was, the higher r_0 was and the lower E was under the same kinetic conditions. When the kinetic parameters of the acylation reactions of PS samples with the same molecular weights with MA and AA were compared, it was determined that with MA, r_0 and K were greater, but E was lower.

There was a difference in r_0 between AA and MA because of the high reaction capability resulting from the MA structure.

By taking into consideration chemical and spectral analyses and kinetic research, we determined that in the chemical modification mechanism with AA, AA

TABLE IV
Kinetics of the Chemical Modification Reaction in the Presence of PS ($M_n = 500,000$) and AA, with $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$

	$[\text{PS}]_0$ (mol/L)	$[\text{AA}]_0$ (mol/L)	$[\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2]_0$ (mol/L)	T (K)	$r_0 \times 10^5$ (mol/Ls)
1	0.360	0.368	0.026	298	1.10
2	0.270	0.368	0.026	298	0.69
3	0.180	0.368	0.026	298	0.64
4	0.361	0.184	0.026	298	0.45
5	0.360	0.276	0.026	298	0.68
6	0.360	0.368	0.026	323	2.1
7	0.360	0.368	0.026	343	3.1
8	0.361	0.368	0.005	298	0.35
9	0.361	0.368	0.053	298	2.0

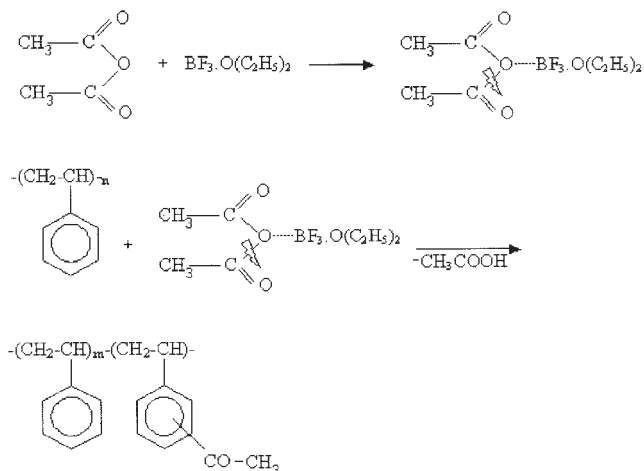
$K \times 10^4$ (L mol ⁻¹ s ⁻¹)			E			
298°C	323°C	343°C	$[\text{PS}]_0$	$[\text{MA}]_0$	$[\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2]_0$	(kJ/mol)
9.1	16.0	23.4	1	1	1	17.15

TABLE V
Kinetics of the Chemical Modification Reaction in the Presence of PS ($M_n = 300,000$) and AA with $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$

	$[\text{PS}]_0$ (mol/L)	$[\text{AA}]_0$ (mol/L)	$[\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2]_0$ (mol/L)	T (K)	$r_0 \times 10^5$ (mol/L s)
1	0.360	0.368	0.026	298	2.30
2	0.270	0.368	0.026	298	1.84
3	0.180	0.368	0.026	298	1.16
4	0.361	0.184	0.026	298	0.85
5	0.360	0.276	0.026	298	1.19
6	0.360	0.368	0.026	323	4.70
7	0.360	0.368	0.026	343	6.20
8	0.361	0.368	0.005	298	0.63
9	0.361	0.368	0.053	298	3.90

$K \times 10^4$ (L mol ⁻¹ s ⁻¹)			E			
298°C	323°C	343°C	$[\text{PS}]_0$	$[\text{MA}]_0$	$[\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2]_0$	(kJ/mol)
6.7	13.6	17.9	1	1	1	12.56

interacted with the cationic catalyst, and a complex was formed, just as in the chemical modification mechanism of PS with MA in the presence of the $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ catalyst.⁸ This complex interacted with PS, and acylation occurred:



CONCLUSIONS

The effects of different molecular weights of PS on chemical modification reactions and reaction kinetics in a cationic catalyst medium with organic anhydrides were investigated, and the following results were determined.

1. Under the optimum conditions found as a result of the chemical modification of PS samples with different molecular weights with maleic and acetic acid, the concentrations of $\text{CO}-\text{CH}=\text{CH}-\text{COOH}$ and CH_3-CO groups connected to the aromatic ring of the polymer changed accord-

ing to the molecular weight of the polymer, and the concentration of functional groups connected to the structure of modified PS increased.

2. The concentration of the functional groups connected to the structure of the polymer changed with the molecular weight of PS, and more functional groups were connected to low-molecular-weight PS.
3. When the kinetic parameters of the acylation reactions of PS samples with the same molecular weights with MA and AA were compared, it was determined that with MA, r_0 and K were greater, but E was lower.

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