

Preparation, Characterization and Modification Kinetics of Modified Polystyrene with Maleic Anhydride

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In this study, the chemical modification reaction of polystyrene (PS) with maleic anhydride (MA) in the presence of borontrifluoride (BF₃) catalyst in chloroform was examined. The modified polystyrene containing (-COCH=CHCOOH) fragments in phenyl rings was characterized by IR and ¹H-NMR spectroscopy. In addition, TGA, AFM analyses and contact-angles for polystyrene and the modified polystyrene were performed. The effects of polystyrene concentration, maleic anhydride concentration, catalyst concentration, solvent volume and temperature on the modification reaction were investigated by determining the amount of the carboxyl group fixed to the aromatic ring of polystyrene. Some kinetic parameters such as the reaction rate, the rate constant, the activation energy for the modification reaction were calculated.

Keywords: polystyrene, maleic anhydride, chemical modification, reaction kinetics

As it is known, functionalized polymers have a great importance for polymer chemistry. The synthesis of functionalized polymers can be carried out by either polymerization of new monomers or preparation of the modified polymers from the proper monomer with appropriate methods [1,2]. These methods are extensively used to increase resistance to heat, air, and strike for the synthesizing of new materials [1-4]. 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 [1, 7, 8].

The free radical-induced grafting of maleic anhydride onto polyolefin has been investigated extensively. This large interest originates in the enhanced adhesion of maleic anhydride functionalized polyolefins to polar materials like polyamide, metals, and glass fibers [9, 10]. The functionalization reaction of polystyrene with the anhydrides occurs by opening the anhydride groups and anchoring the phenyl ring of polystyrene [2, 5, 6]. The incorporation of functional groups to polystyrene caused an increase of adhesion capability, physico-mechanical properties, elasticity [4, 7]. In the previous studies, different modified polystyrenes including sulfonated polystyrene [11], acetylated polystyrene [12] and maleated polystyrene [13] have been reported for the chemical modification of polystyrene.

In this paper, we aimed to investigate chemical modification kinetics of polystyrenes and to determine physicochemical parameters of modified polystyrene. NMR, IR, TGA analyses were performed for the characterization of the modified polystyrene prepared under the optimal conditions. Furthermore, the change in the hydrophilicity and the morphology of the modified polystyrene surface were investigated.

Experimental part

Reagents and Measurements

Polystyrene (M_n : 140000, M_w : 230000), chloroform, maleic anhydride, methyl alcohol, potassium hydroxide and borontrifluoride used in the experiments were purchased

from Merck or Fluka. IR and ¹H NMR spectra were recorded on a Perkin Elmer 1605 IR s and a Varian 400 MHz NMR spectrometer, respectively. Thermogravimetric analysis was performed under argon gas on a Seteram SETSYS thermal analyzer. The samples were heated at 10 °C/min heating rate from 50 to 600 °C. The contact angles of water drops (5 µL) were measured by using a KSV CAM 200 drop sharp analysis in five different positions before and after the chemical modification. Atomic force microscopic (AFM) investigations were carried out with a Veeco diCaliber AFM. The instrument was performed in the contact mode in air at 25°C.

Kinetic procedure

A closed system fixed to the thermostat having external water circulation was used for the reaction and N₂ gas was used in this system for providing an inert medium. Polystyrene and maleic anhydride were dissolved in chloroform, and BF₃ catalyst was added to the reaction mixture (fig. 1). Starting at time zero, and repeating over regular intervals, 1 mL samples were withdrawn from the reaction mixture, and each of these samples were immediately added into 2 mL of deionized water for inhibiting the catalyst's activity. The carboxyl groups fixed to the aromatic ring of polystyrene were titrated with 0.1 N KOH, and the quantity of maleic anhydride was determined from the amount of added KOH. It was found that the initial rate (v_0) of the modification reaction was the slope on t_0 point of the curve obtained from the graph of [MA] - t . Then, the initial rate and the rate constant (k) of the modification reaction were calculated for each experiment study.

Results and discussions

Analysis and characterization

Modified polystyrene was precipitated by using a large amount of methyl alcohol, filtered and dried under vacuum. Afterwards, the modified polystyrene was solved in chloroform, was dripped on the disk formed with KBr crystals and the chloroform on disk evaporated. In the selected IR data for modified polystyrene, characteristic carbonyl stretching band of the modified polystyrene was seen strongly around 1700-1715 cm⁻¹. Furthermore

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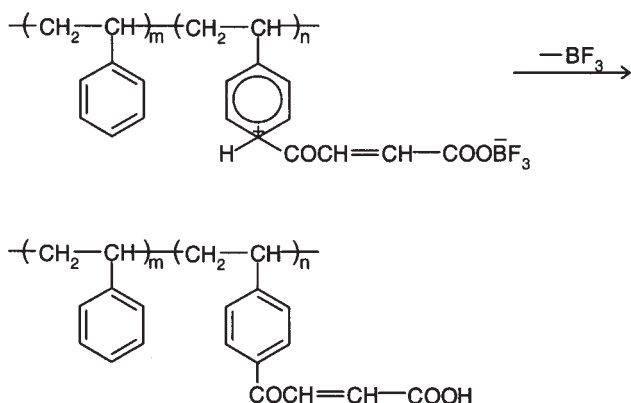
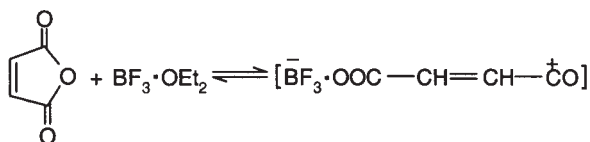


Fig. 1. Chemical modification of polystyrene with maleic anhydride

characteristic stretching of the carbon-carbon double bond (C=C) was seen at 1610-1635 cm⁻¹. On the other hand, in the IR spectra of the modified polystyrene, the new stretching band was seen around 1730-1755 cm⁻¹ attributable to the stretching vibration of the characteristic ester band.

In the ¹H NMR spectra of the modified polystyrene as shown in figure 2., the new peaks numbered with (1) and (2) shows the double bond and -OR (ester) group on the polystyrene backbone, respectively. In addition, the peak numbered with (3) shows the solvent and the other peaks

show structures that are known in the polystyrene chain. These new peaks (1) and (2) indicate that proposed structure of modified polystyrene is corrected. On the other hand, the carboxyl group of phenyl ring turned into ester groups owing to interaction of the catalyst and methanol used in the precipitation process. Furthermore, this situation is corroborated by the presence of the specifically stretching band of the ester in the IR spectra.

TG curve for the modified polystyrene is shown in figure 3. Weight loss of both polymers is observed in two stages: the first, in the range 100-150°C and the second, in the range 400-450°C. The first stage is probably connected with destruction of maleic anhydride formation and the second stage with destruction of the polymer. The first weight loss is related to the decarboxylation of acyl groups with formation of vinylketone (-COCH=CH₂) in the phenyl ring. These groups take place easily in the crosslinking reaction and the crosslinked structure increases the stability of the modified polystyrene against thermal decomposition. These results are in accord with literature [2].

The contact angles for water on polystyrene and modified polystyrene were measured 90.31° (± 0.7°), 62.91° (± 0.3°), respectively, and the contact angle of water on surface of the modified polystyrene was found much lower than that of polystyrene. The increase in the hydrophilicity of the surface after the chemical modification indicated a change in the chemical composition of the phenyl ring of polystyrene. AFM images were recorded to observe the variation on surface before and after the reaction with films prepared from polystyrene and modified polystyrene. We observed a flat surface on polystyrene and the rms roughness of the modified polystyrene was 0.703 μm.

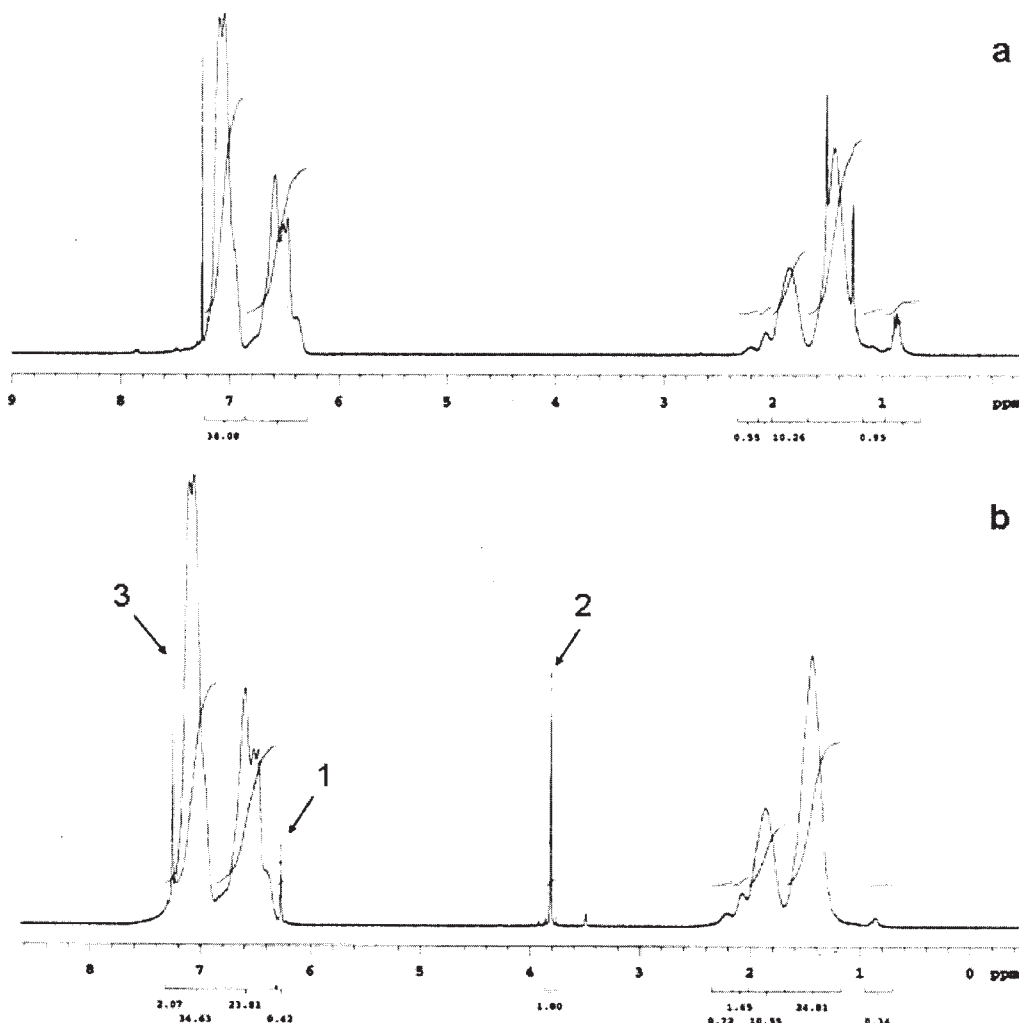


Fig. 2. ¹H NMR spectra of (a) polystyrene and (b) modified polystyrene

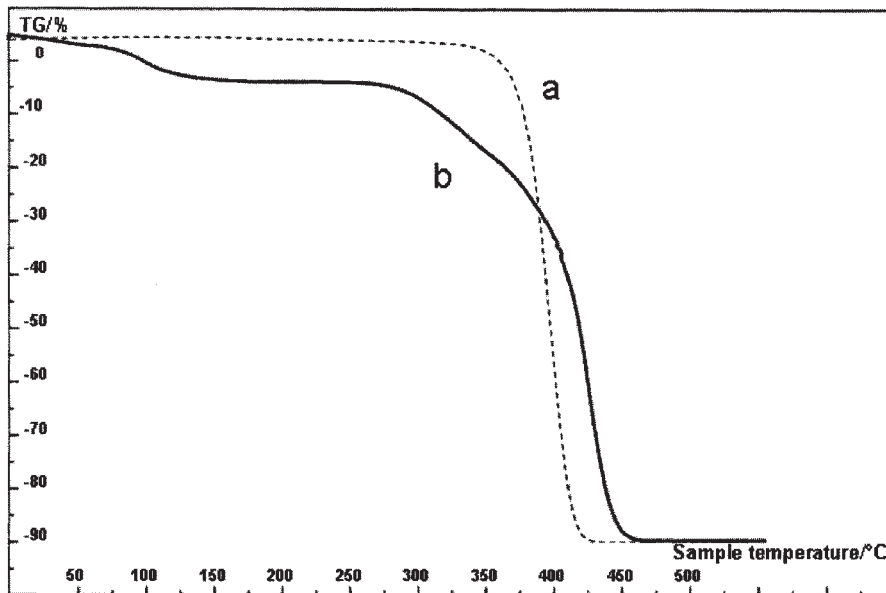


Fig. 3. TGA curve (a) polystyrene, (b) modified polystyrene

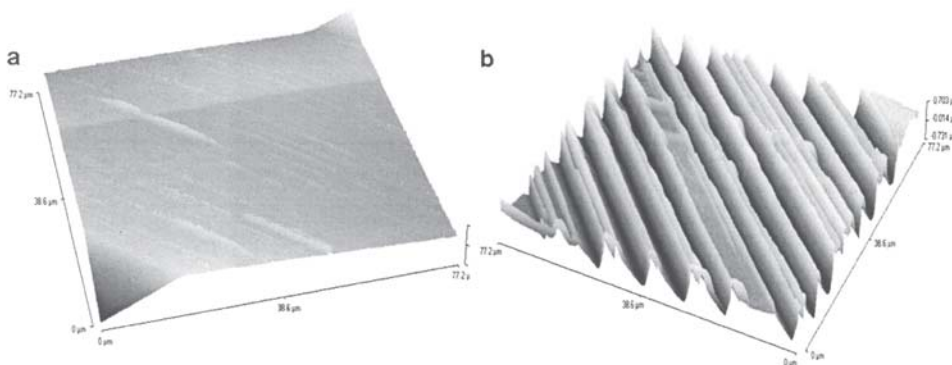


Fig. 4. AFM images of (a) polystyrene and (b) modified polystyrene

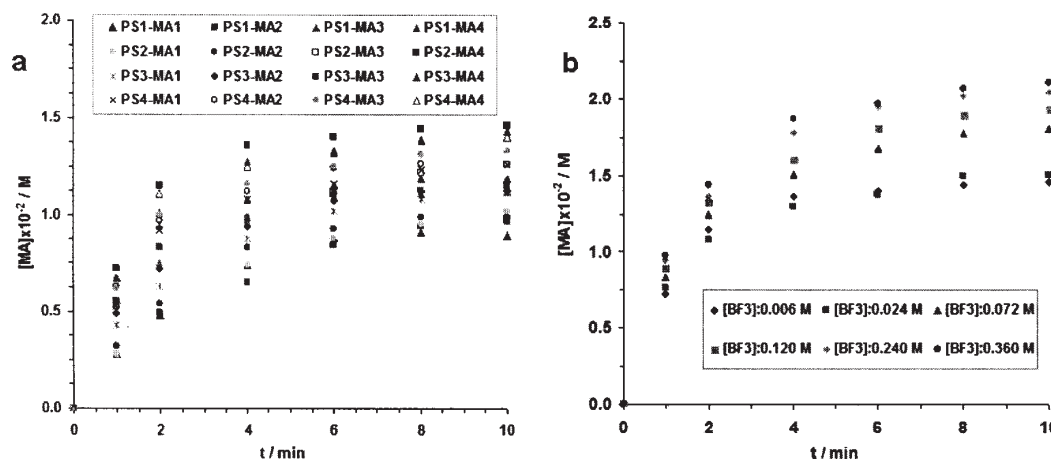


Fig. 5 (a) Effects of polystyrene and maleic anhydride concentrations on modification reaction (PS1: 0.24 M, PS2: 0.36 M, PS3: 0.48 M, PS4: 0.60 M, MA1: 0.06 M, MA2: 0.12 M, MA3: 0.18 M, MA4: 0.24, $[BF_3]_0$: 0.006 M, V_{CHCl_3} : 20 mL, t : 25 °C) (b) Effects of BF_3 concentrations on modification reaction ($[PS]_0$: 0.36 M, $[MA]_0$: 0.24 M, V_{CHCl_3} : 20 mL, t : 25 °C)

Kinetic parameters

In this study, some physicochemical parameters of the modification reaction of polystyrene with maleic anhydride were investigated in the presence of the cationic catalyst. The activity of the cationic catalysts (BF_3 , $TiCl_4$, $AlCl_3$, $SnCl_4$, $ZnCl_2$, $FeCl_3$) was investigated for the modification reaction of polystyrene [5], and the highest carboxyl group ratio in the modified polystyrene was found to occur with BF_3 . It was determined that the modification reaction was the first order according to components in terms of linear curve from the beginning of axis when the reaction rate versus concentrations of $[PS]_0$, $[MA]_0$ and $[BF_3]_0$ was fitted [14, 15]. In these studies, the initial rates were calculated depending on alteration of maleic anhydride concentration. For each study, maleic anhydride concentration – time

graph was drawn. So, it was found that the initial rates of reactions were the slopes on t_0 point of curves obtained from graphs [5, 8, 9]. Effects of maleic anhydride and polystyrene concentrations to the modification reaction rate were investigated and obtained data were shown in figure 5a. The initial rates of were found from the graph for each study and afterwards, the rate constants were calculated and shown in table 1. During the modification reaction of polystyrene with maleic anhydride, the effects of catalyst concentration on the reaction rate were investigated (fig.5b) and the rate constants were calculated and shown in table 2. For the chemical modification reaction of polystyrene with maleic anhydride, chloroform was chosen as the most appropriate in solvents

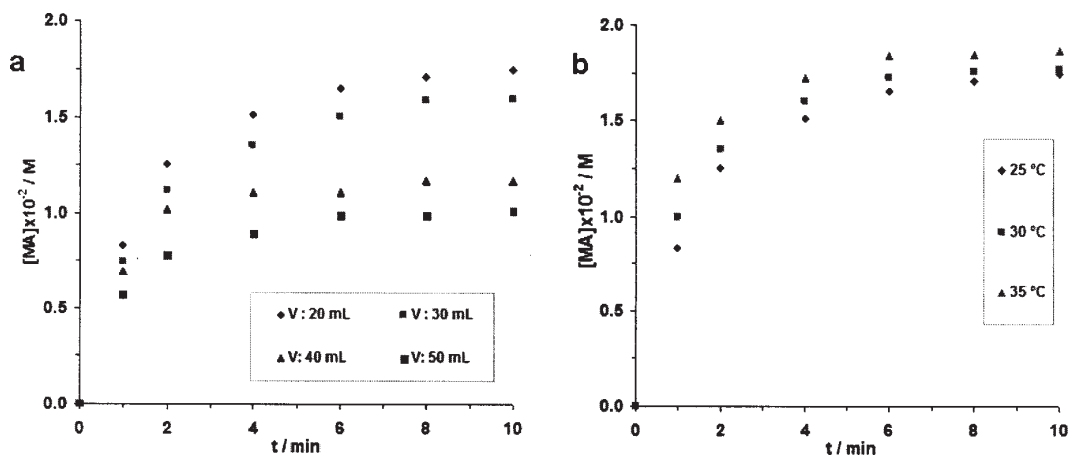


Fig. 6 (a) Effects of solvent volume on the modification reaction ($[PS]_0$: 0.36 M, $[MA]_0$: 0.24 M, $[BF_3]_0$: 0.072 M, V_{CHCl_3} : 20 mL, t : 25 °C) (b) Effect of temperature on the modification reaction ($[PS]_0$: 0.36 M, $[MA]_0$: 0.24 M, $[BF_3]_0$: 0.072 M, V_{CHCl_3} : 20 mL)

Table 1
 v_0 AND k VALUES FOR DIFFERENT CONCENTRATIONS OF POLYSTYRENE AND MALEIC ANHYDRIDE

$[PS]_0$, M	0.24	0.24	0.24	0.24	0.36	0.36	0.36	0.36	0.48	0.48	0.48	0.48	0.60	0.60	0.60	0.60
$[MA]_0$, M	0.06	0.12	0.18	0.24	0.06	0.12	0.18	0.24	0.06	0.12	0.18	0.24	0.06	0.12	0.18	0.24
$v_0(x10^{-3}), M^{-1}min^{-1}$	3.20	2.95	7.45	8.35	2.90	3.70	6.85	8.65	5.45	6.20	6.25	6.50	5.60	7.75	7.40	7.85
$k (x10^{-2}), min^{-1}$	5.33	2.46	4.14	3.48	4.83	3.08	3.81	3.60	9.08	5.16	3.47	2.71	9.33	6.46	4.11	3.27

$[BF_3]_0$, M	0.006	0.024	0.072	0.12	0.24	0.36
$v_0(x10^{-3}), M^{-1}min^{-1}$	8.65	9.80	10.35	11.20	12.20	12.40
$k (x10^{-2}), min^{-1}$	3.60	4.08	4.31	4.67	5.08	5.17

Table 2
 v_0 AND k VALUES FOR DIFFERENT CONCENTRATIONS OF BF_3

$V_{solvent}$, mL	20	30	40	50
$v_0(x10^{-3}), M^{-1}min^{-1}$	10.35	9.20	8.70	7.50
$k (x10^{-2}), min^{-1}$	4.31	3.83	3.63	3.13

Table 3
 v_0 AND k VALUES FOR DIFFERENT CHLOROFORM VOLUMES

temperature, °C	25	30	35
$v_0(x10^{-3}), M^{-1}min^{-1}$	10.35	13.25	16.50
$k (x10^{-2}), min^{-1}$	4.31	5.52	6.88

Table 4
 v_0 AND k VALUES FOR DIFFERENT TEMPERATURES

such as benzene, toluene, dichloroethane and different chloroform volumes were performed (fig. 6a). Initial rates and rate constants obtained were shown in table 3.

The modification reaction was resumed at different temperatures to investigate the effect of temperature on chemical modification reaction rate (fig. 6b). For k values obtained from the curves (table 4), $\ln k - 1/T$ graph was drawn by using Arrhenius equation. Activation energy, E_a , of the modification reaction was found to be 38.47 kJmol⁻¹ from the slope of the plot. We revealed the optimum conditions (PS : 0.36 M, MA : 0.24 M, BF_3 : 7.2×10^{-2} M, V_{CHCl_3} : 20 mL) for the modification reaction according to the experimental results and prepared the modified polystyrene under these conditions for the analysis and the characterization.

Conclusions

Modified polystyrene was prepared from the chemical modification reaction of polystyrene with maleic anhydride

in the presence of BF_3 . The kinetic parameters of the modification reaction were calculated and the most suitable conditions for the modification reaction were determined by using these kinetics parameters. In addition, some physical properties of analysis methods and the modified polystyrene had more stability against thermal destruction than polystyrene and the modified polystyrene had hydrophilic surface after the modification reaction. The results of AFM investigations were explained that there was a structural variation on the polymer surface with the functional groups which were fastened after the modification. Several experimental studies in which modified polystyrene was used in the production of fluorescent matter and of liquid membrane were reported. So, it is expected that the modified polystyrene can be used as a raw matter in chemical research.

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