

Synthesis, Characterization, and Kinetic Study of Functional Polystyrenes

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ABSTRACT: In this study, functionalization of polystyrene (PS) ($M_n = 2.5 \times 10^5$) was carried out with maleic anhydride in the presence of boron trifluoride diethyl etherate ($\text{BF}_3 \cdot \text{OEt}_2$) as catalyst and then functional PS was subjected to condensation reaction with phenyl hydrazine. The structures of both of them were determined by using FTIR, $^1\text{H-NMR}$, elemental analysis, thermogravimetric analysis (TGA) and differential thermal analysis (DTA) techniques. Some physical properties of these two products were investigated and the kinetic parameters of solid

state decomposition reactions were determined from TGA curves. The intrinsic viscosity $[\eta]$ values of modified PS and condensation products (cPs) found to be 1.024 and 0.7036 dL g^{-1} , respectively. According to TGA, the weight losses of modified PS and cPs were found to be 84.03 and 81.86%, respectively, at 500°C. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3454–3460, 2007

Key words: polystyrene; functionalization; physical properties; thermal analysis

INTRODUCTION

The synthesis of polymeric materials by modification method for obtained to the desired properties in polymers is an important topic in polymer chemistry and technology. Modification reactions of polymers can be accomplished by use of a number of different reagents, like epichlorohydrin, organic anhydrides in the various reaction conditions or by the characteristic reactions, such as alkylation, halogenation, nitration, and sulfonation.^{1–5} The reactions of maleic anhydride (MA) with commercial polymers were investigated extensively such as polyethylene,⁶ polypropylene,⁷ polystyrene (PS)^{8–10} in the presence of catalysts. On the other hand, PS have limited some properties such as thermal stability, mechanical strength, adhesion capability, corrosion resistance, and photosensitive, without additional functional groups. For this reason, the desired physical and mechanical properties of PS can be obtained by anchoring some functional groups.^{11–14} Thus, the undesired properties of PS can improve using different reagents by modification reactions.

In this study, side-chain functionalization of PS carries out with MA in the presence of cationic catalyst of Lewis acid type ($\text{BF}_3 \cdot \text{OEt}_2$) and then condensation of modified PS with phenyl hydrazine was

performed to improve the some thermal and physical properties of PS. The solid state decomposition kinetics of both of them was also investigated by nonisothermal thermogravimetry.

EXPERIMENTAL

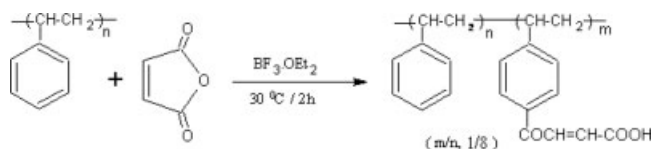
Materials

PS was dissolved in benzene, followed by precipitation in methanol, and was used after drying under vacuum at 50°C. The side-chain modification of PS with MA in the presence of Lewis acid ($\text{BF}_3 \cdot \text{OEt}_2$) was prepared according to published procedures (Scheme 1).¹⁵ MA used was purified by recrystallization from benzene followed by sublimation in vacuum: mp 52.8°C. $\text{BF}_3 \cdot \text{OEt}_2$ was distilled under nitrogen atmosphere. A commercial PS ($M_n = 2.5 \times 10^5$) sample supplied by Petkim Petrochemical A.Ş. Aliğa Complex (Turkey) was used in experimental. Phenyl hydrazine ($\text{NH}_2\text{NHC}_6\text{H}_5$), chloroform, benzene, toluene, dichloromethane, methanol, ethanol, hexane, hydrochloric acid (HCl, 37%), and sodium hydroxide were supplied by Merck Chemical (Germany) and used as received.

Chemical modification of polystyrene with maleic anhydride¹⁵

PS (5.2 g, 0.05 mol) was dissolved in 40 mL of chloroform by stirring in a three-necked flask at 30°C,

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Scheme 1 Synthesis of modified product of PS.

then MA (0.98, 0.01 mol) was added. Catalyst $\text{BF}_3 \cdot \text{OEt}_2$ (1.26 mL, 0.01 mol) was added drop by drop to the mixture for 30 min and the mixture was stirred for 2 h (Scheme 1). After completion of reaction, the product was precipitated with methanol, filtered, and dried under vacuum at 50°C for 5 h. ($-\text{COOH}\%$, 12.5%; acid number (AN):67.32 mg KOH/g)

Calculated: C, 88.04%; H, 8.57%; Found: C, 86.91%; H, 7.09%. FTIR (KBr) ν (cm^{-1}): 3500–3200 (s, O–H), 3150–3100 (m, C–H, aryl), 2900 (s, C–H, aliphatic), 1725 (s, C=O), 1625 (s, C=C, aliphatic), 1575–1555 (s, C=C, aryl), 1100 (C–O). $^1\text{H-NMR}$ (CDCl_3 , δ): 1.6 (2H, CH_2), 2.1 (1H, CH), 3.9 (2H, $-\text{CH}=\text{CH}-$), 6.8 (4H, Ar–H), 7.4 (5H, Ar–H).

Condensation reaction of modified polystyrene

5.2 g (0.05 mol) of modified PS was dissolved in 10 mL of phenyl hydrazine by stirring in a three-necked flask at room temperature and the flask was fitted with a condenser, thermometer, and dyne-stark tube. The reaction mixture was stirred at 140°C for 12 h (Scheme 2). The reaction product was precipitated with methanol and washed with 25 mL of 0.01N HCl, filtered, and dried under vacuum at 53°C for 24 h.

Calculated: C, 87.07%; H, 7.05%; N, 2.74%; Found: C, 89.03%; H, 7.0%; N, 1.7%. FTIR (KBr) ν (cm^{-1}): 3550 (m, O–H), 3336 (s, N–H), 3160–3100 (m, C–H, aryl), 2920 (s, C–H, aliphatic), 1730 (m, C=O), 1650 (s, N=C), 1628 (s, C=C, aliphatic), 1497 (s, C=C, aryl), 1319–1260 (s, C–O). $^1\text{H-NMR}$ (CDCl_3 , δ): 1.6 (2H, CH_2), 1.8 (1H, CH), 3.8 (2H,

$-\text{CH}=\text{CH}-$), 4.9 (1H, NH), 6.8 (4H, Ar–H), 7.2 (5H, Ar–H).

Characterization techniques

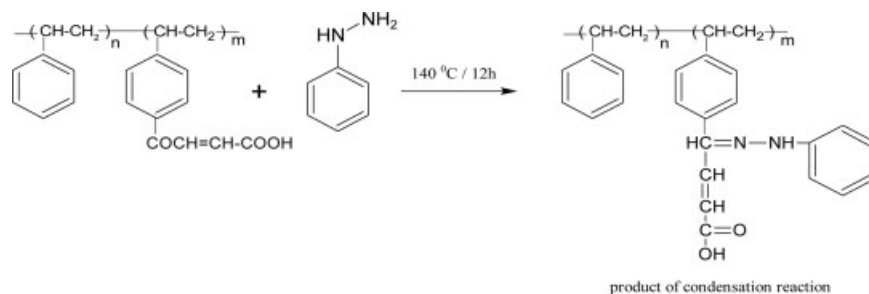
The C, H, and N analyses were performed with a Carlo Erba microanalyser (Italy). IR spectra were recorded on a Pye Unicam SP-3 100 FTIR spectrophotometer using KBr disks ($4000\text{--}400\text{ cm}^{-1}$). Polymers were characterized by using $^1\text{H-NMR}$ spectra (Bruker DPX FT-NMR spectrometer operating at 90 MHz), and they were recorded at 25°C by using CDCl_3 as a solvent. The tetramethylsilane was used as an internal standard. The amounts of the functional groups in the PS were determined by volumetric titration method. Thermal data were obtained by using STA 409C NETZSCH-Geratebau GmbH Thermal Analysis equipment. The TGA-DTA measurements were taken between 20 and 700°C in air atmosphere at a rate of $10^\circ\text{C}/\text{min}$.

Determination of adhesion capability and corrosion resistance

Percentage of coating failure

For the determination of the adhesion capability of the polyfunctional PS to metal (steel of moderate carbon content with dimensions $70 \times 100 \times 1\text{ mm}$), a solution of each polymer was prepared in 10% toluene and deposited as a layer ($120\text{--}140\text{ }\mu\text{m}$) over the metal. This material was first dried in open air and then in an oven at 50°C . The percentage of adhesion capability was determined by the 'lattice notch' method.¹⁶

According to the 'lattice notch' method, a thin polymer layer ($120\text{--}140\text{ }\mu\text{m}$) is formed on the metal surface and the polymer layer is divided into small squares ($2 \times 2\text{ mm}$) by a razor blade. Insulating tape ($10\text{--}100\text{ mm}$) is stuck over these squares and the tape is suddenly pulled. In this process, a portion of small squares is separated from the surface of the metal and another portion remains on the surface. Therefore, the % adhesion is calculated from the



Scheme 2 Synthesis of cP of modified PS.

TABLE I
Algebraic Expression for the Most Frequently Used Mechanisms of Solid State Process

No	Mechanisms	Symbol	Differential form, $f(\alpha)$	Integral form, $g(\alpha)$
1	N and G ($n = 1$)	A_1	$(1 - \alpha)$	$[-\ln(1 - \alpha)]$
2	N and G ($n = 1.5$)	$A_{1.5}$	$(3/2)(1 - \alpha)[- \ln(1 - \alpha)]^{1/3}$	$[-\ln(1 - \alpha)]^{2/3}$
3	N and G ($n = 2$)	A_2	$2(1 - \alpha)[- \ln(1 - \alpha)]^{1/2}$	$[-\ln(1 - \alpha)]^{1/2}$
4	N and G ($n = 3$)	A_3	$3(1 - \alpha)[- \ln(1 - \alpha)]^{2/3}$	$[-\ln(1 - \alpha)]^{1/3}$
5	N and G ($n = 4$)	A_4	$4(1 - \alpha)[- \ln(1 - \alpha)]^{3/4}$	$[-\ln(1 - \alpha)]^{1/4}$
6	Diffusion, 1D	D_1	$1/(2\alpha)$	α^2
7	Diffusion, 2D	D_2	$1/(\ln(1 - \alpha))$	$(1 - \alpha)\ln(1 - \alpha) + \alpha$
8	Diffusion, 3D (cylindrical symmetry)	D_3	$1.5/[(1 - \alpha)^{-1/3} - 1]$	$(1 - 2\alpha/3) - (1 - \alpha)^{2/3}$
9	Diffusion, 3Dsphere symmetry)	D_4	$[1.5(1 - \alpha)^{2/3}][1 - (1 - \alpha)^{1/3}]^{-1}$	$[1 - (1 - \alpha)^{1/3}]^2$
10	Diffusion, 3D (Anti-Jander equation)	D_5	$(3/2)(1 + \alpha)^{2/3} [(1 + \alpha)^{1/3} - 1]^{-1}$	$[(1 + \alpha)^{1/3} - 1]^2$
11	Diffusion, 3D (Zhuralev, Lesokin and Tempelmen equation)	D_6	$(3/2)(1 - \alpha)^{4/3} [1/(1 - \alpha)^{1/3} - 1]^{-1}$	$[[1/(1 - \alpha)^{1/3} - 1]^2$
12	Contracted geometry shape (contracting linear)	R_1	$2(1 - \alpha)^{1/2}$	$1 - (1 - \alpha)^{1/2}$
13	Contracted geometry shape (cylindrical symmetry)	R_2	$3(1 - \alpha)^{2/3}$	$1 - (1 - \alpha)^{1/3}$
14	Contracted geometry shape (sphere symmetry)	R_3	$3(1 - \alpha)^{2/3}$	$1 - (1 - \alpha)^{1/3}$
15		P_1	1	A
16		P_2	$2\alpha^{1/2}$	$\alpha^{1/2}$
17		P_3	$(1.5)\alpha^{2/3}$	$\alpha^{1/3}$
18		P_4	$4\alpha^{3/4}$	$\alpha^{1/4}$
19	Chemical reaction ($n = 2$)	C_2	$(1 - \alpha)^2$	$(1 - \alpha)^{-1} - 1$
20	Chemical reaction ($n = 1$ or $n = 1.5$)	$C_{1/1.5}$	$2(1 - \alpha)^{3/2}$	$(1 - \alpha)^{-1/2}$
21	Random nucleation with two nucleus on the individual	F_2	$(1 - \alpha)^2$	$1/[(1 - \alpha)]$
22	Random nucleation with two nucleus on the individual	F_3	$1/[2(1 - \alpha)]^3$	$1/[(1 - \alpha)^2]$

N, nucleation; G, growth; 1D, one dimensional diffusion; 2D, two dimensional diffusion; 3D, three dimensional diffusion.

number of small squares still remaining on the metal surface.

Corrosion resistance

Thin polymer films (120–140 μm) were formed over metal (plates of steel of moderate carbon content with dimensions $70 \times 150 \times 1$ mm) from the prepared polymer solution and were subjected to 10% NaOH, 10% HCl, 3% NaCl, pure water, and open air for 7 days. Then the plates (metals covered with polymer) were removed from these environments and the amount of decomposition observed by the naked eye was taken as a measure of the corrosion resistance.

Percentage of absorbed water

In addition, the percentage of water absorption was determined by exposing samples of the polymer to water at 20°C for 24 h and then removing the sample from the water and weighing the polymer. The sample was then dried over a desiccant in vacuum at 50°C and weighed. The difference between wet and dry weights gives in percentage of absorbed water.

Kinetic models

In thermogravimetric measurements, the conversion is typically calculated as:

$$\alpha = \frac{W_0 - W_t}{W_0 - W_\infty} \quad (1)$$

where W_0 , W_t , W_∞ are the initial, the actual and final weights of samples, respectively. Reaction rate is defined as the derivative of conversion according to time. The rate of conversion, $d\alpha/dt$ is a linear func-

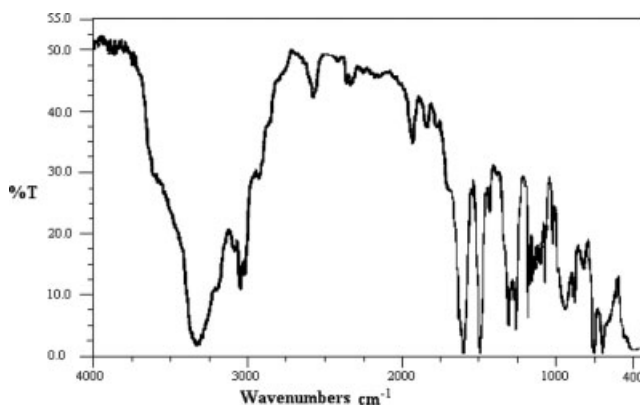


Figure 1 The FTIR spectrum of cP.

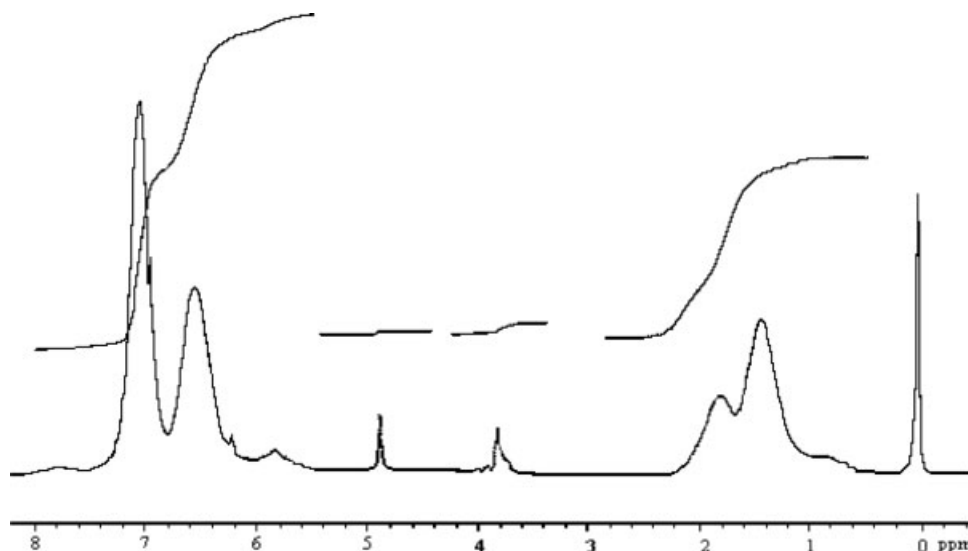


Figure 2 The ^1H -NMR spectrum of cP.

tion of a temperature-dependent rate constant, k , and a temperature-independent function of conversion, α , that is:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (2)$$

where $f(\alpha)$ depends on the mechanism of the decomposition reaction. $k(T)$, the temperature dependence of the rate of weight loss, is often modeled successfully by the Arrhenius expression.

$$k(T) = Ae^{\frac{-E}{RT}} \quad (3)$$

where E , A , R , and T are the activation energy (kJ mol^{-1}), pre-exponential factor (min^{-1}), gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and absolute temperature (K), respectively. The simplest and most frequently used model for $f(\alpha)$ in the analysis of TGA data is:

$$f(\alpha) = (1 - \alpha)^n \quad (4)$$

where n represent the order of reaction, and then eq. (2) can be expressed as:

$$\frac{d\alpha}{dt} = Ae^{\frac{-E}{RT}}(1 - \alpha)^n \quad (5)$$

The rate of conversion, $d\alpha/dt$, for TGA experiment at constant rate of temperature change, $\beta = dT/dt$,

may be expressed by

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = Ae^{\frac{-E}{RT}}(1 - \alpha)^n \quad (6)$$

The integrated form of eq. (6), introducing the initial condition of $\alpha = 0$ at $T = T_0$ is:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^\alpha \frac{d\alpha}{(1 - \alpha)^n} = \frac{A}{\beta} \int_{T_0}^T e^{\frac{-E}{RT}} dT \quad (7)$$

where $g(\alpha)$, β are the integral function of conversion and heating rate, respectively.

Several techniques using different approaches have been developed for solving the integral of eq. (7) and the differential of eq. (2). Also, the different expressions for $g(\alpha)$ and $f(\alpha)$ derived.¹⁷⁻²² These functions given Table I and were satisfactorily used for the estimation of the reaction solid state mechanisms from nonisothermal TGA experiments.

Coats and Redfern method²³

Using an asymptotic approximation for resolution of eq. (7), the following equation can be obtained:

$$\ln \frac{g(\alpha)}{T^2} = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (8)$$

TABLE II
Some Physical Parameters of Polymers

Compound	ρ (g cm^{-3})	$[\eta]$ (dL g^{-1})	Titration method δ (cal. cm^{-3}) ^{1/2}	Swelling method δ (cal. cm^{-3}) ^{1/2}
Polystyrene	1.04	—	—	—
Modified polystyrene	1.10	1.024	9.33	9.71
Condensation product	1.21	0.7036	9.33	9.72

TABLE III
The Adhesion Capability and Corrosion Resistance of Polymers

Functional group	Adhesion capability (%)	Corrosion resistance					Water absorption (%)
		3% NaCl	10% NaOH	10% HCl	Pure water	Air	
–COOH	92	++	+	++	+	++	0.35
–C=N–, –COOH	60	++	+	±	++	++	0.72

±, little resistance; +, medium resistance; ++, high resistance.

The authors supposed that $\ln(1 - \frac{2RT}{E}) \rightarrow 0$ for the Doyle approximation,²⁴ obtaining in natural logarithmic form:

$$\ln \frac{g(\alpha)}{T^2} \cong \ln \left[\frac{AR}{\beta E} \right] - \frac{E}{RT} \quad (9)$$

The expression of $g(\alpha)$ for different mechanisms have been listed in Table I and activation energy for each decomposition mechanisms can be obtained from the slope of a plot of $\ln[g(\alpha)/T^2]$ versus $1000/T$.

MacCallum and Tanner method²⁵

MacCallum and Tanner method provides an approximation integrated from the rate of degradation as a function of temperature. The rate of degradation can be thus expressed by:

$$\log g(\alpha) = \log \frac{AE}{\beta R} - 0.4828E^{0.4351} - \left(\frac{0.449 + 0.217E}{10^{-3}T} \right) \quad (10)$$

A plot of $\log g(\alpha)$ versus $1/T$ can give E from the slope, and A from the intersection of the Y-axis.

Madhusudanan–Krishnan–Ninan method²⁶

MKN method is similar to Coats–Redfern and MacCallum–Tanner method.

$$\ln \left[\frac{g(\alpha)}{T^{1.8843}} \right] = \ln \left(\frac{AE}{\beta R} \right) + 3.6012 - 1.8843 \ln E - 0.12051 \left(\frac{E}{T} \right) \quad (\text{by series solution}) \quad (11)$$

$$\ln \left[\frac{g(\alpha)}{T^{1.9206}} \right] = \ln \left(\frac{AE}{\beta R} \right) + 3.7678 - 1.9206 \ln E - 0.12040 \left(\frac{E}{T} \right) \quad (\text{by approximation}) \quad (12)$$

A plot of $\ln[g(\alpha)/T^{1.8843}]$ versus θ will give straight line and activation energy, E and pre-exponential factor; A can be calculated from here. Also, this situation can be applied to eq. (12).

RESULTS AND DISCUSSION

Modified products of PS were characterized by various instrumental methods. The FTIR spectrum of cP is shown in Figure 1 if a comparison is made among the FTIR spectrum of mPS with that of PS, we will see that the spectra of mPS have given bands 3500 cm^{-1} (O–H), 1725 cm^{-1} (C=O), 1625 cm^{-1} (C=C), 1100 cm^{-1} (C–O), which are in good agreement with the FTIR spectrum given by Kurbanova et al.¹⁵ The FTIR spectrum of cP exhibits FTIR bands 3336 and 1650 cm^{-1} because of NH and C=N groups, respectively, in addition to characteristic bands of mPS.

The $^1\text{H-NMR}$ spectrum of cP is shown in Figure 2. $^1\text{H-NMR}$ spectrum of (mPS) shows signals at 7.4 ppm for *meta* and *para* protons, and signal at 6.8 ppm for *ortho* protons in aromatic ring, at 3.9 ppm for methine protons of anhydride group, at 1.6–1.9 ppm for protons methine and methylene protons in polymer chain. In addition to this signals, $^1\text{H-NMR}$ spectrum of cP showed signal at 4.9 ppm for proton of NH group. However, it can not be showed any signal for hydroxyl of anhydride group because of dimerisation. On the other hand the volumetric analysis, elemental analysis and degradation studies were showed that the modified mPS and cP have hydroxyl groups.

Condensation reaction of mPS with phenyl hydrazine was carried out at 140°C being elimination temperature of carboxyl group in polymer and the existence of carboxyl in this temperature was determined by the decomposition of polymer using a programmed furnace, liquid nitrogen, and IR equip-

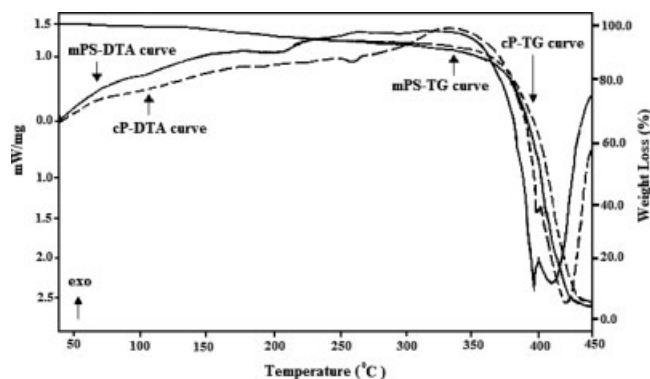


Figure 3 TGA–DTA curves of polymers.

TABLE IV
TGA and DTA Data of Polymers

Polymers	First stage decomposition			Second stage decomposition				Residue after 500°C
	T_{pk} (°C)	T_{st} (°C)	Weight loss (%)	T_{pk} (°C)	Heat flow	T_{st} (°C)	Weight loss (%)	
mPS	194 (Endo)	120	11.87	397, 413	Endo	293	84.03	4.1
cP	260 (Endo)	140	10.9	399, 425	Endo	335	81.86	7.24

T_{pk} , peak temperature (DTA curves), T_{st} , initial decomposition temperature (TGA curves).

ment. FTIR spectrum of condensed decomposition products shows at 2365 cm^{-1} a strong band of CO_2 .

Physical and mechanical parameters

Some physical and mechanical parameters like corrosion resistance, adhesion capability, water absorption (%), densities (ρ), solubility parameters (δ) (according to swelling¹² and titration²⁷ method) of polymers at 20°C and limit viscosity numbers $[\eta]$ of polymers at 25°C were determined in this study. The density of polymers was found by applying floating method.²⁸ The limit viscosity numbers of mPS and cP were determined in toluene, and also the solubility parameter of each product was determined by using both titration method and swelling method. The percentage of adhesion capability was determined by "lattice notch" method.¹⁶ Thin polymer films were formed for corrosion resistance of polymers over metal which contained carbon and were subjected to 10% NaOH, 10% HCl, and 3% NaCl, and open air for seven days. In addition, the percentage of water absorption was determined by exposing samples of the polymer to water at 20°C for 24 h. These values are shown in Tables II and III.

As expected, the density of cP is higher than that of mPS. Viscosity-average molecular weight of mPS and cP, M_v , was separately calculated from Mark-Houwink equation using an Ubbelohde viscosimeter and found to be 196,000 and 125,000 g mol^{-1} , respectively.

At the same time, the number of carboxyl groups ($-\text{COOH}$, %) and acid number (AN) in the mPS obtained via the chemical modification with MA of PS in the presence of the cationic catalyst was found to be 12, 5%, 67.32 mg KOH/g, respectively. That is to say, the ratio of the contents of unmaleated PS (n) and maleated PS (m) units (m/n) was found to be 8:1 (Scheme 1). This analysis was carried out using titration method.

Thermal analysis

The TGA of functional PSs were performed under an air atmosphere in a temperature range 20–450°C to the thermal stability and kinetic parameters.

Figure 3 shows the TGA–DTA curves for polymers and the relevant data given in Table IV. According to the TGA curves, polymers degrade in two stages. In the first stages which have long decomposition period, the observed weight losses, 11.87% for mPS and 10.9% for cP, probably were related to the decarboxylation reaction of unsaturated acyl groups. Also, the weight losses in the second stages because of the decomposition of polymer backbone and vinyl keton groups were formed with the elimination of unsaturated acyl groups in the side chain. According to the DTA curves of mPS and cP, endothermic peaks observed in 397, 413°C and 399, 425°C, respectively at the second stage decomposition.

TABLE V
Kinetic Parameters and Correlation Coefficient (r) Calculated Using Coats–Redfernd (CR), MacCallum–Tanner (MT), and Madhusudanan–Krishnan–Ninan (MKN) for the First and Second Stage of Modified Polystyrene (mPS)

Model	E_a (kJ/mol)	Log A	r	Method
First stage decomposition				
C_2	52.9	6.41	0.99879	CR
D_6	75.1	8.15	0.98412	
F_3	73.4	10.01	0.95587	
C_2	53.2	5.23	0.99884	MKN (by series solution)
D_6	75.3	6.59	0.98437	
F_3	73.6	8.48	0.95624	
C_2	53.13	5.14	0.99879	MKN
D_6	75.30	6.48	0.98427	(by approximation)
F_3	73.60	8.37	0.95613	
C_2	66.2	10.84	0.99899	MT
D_6	87.5	12.30	0.98762	
A_1	40.6	7.40	0.96752	
Second stage decomposition				
A_1	138.70	10.58	0.99774	CR
$A_{1,5}$	88.88	6.44	0.99759	
A_2	63.98	4.32	0.99734	
A_1	139.05	8.51	0.99779	MKN
$A_{1,5}$	89.34	4.86	0.99764	(by series solution)
A_2	64.48	4.36	0.99744	
A_1	138.99	8.39	0.99779	MKN
$A_{1,5}$	89.22	4.78	0.99759	(by approximation)
A_2	64.34	4.36	0.99739	
A_1	152.17	14.57	0.99809	MT
A_2	80.22	8.92	0.99808	
A_4	44.25	6.22	0.99808	

TABLE VI
Kinetic Parameters and Correlation Coefficient (r)
Calculated Using Coats–Redfern (CR),
MacCallum–Tanner (MT), and Madhusudanan–
Krishnan–Ninan (MKN) for the First and Second Stage
of Condensation Product (cP)

Model	E_a (kJ mol ⁻¹)	Log A	r	Method
First stage decomposition				
D_4	106.28	11.58	0.99040	CR
A_1	60.40	6.92	0.98974	
R_3	49.61	4.95	0.98888	
D_4	106.48	9.72	0.99050	MKN
A_1	60.69	5.58	0.98984	(by series solution)
R_3	49.93	4.52	0.98904	
D_4	106.46	9.61	0.99045	MKN
A_1	60.625	5.48	0.98979	(by approximation)
R_3	49.84	4.51	0.98898	
D_4	122.68	15.43	0.99167	MT
A_1	76.52	11.22	0.99166	
R_3	65.66	9.40	0.99166	
Second stage decomposition				
A_1	230.67	17.78	0.99844	CR
$A_{1,5}$	150.13	11.31	0.99839	
A_2	109.86	8.04	0.99829	
A_1	230.86	15.27	0.99844	MKN
$A_{1,5}$	150.47	9.17	0.99839	(by series solution)
A_2	110.28	6.17	0.99829	
A_1	230.88	15.15	0.99844	MKN
$A_{1,5}$	150.41	9.06	0.99839	(by approximation)
A_2	110.19	6.06	0.99829	
A_1	240.92	21.36	0.99860	MT
$A_{1,5}$	163.37	15.25	0.99859	
A_2	124.60	12.22	0.99859	

The kinetic parameters were determined by Coats and Redfern (CR), Madhusudanan–Krishnan–Ninan (MKN), and MacCallum–Tanner method (MT). The algebraic expression of integral $g(\alpha)$ functions for the most common mechanism operating in solid-state decompositions tested in the present work are listed in Table I. The kinetic parameters were calculated from the linear plots of the left-hand side of kinetic eqs. (9)–(12) against $1/T$ for earlier methods. The E and A values were calculated, respectively, from the slope and intercept of the straight lines. Values of the kinetic parameters and linear regression coefficients obtained for each decomposition stage are listed in Tables V and VI. The three kinetic functions which have higher linear regression coefficient are given in Tables. One should note that there is a good agreement between the results obtained for the mechanisms and activation energy of the first step and second step of polymers in Coats–Redfern and Madhusudanan–Krishnan–Ninan methods.

CONCLUSION

Side-chain functionalization of PS with MA in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ as catalyst and the condensation of this product with phenyl hydrazine were performed to improve the some thermal and physical properties of PS. Viscosity molecular weights, the glass transition temperatures of mPS and cP found be 196,000, 125,000 g mol⁻¹; 165°C and 253°C, respectively. Analysis of the experimental results suggested that the actual decomposition mechanisms of mPS and cP were C_2 , A_n , and D_n type.

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