# Styrene–Maleic Anhydride Copolymers: Synthesis, Characterization, and Thermal Properties

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## SYNOPSIS

Radical copolymerization of styrene and maleic anhydride have been carried out in $N,N$-dimethylformamide at 60°C using 2,2'-azobisisobutyronitrile as initiator. The copolymer compositions were determined using an aqueous conductometric direct titration method. Monomer reactivity ratios were calculated by Fineman–Ross, Kelen–Tudos, and conversion-based Kelen–Tudos methods. Gel permeation chromatography was used to determine molecular weights and polydispersity indexes. The thermal degradation and energy of activation of the degradation process were determined by several thermogravimetric analysis and differential scanning calorimetric models. The thermal degradation of the copolymer is a two-stage process, the major degradation being the second stage. The copolymer degrades at a lower temperature than polystyrene. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

The interest shown in the study of free radical copolymerization of styrene (St) with symmetrically 1,2-disubstituted ethylene having electron withdrawing groups such as maleic anhydride (MAn) arises from both academic and industrial demands.[1–5] Because the classical schemes of Mayo–Lewis and Alfrey–Goldfinger are inadequate to explain the copolymerization behavior for truly alternating St–MAn systems, other methods (e.g., the penultimate group effect model[6,7] and the charge–transfer complex formation model[8,9]) have been derived to explain the kinetic anomalies of alternating behavior. Studies[10,11] reveal that the alternating tendency in copolymerization can be explained by assuming the participation of 1 : 1 charge–transfer complex of St and MAn in the propagation step. Though the charge–transfer complex model provides[2] a better understanding for the polymerization kinetics than the penultimate group model, neither model could be distinguished by using composition data alone.[3,12,13] Until now, no reliable values of the reactivity ratios for St–MAn system existed in the literature, and limited attempts[5,14,15] have been made to describe the effect of complex formation on the classical reactivity ratios.

Dodgson and Ebdon[1] have interpreted the copolymer composition by using both the penultimate and complex models, in which it was assumed that no homopolymerization of MAn occurred. However, they preferred penultimate group model to describe the copolymer composition and showed that complex participation plays a very small part in leading to alternating behavior in the system. Brown and Fujimori,[4] by using the nonlinear least square (NLLS) optimization method, have shown that although their data and the data of Dodgson and Ebdon are comparable, yet the penultimate model is inadequate to describe the kinetics of the system. Barb[7] considered that the terminal model was inadequate and proposed the penultimate group effect model for styrene-ended radicals to explain the composition data from copolymerization. In a strong solvent, chain transfer to solvent can occur easily[16] and copolymerization involves propagation in part via 1 : 1 St–MAn donor acceptor complex. Deb and Meyerhoff also presented the kinetics of St–MAn copolymerization in terms of the charge–transfer complex model and the participation of the complex in the propagation step.[17,18]

Thermogravimetric studies of polystyrene (PSt) and its copolymers with MAn have been discussed by several investigators.[19,20] In a styrene-containing co-

polymer, ionic groups are more effective in raising the glass transition temperature ($T_g$) than for hydrogen bonding interactions.[21]

It is evident that the copolymerization kinetics of the St–MAn system in different types of solvents are not clear and the reports on the high conversion copolymerization range are scanty.[22,23] The objective of the present work is to study the copolymerization of St and MAn initiated by 2,2′-azobisisobutyronitrile (AIBN) in an amphoteric solvent such as $N,N$-dimethylformamide (DMF). This paper reports the use of various methods to determine reactivity ratios of the styrene–maleic anhydride system. The degradation kinetics of the copolymer were also investigated with several thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) models applicable to dynamic data.

## EXPERIMENTAL

Maleic anhydride was recrystallized twice from methanol and dried under vacuum. Inhibitor-free styrene was distilled under vacuum and the middle fraction was collected. AIBN was recrystallized from methanol and dried in a desiccator. DMF and tetrahydrofuran (THF) were purified by the standard methods.

The copolymerizations were followed dilatometrically and gravimetrically in high-vacuum sealed ampoules. For gravimetric work, the requisite amounts of monomer, initiator, and solvent were charged in ampoules and the ampoules were flushed with oxygen-free nitrogen for 1 h. The ampoules were then tightly sealed with a high-vacuum stopper and polymerized at 60°C for a definite period of time. After the desired time period the copolymers were isolated by precipitation with methanol containing traces of hydroquinone. The copolymers were then filtered and dried under vacuum. Conversion and rates of polymerization were calculated from the weight of the dried copolymer. The dilatometric measurement showed no induction period and the rates as obtained dilatometrically and gravimetrically were in good agreement.

For the calculation of reactivity ratios, the copolymer composition was determined by estimating the anhydride content conductometrically[24] with a Toshniwal digital conductivity meter.

Gel permeation chromatography (GPC) was performed using a Waters model 510 solvent delivery system at a flow rate of 1.0 mL min$^{-1}$ through a set of four ultrastyragel columns (Waters) of exclusion sizes $10^6$, $10^5$, $10^4$, and 500 Å. The analysis was performed at room temperature using purified high-performance liquid chromatography (HPLC) grade THF as eluent. A Waters differential refractometer model R401 was used as detector. Sample concentration was 0.2% w/v, and the volume of polymer injected was 50 $\mu$L. The GPC curves were analyzed with the calibration curve obtained by 9 narrow-MWD polystyrene (Waters) samples.

Differential scanning calorimetry (DSC) was performed on a Perkin Elmer PC series DSC 7 with 3–5 mg of polymer samples weighed in aluminium pans at a heating rate of 10°C min$^{-1}$. All experiments were carried out in a nitrogen atmosphere and the measurement was started as soon as the heat flow in the DSC cell had stabilized.

Thermogravimetry (TG) and differential thermogravimetry (DTG) were performed using a Shimadzu Thermal Analyzer 30 at a heating rate of 10°C min$^{-1}$ using 5 ± 1 mg of powdered samples in the temperature range from 30°C to 500°C.

## RESULTS AND DISCUSSION

In order to study the composition of the copolymer and the percent of conversion, copolymerization of St and MAn was done with AIBN as initiator at 60°C in DMF. Table I shows the composition of the monomer feed and of the copolymer formed. There is a gradual increase in MAn content in the copolymer with an increase in the molar concentration of MAn in the feed. It was found that copolymer composition remained approximately unimolar up to a 4 : 1 feed ratio of [St] : [MAn]. However, it was reported[25] that when a very high concentration of styrene was used (22 : 1 molar ratio of [St] : [MAn]), the copolymer composition became 2 : 1 and a mixture of homopolymers of styrene and St–MAn copolymers was obtained. Molecular weight and molecular weight distribution of the copolymers are also presented in Table I, and the GPC chromatogram of a typical ST–MAn copolymer is shown in Figure 1. It was observed that number average molecular weight ($\bar{M}_n$) is higher for the copolymer with higher MAn mole fraction in the feed. The values indicate that all of the polymers are polydisperse in nature but no particular trend was observed in polydispersity indexes of copolymers. The higher polydispersity index value may indicate that, in the termination of the copolymer chain, disproportionation is the predominant rather than addition mechanism.

To determine the copolymerization behavior, the reactivity ratios for the St–MAn system were cal-

**Table I  Copolymerization of Styrene (St) and Maleic Anhydride (MAn): Copolymer Composition and Molecular Weights**

| Feed Composition in Mol Fractions | | Conversion (%) | Copolymer Composition in Mol Fractions | | $\bar{M}_n$ | $\bar{M}_w$ | $\bar{M}_w/\bar{M}_n$ |
| St ($M_1$) | MAn ($M_2$) | | St ($m_1$) | MAn ($m_2$) | | | |
| --- | --- | --- | --- | --- | --- | --- | --- |
| 0.107 | 0.893 | 12.5 | 0.505 | 0.495 | 7,700 | 37,400 | 4.8 |
| 0.200 | 0.800 | 10.7 | 0.505 | 0.495 | 6,300 | 13,400 | 2.2 |
| 0.362 | 0.638 | 20.8 | 0.510 | 0.490 | 5,500 | 14,300 | 2.6 |
| 0.400 | 0.600 | 25.2 | 0.515 | 0.485 | 5,400 | 14,600 | 2.7 |
| 0.500 | 0.500 | 28.0 | 0.520 | 0.480 | 4,800 | 11,200 | 2.3 |
| 0.574 | 0.426 | 26.4 | 0.540 | 0.460 | 4,700 | 10,700 | 2.3 |
| 0.690 | 0.310 | 21.8 | 0.560 | 0.440 | 4,400 | 15,500 | 3.5 |
| 0.738 | 0.262 | 24.3 | 0.600 | 0.400 | 4,300 | 17,200 | 4.0 |

Temperature = $60 \pm 0.1°C$; [AIBN] = $8.12 \times 10^{-2}$ mol $L^{-1}$; solvent = DMF.

culated by using a number of well-known linear methods. Most widely used linear methods are derived by Fineman–Ross[26] and Kelen–Tudos,[27] but both methods disregard the error structure.[28]

Fineman and Ross[26] linearized the original Mayo–Lewis equation as:

$$G = r_1 F - r_2 \qquad (1)$$

where $G = x_0(1 - 1/y)$ and $F = x_0^2/Y$, with $x$ and $y$ representing the mol ratios of monomers in the feed and the mol ratios in the copolymer, respectively. The reactivity ratios $r_1$ and $r_2$ can be obtained from the plot of $G$ versus $F$ (Fig. 2). The ordinate intercept is $-r_2$ and the slope of the line is $r_1$.

The Fineman–Ross method is no longer considered proper except for a quick determination of
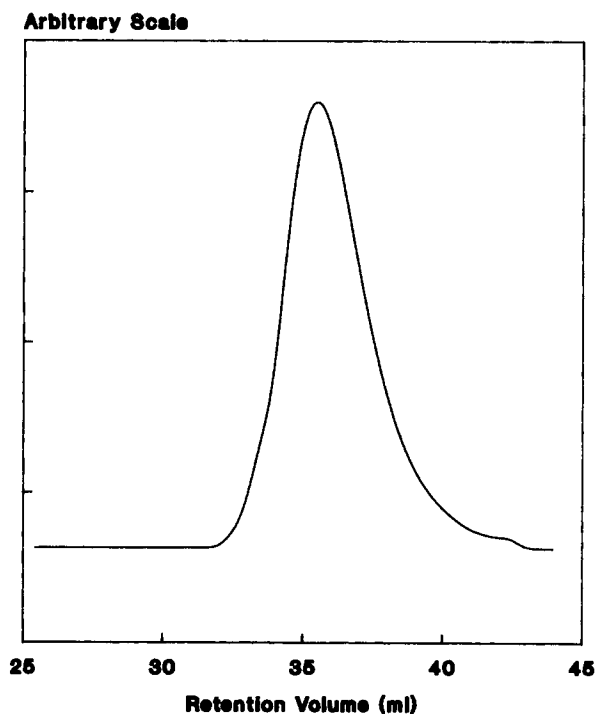
**Arbitrary Scale**



**Figure 1**  Gel permeation chromatogram of a typical St–MAn copolymer prepared with AIBN as initiator in DMF at 60°C.
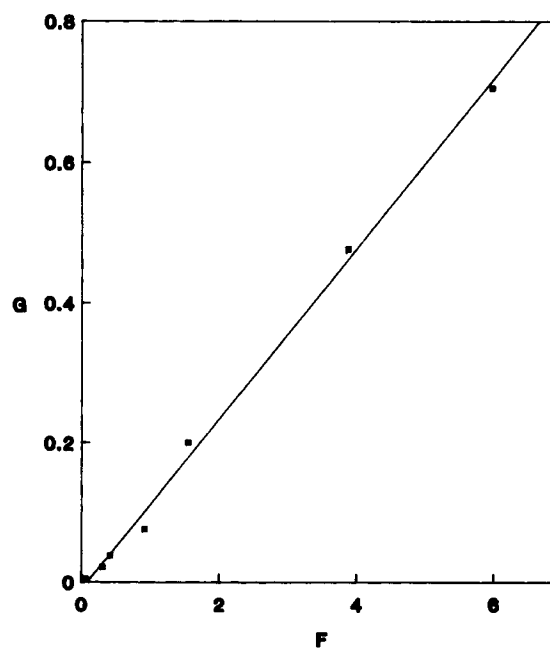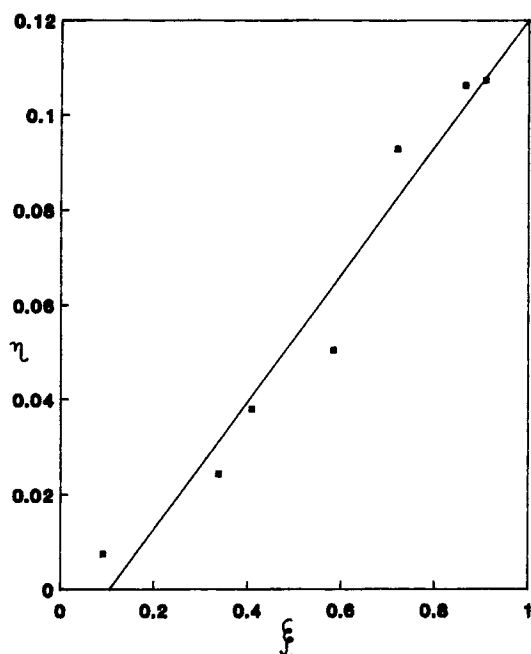


**Figure 2**  Fineman–Ross plot.

**Figure 3**   Kelen–Tudos plot.



**Figure 4**   Kelen–Tudos plot based on conversion data.

reactivity ratios of monomer pairs; therefore, the slope of the best visual fit of the Fineman–Ross plot is used to obtain the correct values of reactivity ratios.[29]

Kelen–Tudos also proposed[27] a simple graphical linear method for the determination of reactivity ratios; this equation can be expressed as:

$$\eta = \zeta(r_1 + [r_2/\alpha]) - r_2/\alpha \qquad (2)$$

where the transformed variables $\eta$ and $\zeta$ can be defined as $\eta = G/(\alpha + F)$ and $\zeta = F/(\alpha + F)$. $\alpha$ is a symmetrical parameter ($\alpha > 0$) which is defined as $(F_{min} * F_{max})^{0.5}$, where $F_{min}$ and $F_{max}$ are the lowest and highest values of $F$. From the Kelen–Tudos plot (Fig. 3) the values of $r_1$ and $r_2/\alpha$ were obtained from the intercepts at $\zeta = 1$ and $\zeta = 0$, respectively. The experimental data were also evaluated by the method of least squares.[27(a)] The values of $r_1$ and $r_2$ calculated by the least-square method are comparable with those obtained by the graphical method.

Both methods described above are applicable only for low conversion and azeotropic copolymerizations. Kelen and Tudos modified their equation of low conversion polymerization for high conversion data by redefining $F$ and $G$ as $F = (m_1/m_2)/(\log z_1/\log z_2)$ and $G = (m_1/m_2 - 1) \times (\log z_1/\log z_2)$ where $z_1 = M_{1F}/M_{10}$ and $z_2 = M_{2F}/M_{20}$. $M_{10}$, $M_{1F}$, $M_{20}$, and $M_{2F}$ represent the initial and final concentrations of monomer 1 and monomer 2, respectively. The modified method of Kelen–Tudos can be used with rel-
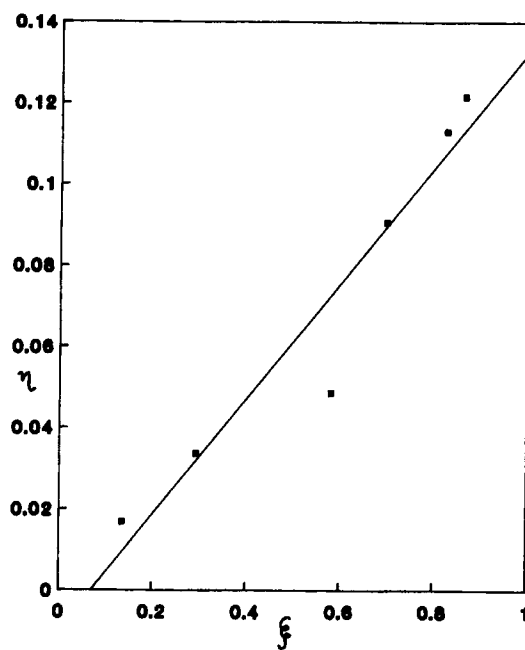
atively high conversion data. Figure 4 shows the Kelen–Tudos plot based on conversion data. The copolymerization reactivity ratios were also determined directly by a linear least-square method applicable to the high conversion equation. The reactivity ratios determined by the above methods are summarized in Table II.

The 95% confidence limits for the above estimates were calculated according to the standard procedure given by Kelen–Tudos. Considering the joint confidence limits, it is recommended[29] that an NLLS method or Kelen–Tudos procedure may be used to determine reliable reactivity ratio values.

**Table II   Reactivity Ratios of Styrene (St) and Maleic Anhydride (MAn) by Different Methods**

| Method | $r_{St}$ | $r_{MAn}$ |
|---|---|---|
| Fineman–Ross | $0.121 \pm 0.003$ | $0.009 \pm 0.001$ |
| Kelen–Tudos (graphical) | $0.120$ | $0.008$ |
| Kelen–Tudos (Least Square Method) | $0.124 \pm 0.014$ | $0.016 \pm 0.001$ |
| Conversion-based Kelen–Tudos (Graphical) | $0.124$ | $0.006$ |
| Conversion-based Kelen–Tudos (Least Square Method) | $0.132 \pm 0.008$ | $0.006 \pm 0.003$ |

For a system with the simple binary copolymerization method, Kelen–Tudos introduced a quantitative measure of the confidence, $\delta$, which is defined by the relative value of confidency intervals:

$$\delta = (\Delta r_1 \Delta r_2 / r_1 r_2) \qquad (3)$$

In a high conversion system, Kelen–Tudos defined a class I system as one that is strictly linear and has a $\delta$ value less than 1. A class I(i) system is linear and consistent with the two-parameter model but gives poorer parameter estimation because of the wide scattering of experimental points. A $\delta$ value of 0.024 was calculated for the St–MAn system by using the reactivity ratios determined by the Kelen–Tudos procedure. Figure 4 gives a correlation coefficient of 0.98, which indicates that St–MAn is a class I copolymer system as defined by Kelen–Tudos.[27]

TGA which measures the weight loss kinetics at elevated temperatures has been used to predict the stability of polymeric materials because it is very simple and accurate. The TGA traces of PSt and of St–MAn copolymer prepared with 1 : 1 molar feed ratio are represented in Figure 5. PSt showed the characteristic one-step nature of decomposition in the temperature range of 220–400°C. The copolymer undergoes a two-stage weight loss in the temperature range of 80–375°C, where the major portion decomposes in the second stage. The first-stage weight loss was approximately 5–10% at 80–175°C. Pure PSt has higher initial thermal stability than the copolymers, while increasing MAn content decreases the final decomposition temperature of the copolymer. Second-stage degradation of the copolymers occurs at 265–375°C. The temperature of maximum weight loss decreases with increasing MAn content and lies between 310–340°C, whereas the temperature of maximum weight loss for PSt is 360°C. TGA shows that the incorporation of MAn moiety into PSt decreases the thermal stability of PSt. As the compositions of the copolymers are practically invariable with varied monomer feed ratios, the variations of thermal stability of the copolymers are also not appreciable. PSt decomposes mainly by depropagation,[30] and the controlling factor in decomposition is the nature of side groups attached to the carbon atom at which the chain scission occurs. Thus the incorporation of anhydrous MAn might be responsible for the early degradation of the copolymer.[31]

It is assumed that in the majority of polymers that undergo isothermal decomposition, the rate of decomposition is proportional to the concentration of nondegraded materials. Kinetic param-
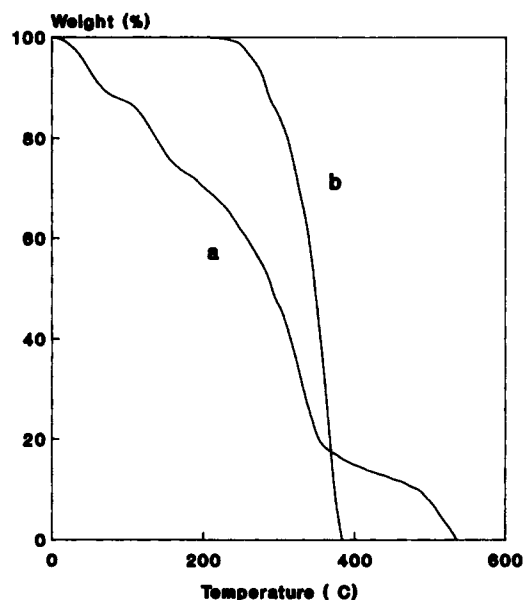


**Figure 5** Typical TGA thermograms of St–MAn copolymer (a) and PSt (b) at a heating rate of 10°C min⁻¹ in nitrogen.

eters for the St–MAn copolymerization system from weight loss curves of copolymer with 1 : 1 molar feed ratio were evaluated by three methods for two weight-loss regions. In this study a first-order reaction was assumed to be applicable for the system and all methods were evaluated assuming first-order kinetics.

A reaction rate is defined as the derivative of conversion with respect to time. In a TGA, conversion is defined[32] as the rate of final mass loss to total mass loss corresponding at a particular stage of degradation process, i.e.,

$$\beta = W/W_r \qquad (4)$$

where $W_r = W_\infty - W$; $W_\infty$ = mass loss at the end of the particular stage of reaction; and $W$ = mass loss up to time $t$.

The rate of conversion in a dynamic TGA experiment at a constant heating rate can be expressed as:

$$d\beta/dt = Q(d\beta/dT) = k(T)f(\beta) \qquad (5)$$

where $Q$ is the heating rate, $k(T)$ is the rate constant and $f(\beta)$ is the conversion functional relationship.

Arrhenius expression, which describes the temperature dependence of the rate constant, may be expressed as:
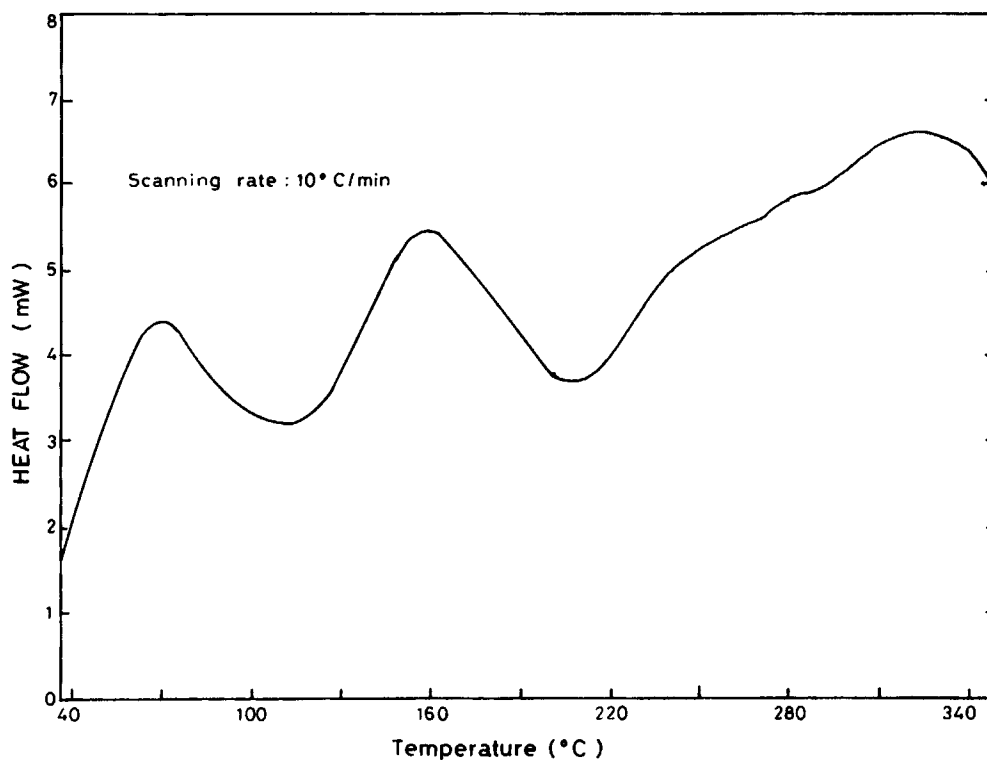
**Figure 6** DSC thermogram of a typical St–MAn copolymer at a heating rate of 10°C min⁻¹ in nitrogen.

$$k(T) = A \exp(-E/RT) \qquad (6)$$

where $A$ is the pre-exponential factor, $E$ is the activation energy, and $R$ is the Universal gas constant.

The integral form of the rate equation in a dynamic heating expression experiment may be expressed as:[32]

$$g(\beta) = (AE/QR)p(x) \qquad (7)$$

where $p(x) = \int_{\infty}^{x}(\exp(-x)/x^2)dx$ and $x = E/RT$.

$g(\beta)$ is the integral form of conversion dependence function.

Several methods using different approaches have been developed for solving the integral $p(x)$ equation. In the present investigation, three different nonisothermal methods are used for the computation of the kinetic parameters. All linear plots drawn by methods of least-square and corresponding correlation coefficients were also calculated. The equations employed are the differential method of Freeman and Carroll,[33] the integral method of Coats and

**Table III** Thermal Decomposition Temperatures, Activation Energies, and Correlation Coefficients of Polystyrene and Styrene–Maleic Anhydride (St–MAn) Copolymer by Various Methods

| Polymer | Stage of Decomposition | Temperature Range | Activation Energies, $E$ (kJ mol⁻¹) and Correlation Coefficients, $r$ | | | | | |
| | | | F and Cᵃ | | C and Rᵇ | | H and Mᶜ | |
| | | | $E$ | $r$ | $E$ | $r$ | $E$ | $r$ |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Polystyrene | Single | 220.0–400.0 | 140.6 | 0.98 | 148.6 | 0.98 | 158.2 | 0.96 |
| St–MAn Copolymer | Stage I | 80.0–175.0 | 115.2 | 0.97 | 117.9 | 0.98 | 120.6 | 0.94 |
| | Stage II | 265.0–375.0 | 147.8 | 0.98 | 156.6 | 0.98 | 172.8 | 0.98 |

ᵃ Freeman and Carroll method.
ᵇ Coats and Redfern method.
ᶜ Horowitz and Metzger method.

Redfern,[34] and the approximation method of Horowitz and Metzger.[35]

## Differential Method of Freeman and Carroll

The final equation derived from the modified treatment of the Freeman and Carroll method can be represented in the form:

$$\log[Q(dW/dT)/W_r]$$
$$= (-E/2.303RT) + \log A \quad (8)$$

$E$ and $A$ can be calculated from the slope and intercept, respectively. The activation energies for the two weight-loss degradation stages of St–MAn copolymer determined by this method were 115.2 and 147.8 kJ mol$^{-1}$ from the slopes of two linear lines. The decomposition of PSt occurred in a single stage with an activation energy of 140.6 kJ mol$^{-1}$.

The relationship by which the DSC data are fitted to Perkin-Elmer power compensated DSC software is based on the modified treatment of Freeman and Carroll. It is assumed that fraction-reacted $W$ as a function of temperature is directly proportional to the fractional area between the DSC peak and baseline. In the Perkin-Elmer DSC software, the kinetic parameters are determined by the multilinear regression method using partial area peak data of the corrected heat-flow effect. One major advantage of this software is the statistical treatment of the data which gives the confidence limits for all kinetic parameters.

The $T_g$ of polystyrene and styrene–maleic anhydride copolymer with 1 : 1 molar feed ratio were determined at a heating rate of 10°C min$^{-1}$ in the temperature range of 30–350°C. The $T_g$ of PSt is 101°C and for the copolymer is 63.9°C. Styrene–maleic anhydride copolymer with 1 : 1 molar feed ratio also shows two thermal transitions at 157.9°C and 322.4°C (Fig. 6). The activation energies of these two transitions were found to be 130.55 ± 1.91 kJ mol$^{-1}$ and 192.21 ± 4.11 kJ mol$^{-1}$, respectively. In both transitions, the orders of reaction were 1.14 ± 0.02 and 0.92 ± 0.02, respectively. This shows that the decomposition process is not too complex. Since the copolymer undergoes degradation on heating, the reverse run did not reproduce the heating curves. As shown in TGA thermogram, the weight loss at the third endotherm region accounts for about 80% of the degradation.

## Integral Method of Coats and Redfern

For a first-order reaction process, Coats and Redfern provided an approximation to the integral of Eq. (7) in the form:

$$\log[-(\log(1-\beta)/T^2]$$
$$= \log\frac{AR}{QE}(1-2RT/E) - E/2.303RT \quad (9)$$

Since $(1-2RT/E) \approx 1$, a plot of the left-hand side of Eq. (9) versus $1/T$ should result a straight line with a slope of $-E/2.303R$. The activation energies for two weight-loss degradation stages of the copolymer determined from the slopes of two linear portions of the graph by this method were 117.9 and 156.6 kJ mol$^{-1}$; that of PSt for its single-stage degradation was 148.6 kJ mol$^{-1}$.

## Approximation Method of Horowitz and Metzger

For a first-order process, Horowitz and Metzger derived the following relation by using a series of approximations. The final result may be expressed as:

$$\ln\ln[1/(1-\beta)] = E\theta/RT_m^2 \quad (10)$$

where $\theta = T - T_m$ and $T_m$ is the temperature at which maximum degradation rate is exhibited. Thus a plot of $\ln\ln[1/(1-\beta)]$ against $\theta$ should give a straight line with a slope of $E/RT_m^2$ and allows the activation energy to be determined from the slope. Activation energies of the copolymer determined by Horowitz and Metzger's method for two weight-loss degradation stages were 120.6 and 172.7 kJ mol$^{-1}$ from the slopes of two linear portions of the graph. For PSt the calculated value of activation energy by this method was 158.2 kJ mol$^{-1}$.

Table III shows the activation energy $E$ and the values of the correlation coefficient $r$ obtained by three different methods employed in this work. The activation energy of St–MAn copolymer for the first stage may be assumed to be between 115.0 and 125.0 kJ mol$^{-1}$, while that of the second stage is between 145.0 and 175.0 kJ mol$^{-1}$. From Table III it is apparent that highest correlation coefficient was obtained by using the Coats and Redfern method. This substantiates the observation of Zsako,[36] who suggested that the Coats–Redfern method is superior to other methods because it shows the best linearity of the data.

Director, RRL–Jorhat, for permission to publish these results.

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