Thermal degradation kinetics of poly \{N-[(4-bromo-3,5-difluorine)-phenyl]maleimide-co-styrene\} in nitrogen

Yanxun Li, Li Xu, Xinding Yao, Tingliang Luo, Guoji Liu*
College of Chemical and Energy Engineering, Zhengzhou University, Zhengzhou 450001, P.R. of china

*E-mail: guojiliu@zzu.edu.cn

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Abstract. The nonisothermal degradation kinetics of the copolymer poly\{N-[(4-bromo-3,5-difluorine)phenyl]maleimide-co-styrene\}, which was synthesized with N-[(4-bromo-3,5-difluorine)phenyl]maleimide and styrene, were studied by thermogravimetry/derivative thermogravimetry techniques. The kinetic parameters, including the activation energy and the pre-exponential factor of the copolymer degradation process, were calculated by the Kissinger and Flynn-Wall-Ozawa methods. The thermal degradation mechanism of the copolymer was also studied with the Satava-Sestak method. The results show that the activation energies were 165.97 kJ/mol with the Kissinger method and 169.04 kJ/mol with the Flynn-Wall-Ozawa method. The degradation of the copolymer followed a kinetic model of a nucleation and growth and the kinetic equation could be expressed as \( G(\alpha) = [-\ln(1-\alpha)]^{1/2} \) [where \( G(\alpha) \) is the integral function of conversion and \( \alpha \) is the extent of conversion of the reactant decomposed at time \( t \)]. The reaction order was 1/2.

1. Introduction

At present there is a considerable interest not only in the synthesis of new type of the plastic materials, but also in the modification of exiting polymers in order to vary its properties to meet requirements for new applications. One of the existing methods of improving polymer properties is the copolymerization. Polystyrene (PS) is a clear, colorless polymer used extensively for low-cost applications. It is available commercially in both pellet and sheet form. But there are some serious deficiencies such as low impact strength, poor weatherability and poor chemical resistance. So it is important to correct these shortcomings by modification.

N-substituted phenyl maleimide is a type of heat-resistant monomer which has a planar five-ring. The heat resistance can be improved greatly if it is embedded in the polymer chain to increase the internal rotation resistance of the chain [1-3]. As a result, it is mainly used as heat-resistant polymer modifier [4-6]. When it is adopted as the modifier, not only the heat resistance can be improved, but also processability, hot melting and abrasion resistance property will be enhanced. Furthermore, with the introducing of fluorine atom or bromine atoms, fluorine- and bromine-substituted phenyl maleimide could be obtained. Due to the fluorine atom in the polymer chain, a series of properties of the fluorine-substituted phenyl maleimide polymers, such as the thermal stability, weatherability, oxidation resistance, corrosion resistance, water resistance, oil resistance and abrasion resistance, can
be improved [7,8]; Bromine-substituted phenyl maleimide is regarded as a kind of monomer with good heat resistance and flame-retardant which is used as heat-resistant polymer modifier widely [9].

In this article, we synthesized a novel heat-resistant copolymer poly{N-[(4-bromo-3,5-difluorine)phenyl]maleimide-co-styrene} with N-[(4-bromo-3,5-difluorine)phenyl]maleimide (BDPM) and styrene, and its thermal stability was investigated with thermogravimetric analysis (TGA) under dynamic conditions under a N$_2$ atmosphere. The thermal stability was a crucial factor for determining the processing method and the application of the copolymer.

TGA has been widely used for rapidly assessing the thermal stability of various substances, including polymer pyrolysis [10,11]. The kinetic parameters of the decomposition process, such as the rate constants, activation energies, reaction orders, and pre-exponential factors, were assessed with the data from thermograms. Many kinetic analytical methods have been established for the analysis of the TGA data [12-15]. We used the Kissinger and Flynn-Wall-Ozawa (FWO) methods to calculate the activation energy and the pre-exponential factor of the copolymer and the Satava-Sestak method to study the thermal degradation mechanism of the copolymer.

2. Materials and methods

2.1. Materials

2.1.1. Synthesis of N-[(4-bromo-3,5-difluorine)-phenyl]maleimide.

The N-[(4-bromo-3,5-difluorine)-phenyl]maleimide was prepared according to our previous report [16]: 80 ml toluene, 15 ml DMF, and 4.54 g maleic anhydride were put into a 250 ml 4-mouth flask respectively, then 8.00 g 4-bromo-3,5-difluoroaniline was added to three flasks in batches, the mixture was maintained for 1.5 h at the temperature of 293.15 K. Then, 0.88 g of toluene-p-sulfonic acid and an appropriate amount of inhibitor were added to the reaction flask, the mixture was maintained for hours at the temperature of 383.15 K until there is no water drops appear in the water separator. Toluene was removed by distillation, and then cooled to room temperature, N-[(4-bromo-3,5-difluorine)-phenyl]maleimide were obtained by filtering, washing and drying.

2.1.2. Synthesis of poly{N-[(4-bromo-3,5-difluorine)phenyl]maleimide-co-styrene}.

The copolymer poly{N-[(4-bromo-3,5-difluorine)phenyl]maleimide-co-styrene} was prepared by ourselves as following method: Styrene and BDPM were added to a 50 mL, double-jacketed glass reactor equipped with a magnetic stirrer. Azobisisobutyronitrile was dissolved in 1,4-Dioxane and then added to the flask. The reaction was kept at 70°C for 5 h to obtain a semitransparent emulsion, the whole reaction mixture was poured into methanol, and the polymer was isolated by filtration, dissolved in 1,4-Dioxane, reprecipitated, to remove the unreacted monomer and the homopolymer byproduct, and dried in vacuum at 60°C for 24 h to obtain a white powder.

2.2. FTIR measurements

Fourier transform infrared (FTIR) spectra was recorded on a FTIR Nicolet IMP410 spectrometer (America). The sample was prepared in KBr pellets, and the spectrum was obtained in the range 400-4000 cm$^{-1}$.

2.3. TG and DTG measurements

The TG and derivative thermogravimetry (DTG) analyses for the copolymer were conducted on a Netzsch STA 409 PG/PC thermal analyzer (Germany) with a heating rate of 10°C/min in nitrogen. In the dynamic model, heating rate of 5, 10, 15, and 20°C/min were conducted under a nitrogen atmosphere. In all the experiment, a nitrogen steam was continuously passed into the furnace at a flow rate of 30 mL/min from 40°C to 800°C. 7.5 to 8.5 mg of copolymer was analyzed in each run.
3. Results and discussion

3.1. FTIR of poly{N-{(4-bromo-3,5-difluorine)phenyl}maleimide-co-styrene}

Figure 1 shows the FTIR spectra of polystyrene and poly{N-{(4-bromo-3,5-difluorine)phenyl}maleimide-co-styrene}. Compared with the FTIR spectrum of polystyrene, there were strong absorptions at 1715 cm\(^{-1}\) in the FTIR spectrum of poly{N-{(4-bromo-3,5-difluorine)phenyl}maleimide-co-styrene}, which were the characteristic absorption peak of C=O bond. This indicated that the monomer, N-{(4-bromo-3,5-difluorine)phenyl}maleimide, was incorporated into the copolymer.

![Figure 1](image1.png)

**Figure 1.** FTIR spectra of (1) polystyrene and (2) poly{N-{(4-bromo-3,5-difluorine)phenyl}maleimide-co-styrene}.

3.2. TGA and DTG curves

Figure 2. TGA curves of poly{N-{(4-bromo-3,5-difluorine)phenyl}maleimide-co-styrene} at different \(\beta\) values.

The TGA and DTG curves for the poly{N-{(4-bromo-3,5-difluorine)phenyl}maleimide-co-styrene} are illustrated in Figure 2 and 3, respectively. As shown, there was a region of major decomposition, and the TG curves shifted toward the high-temperature zone as \(\beta\) increased from 5 to 20\(^\circ\)C/min because of the heat lag of the process. The decomposition behaviors at different \(\beta\) values were similar to one another, as indicated in Figure 3. As shown in Figure 4, there was a region of main weight loss. The main region was between 390 and 470\(^\circ\)C with 90 wt % loss, whereas the first weight loss period of polystyrene ranged from 350 to 450\(^\circ\)C with 100 wt % loss [17], which showed that the weight loss temperature range of poly{N-{(4-bromo-3,5-difluorine)phenyl}maleimide-co-styrene} was wider than...
that of polystyrene. This indicated that the N-[(4-bromo-3,5-difluorine)phenyl]maleimide group in poly{N-[(4-bromo-3,5-difluorine)phenyl]maleimide-co-styrene} made the thermal stability of polystyrene increase and delayed the thermal decomposition rate of the poly{N-[(4-bromo-3,5-difluorine)phenyl]maleimide-co-styrene}. This weight loss corresponded to the decomposition of the main chain. There was about 7 wt % char residue left at 650°C, which indicated a good thermal stability of the copolymer.

Figure 3. DTG curves of poly{N-[(4-bromo-3,5-difluorine)phenyl]maleimide-co-styrene} at different β values.

Figure 4. TGA and DTG curves of poly{N-[(4-bromo-3,5-difluorine)phenyl]maleimide-co-styrene} at β=10°C/min.

Figure 5. Plots of ln(β/TP²) versus 1/TP by the Kissinger method and log β versus 1/TP by the FWO method.
3.3. Theoretical background

According to the reaction theory, the kinetic equation for solid degradation, \( B(s) \rightarrow D(s) + C(g) \) [where \( B(s) \) is the solid reactant and \( D(s) \) and \( C(g) \) are the remaining solid and gas products, respectively], can usually be expressed as follows:

\[
\frac{d\alpha}{dt} = kf(\alpha)
\]

where \( \alpha \) is the extent of conversion of \( B(s) \) decomposed at time \( t \), \( f(\alpha) \) is the reaction mechanism function, and \( k \) is the reaction rate constant. \( k \) obeys an Arrhenius equation:

\[
k = A\exp(-E / RT)
\]

where \( A \) is the pre-exponential factor, \( E \) is the apparent activation energy, \( R \) is the gas constant, and \( T \) is the absolute temperature. Combining eqs. (1) and (2) gives the following equation:

\[
\frac{d\alpha}{dt} = A\exp(-E / RT)f(\alpha)
\]

If the temperature of the sample is controlled at a constant heating rate (\( \beta = dT/dt \)), the reaction rate can be defined as follows:

\[
\frac{d\alpha}{dt} = (A / \beta)\exp(-E / RT)f(\alpha)
\]

There are many methods for studying the kinetics of the degradation of solid materials. In this study, we used the Kissinger method [12], FWO method [13,14], and Satava-Sestak method [15] to study the degradation kinetics of the copolymer.

Through separating the variable and rearranging with the integral or differential functions of eq. (4), the Kissinger equation [eq. (5)] and the FWO equation [eq. (6)] can be gained, respectively, as follows:

\[
\ln \frac{\beta}{T^2_p} = \ln \frac{AR}{E} - \frac{E}{RT_p}
\]

\[
\log(\beta) = \log\left(\frac{AE}{RG(\alpha)}\right) - 2.315 - 0.4567\frac{E}{RT}
\]

where \( G(\alpha) \) is the integral function of conversion and \( T_p \) is the temperature at the maximum weight loss. In this method, four or more thermal degradation curves are used, and the activation energy and the pre-exponential factor can be determined from the slope and the ordinate of the linear plot of \( \ln(\beta/T^2_p) \) versus \( 1/T_p \), respectively. The Kissinger method is suitable for computing the kinetic parameters when the thermal degradation rate is fast.

Equation (6) is one of the integral methods that can be used to determine the activation energy without knowledge of the reaction order or the reaction mechanism. It is a relatively simple method for determining the activation energy directly from data of the weight loss versus the temperature obtained at several \( \beta \) values. The activation energy can be determined from the slope of the linear plot of \( \ln \beta \) versus \( 1/T_p \). Compared to other kinetic methods, the FWO method avoids possible error resulting from different assumptions of the reaction mechanism function. Therefore, it can be used to
validate the activation energy computed by different assumptions of the reaction mechanism function. It can be used to obtain the kinetic parameters of any point on the thermogravimetry (TG) curves.

Rearranging eq. (6), we obtain the Satava–Sestak equation:

$$\log G(\alpha) = \log\left(\frac{A_S E_S}{R \beta}\right) - 2.315 - 0.4567 \frac{E_S}{R T}$$

(7)

where $A_S$ is the pre-exponential factor obtained from Stava-Sestak equation and $E_S$ is the apparent activation energy obtained from Stava-Sestak equation.

Thirty types of kinetic model functions [18] were used in the Satava-Sestak method. The $E_S$, $A_S$, and linear correlation coefficient ($r$) values of different model functions were calculated from a plot of $\log G(\alpha)$ against $1/T$. It could also be used to obtain the kinetic parameters of any point on the TG curves.

3.4. Kinetic analysis

3.4.1. Evaluation of activation energy.

The Kissinger method is suitable for computing the kinetic parameters of a region at which the thermal degradation rate is fast. The FWO and Satava–Sestak methods can be used to calculate the kinetic parameters of any region in the TG curves. Table 1 shows the parameters computed from the TG curves.

| $\beta$ (K·min$^{-1}$) | $T_d$ (°C) | $1/T_d$ ($1 \times 10^{-3}$ K$^{-1}$) | Kissinger method: $\ln(\beta/T_d^2)$ (K$^{-1}$·min$^{-1}$) | FWO method: $\log \beta$ |
|-------------------------|-----------|---------------------------------|-------------------------------------------------|----------------|
| 5                       | 420.5     | 1.442                           | -11.475                                         | 0.699         |
| 10                      | 434.3     | 1.414                           | -10.821                                         | 1.000         |
| 15                      | 445.5     | 1.391                           | -10.447                                         | 1.176         |
| 20                      | 452.9     | 1.377                           | -10.180                                         | 1.301         |

According to Kissinger method, by plotting $\ln(\beta/T_d^2)$ versus $1/T_d$, the regression curves can be generated by the least square method, as shown in Figure 5. The apparent activation energy calculated with the Kissinger method ($E_k$), 165.97 kJ/mol, and the pre-exponential factor obtained with the Kissinger method, 6.75 $\times$ 10$^{11}$, were obtained. The reported activation energies of decomposition of polystyrene were 67.8 kJ/mol by other researcher [17], which were smaller than that of the copolymer. The activation energy of the polymer is determined by the energy required by the step of decomposition of the main chain. In the copolymer, the N-[(4-bromo-3,5-difluorine)phenyl]maleimide have rigid imide ring in the backbone, which mean that the decomposition of the copolymer need high temperature, this resulted in increased activation energy. In other words, to achieve decomposition, more energy was required. The result showed that the stability of the copolymer synthesized in this study was better than that of the polystyrene. With the FWO method, through the plotting of $\log \beta$ against $1/T_d$, the regression curves were generated with the least-square method, as shown in Figure 5; the obtained value of the apparent activation energy calculated with the FWO method ($E_o$), 169.04 kJ/mol, was in good agreement with $E_k$, and this indicated that the selection of the thermal degradation kinetics was reasonable.

3.4.2. Evaluation of the thermal degradation mechanism.
In the Satava-Sestak equation [eq. (7)], \( \log(\frac{A \varepsilon}{R \beta}) \) is not affected by temperature. Thus, at the given value of \( \beta \), a plot of \( \log(G(\alpha)) \) against \( \frac{1}{T} \) should be a straight line with a slope of \( -0.4567 \frac{\varepsilon}{R} \). Therefore, the function that shows a linear relation should be the fitting function. When many \( G(\alpha) \) functions show the linear relation, those \( G(\alpha) \) functions that meet \( E \approx E_0 \) should be selected. For the 30 types of thermal degradation mechanism functions (Table 2), the thermal degradation data from the TG curves at the different \( \beta \) values were computed by the Satava–Sestak method. As a result, the number 11 function was the most suitable kinetic model function; that is, \( G(\alpha) = \left[-\ln(1-\alpha)\right]^{1/2} \). \( |r| \) was larger than 0.96, and the standard deviation (SD) was less than 0.07; this indicated good linearity, as shown in Tables 1 and 3. Therefore, the obtained kinetic equation of the thermal degradation of the poly{N-[4-bromo-3,5-difluorine)phenyl]maleimide-co-styrene} was \( G(\alpha) = \left[-\ln(1-\alpha)\right]^{1/2} \). This showed that the degradation of the copolymer followed a kinetic model of the nucleation and growth, and the order of the reaction was 1/2.

### Table 2. Thirty Types of Thermal Degradation Mechanism Functions

| No. | Differential function: \( f(\alpha) \) | Integral function: \( G(\alpha) \) |
|-----|-------------------------------------|----------------------------------|
| 1   | \( 1/2 \alpha \) \(^-1 \)          | \( \alpha + (1-\alpha)\ln(1-\alpha) \) |
| 2   | \( 3/(1-\alpha)^{1.5} \) \(^{-1} \) | \( (1-\alpha)^2/(3(1-\alpha)^2) \) |
| 3   | \( 3/2(1+\alpha)^2(1+\alpha)^{1.5} \) \(^{-1} \) | \( [1+\alpha]^2 \) |
| 4 and 5 | \( 3/(1-\alpha)^{\frac{3}{2}} [1-(1-\alpha)^{\frac{3}{2}} - (n=2, 1/2) \) | \( [1-(1-\alpha)^{\frac{3}{2}}]^{n=2, 1/2} \) |
| 6   | \( 4(1-\alpha)^{\frac{1}{2}} [1-(1-\alpha)^{\frac{3}{2}} ]^{1/2} \) | \( [1-(1-\alpha)^{\frac{3}{2}}]^{1/2} \) |
| 7   | \( 3/(1-\alpha)^{\frac{3}{2}} [1-(1-\alpha)^{\frac{3}{2}} - 1 \) \^-1 \) | \( [(1/(1+\alpha))^{\frac{3}{2}} - 1]^{1/2} \) |
| 8   | \( 4(1-\alpha)^{\frac{3}{2}} [1-(1-\alpha)^{1/3} - 1 \) \^-1 \) | \( -\ln(1-\alpha) \) |
| 9   | \( 1/2 \alpha \) \(^{-1} \) | \( \alpha + (1-\alpha)\ln(1-\alpha) \) |
| 10–16 | \( 1/(n+1)(1-\alpha)[\ln(1-\alpha)]^{(n=2/3, 1/2, 1/3, 4, 1/4, 2/3) \) | \( [-\ln(1-\alpha)]^{n=2/3, 1/2, 1/3, 4, 1/4, 2, 3} \) |
| 17–22 | \( 1/(n+1)(1-\alpha) \) \(^{-n-1} \) \(^{n=1/2, 3, 2, 4, 1/3, 1/4} \) | \( 1-(1-\alpha)^{n=1/2, 3, 2, 4, 1/3, 1/4} \) |
| 23–27 | \( 1/n(1-\alpha) \) \(^{-n-1} \) \(^{n=1, 3/2, 1/2, 1/3, 1/4} \) | \( \alpha^n=1, 3/2, 1/2, 1/3, 1/4 \) |
| 28   | \( 1-\alpha \) \(^2 \) | \( (1-\alpha)^2 \) |
| 29   | \( 1-\alpha \) \(^2 \) | \( (1-\alpha)^2 \) |
| 30   | \( 2\alpha \) \(^{3/2} \) | \( (1-\alpha)^{3/2} \) |

### Table 3. Results of the Satava-Sestak Method

| \( \beta \) (K/min) | E(kJ/mol) | \( \log A_\varepsilon \) | \( r \) | SD |
|---------------------|-----------|-----------------|------|----|
| 5                   | 163.57    | 11.56           | 0.9716 | 0.0614 |
| 10                  | 155.29    | 10.99           | 0.9646 | 0.0674 |
| 15                  | 158.52    | 11.25           | 0.9725 | 0.0608 |
| 20                  | 161.33    | 11.46           | 0.9698 | 0.0635 |

### 4. Conclusions

The thermal degradation process of poly{N-[4-bromo-3,5-difluorine)phenyl]maleimide-co-styrene} was studied by the TG-DTG method. The results show that the activation energies obtained by the Kissinger and FWO methods were 165.97 and 169.04 kJ/mol, respectively. The degradation of the copolymer followed a kinetic model of the nucleation and growth, the kinetic equation could be expressed as \( G(\alpha) = \left[-\ln(1-\alpha)\right]^{1/2} \), and the reaction order was 1/2.
Reference

[1] Mokhtar S M, Abd-Elaziz S M, Gomaa F A 2010 *Journal of Fluorine Chemistry* **131** 616
[2] Matsumoto A, Kubota T, Otsu T 1990 *Macromolecules* **23** 4508
[3] Otsu T, Matsumoto A, Kubota T, Mori S 1990 *Polym Bull* **23** 43
[4] Chung C M, Ahn K D 1997 *Macromol Symp* **118** 485
[5] Kita Y, Kishino K, Nakagawa K 1997 *J. Appl. Polym. Sci.* **63** 1055
[6] Matsumoto A, Kimura T 1998 *J. Appl. Polym. Sci.* **68** 1703
[7] Lee J R, Jin F L, Park S J, Park J M 2004 *Surf. Coat. Technol.* **180** 650
[8] Pomes V, Fernandez A, Costarramone N, Grano B, Houi D 1999 *Colloid Surf.* **159** 481
[9] Rytte A 1999 *Angew. Makromol. Chem.* **267** 67
[10] Li L Q, Guan C X, Zhang A Q, Chen D H, Qing Z B 2004 *Polym. Degrad. Stab.* **84** 369
[11] Liu B Y, Li Y, Zhang L, Yan W D, Yao S H 2007 *J. Appl. Polym. Sci.* **103** 3003
[12] Kissinger H E 1957 *Anal. Chem.* **29** 1702
[13] Flynn J H, Wall L A 1966 *J. Polym. Sci. Part B: Polym. Lett.* **4** 323
[14] Ozawa T 1965 *Bull. Chem. Soc. Jpn.* **38** 1881
[15] Satava V, Sestak J 1975 *J. Therm. Anal.* **8** 477
[16] Li Y X, Xu L, Yao X D, Luo T L, Liu G J 2011 *J. Chem. Eng. Data* **56** 158
[17] Nishizaki H, Yoshida K, Wang J H 1980 *J. Appl. Polym. Sci.* **25** 2869
[18] Hu R Z, Shi Q Z 2001 *Thermal Analysis Kinetics* （Beijing: Science）pp 56–67