

# Thermal analysis and isoconversional kinetic study of thermal decomposition of polycyclohexene oxide polystyrene (PCHO-PST) comb-shaped polymer

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Accepted: November 13, 2021

In this study we aimed to investigate the thermal and the kinetic parameters of the thermal decomposition reaction of poly cyclohexene oxide polystyrene (PCHO-PSt) comb-shaped polymer. The polymer of epoxy end-functionalized polystyrene was synthesized by atom transfer radical polymerization (ATRP) and the glass transition of polystyrene present as a unit in the polymer was determined. The thermal characteristics of the polymer were evaluated through thermal analysis, differential thermal analysis (DTA), thermogravimetric analysis-derivative thermogravimetry (TG-DTG) under nitrogen atmosphere at 3, 5, 7 and 10 °C min<sup>-1</sup> from 30 °C to 600 °C. The obtained results were supported by differential scanning calorimetry (DSC). The glass transition of the PCHO-PSt was seen at 79 °C. The crystallization and melting temperatures of the PCHO-PSt were determined as 142 and 240 °C, respectively. The polymer decomposition was seen in the range of 320-350 °C depending on the heating rate. Based on the isoconversional method, the activation energy was calculated by the free model approach of the Ozawa-Flynn-Wall method (OFW). The highest activation energy was found as 160.82 kJmol<sup>-1</sup> at 30% conversion. It was found that the activation energy decreased as conversion increased.

**Keywords:** Comb-shaped polymer, TGA-DTA, DSC, Pyrolysis, Activation energy

## INTRODUCTION

The polymers bearing an end-functional group are important because of their use as forerunners of block and graft polymers. Atom transfer radical polymerization (ATRP) method was preferred to synthesize these polymers because of its easy experimental setup, use of inexpensive catalyst, without the formation of side products. Also, the polymers synthesized using ATRP have been used for coating and adhesives, in medical and environmental fields.

The reaction kinetics gives information about the durability and decomposition temperature of a polymer under various thermal conditions [1]. To determine the kinetic data of polymer decomposition, thermal analysis methods are generally used. Thermogravimetric-differential thermal analysis (TG-DTA), as well as differential scanning calorimetry (DSC) are counted in among these methods. Mostly, in the evaluation of data these methods are performed together as they complete each other. Measurements are based on the weighing of the polymer mass with time in TG analysis (TGA). The temperature is different between a reference material and the worked material. In DTA this difference is quantified as a function of temperature or time and is given in related plots as heat flow. In this way, we can get

information about the heat absorbed or emitted by a chemical system by determining DTA data.

DSC data are utilized for determination of the crystallization temperature ( $T_c$ ), the melting point ( $T_m$ ), the heat of fusion ( $\Delta H_f$ ), the heat of crystallization ( $\Delta H_c$ ), and glass transition ( $T_g$ ) of polymers. Also, DSC may be performed to determine the unique features of particular polymers, polymer additives that show thermal transitions and polymer alloys. Some materials do not show a net transition case as they are heated. In this case they are present in glassy state. This state is seen in amorphous materials, named as glass transition [2].

## Kinetics

The decomposition mechanism of a polymer or a composite can be impossible to understand and it can't be solved in this situation. Isoconversional methods are suggested to study the kinetics of a non-isothermal process [3]. In isoconversional method, it is assumed that the basic kinetic equation for solid state decomposition reaction is a function of temperature and conversions [4]. This case can be expressed by:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

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In here  $f(\alpha)$  is the conversion function,  $\alpha$  is the degree of conversion. A temperature dependence of the rate constant is expressed by  $k(T)$ . The Arrhenius equation means this dependence as follows:

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

As known, the  $R$ ,  $T$ ,  $A$  and  $E$  terms in the equation mean universal gas constant, temperature, pre-exponential factor and energy of activation, respectively. Then Eqn. 1 can be rewritten as:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (3)$$

As Eqn. 3 can be difficult to measure accurately, the temperature dependence in Eqn. 3 can be rewritten as:

$$\beta \frac{d\alpha}{dT} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (4)$$

where  $\beta = \frac{T-T_0}{t} = \frac{dT}{dt} = \text{constant}$  is the linear heating rate in  $^{\circ}\text{C}/\text{min}$ .

In the literature, many researchers have investigated the thermal decomposition processes of polymers and ligands [5, 6]. Kinetic parameters such as  $A$  and  $E$  were determined by kinetic methods such as Kissinger and Crane and Ozawa–Flynn–Wall. These methods are isoconversional. During applying the methods, conversion was constant, temperature was not. Sahin *et al.* [7] investigated the thermal decomposition of derivatives of boron using Coats-Redfern thermal analysis. Recently, researchers prepared nanocomposites from polymer-nanoparticles couples such as polystyrene (PS)-ZnO [8] and polyethylene-graphene [9] and the thermal stability of these nanocomposites was investigated and the influence of nanoparticles was reported. TG-DTA data were used to evaluate the results during the investigation of these properties of nanocomposites.

In this study, the thermal decomposition of the PCHO-PSt comb-shaped polymer bearing epoxy end-functionalized polystyrene and the change in  $T_g$  of PSt when it was used as a unit of the polymer were investigated.

## EXPERIMENTAL

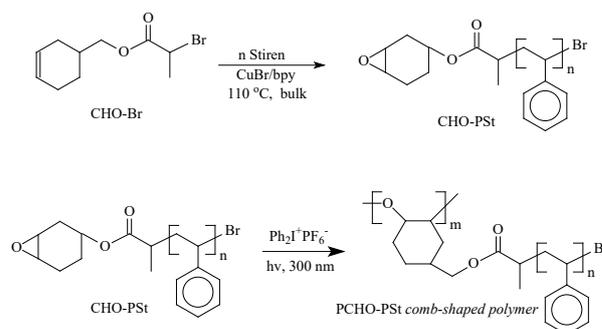
### Material and methods

Calcium hydride ( $\text{CaH}_2$ ) was used to distill cyclohexene oxide (CHO) and styrene (St) and they were held at  $+4^{\circ}\text{C}$  in an atmosphere of nitrogen before the process. Also, in the process compounds

such as pyridine,  $\text{CuBr}$ , 3-chloroperoxybenzoic acid, 2-bromopropanoyl bromide, sodium bicarbonate ( $\text{NaHCO}_3$ ) and 3-cyclohexene-1-methanol were used. The polymerization was carried out *via* ATRP. Dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) was used as a solvent. In this stage chemicals such as diphenyliodonium hexafluorophosphate ( $\text{Ph}_2\text{I}^+\text{PF}_6^-$ ), and 2,2-bipyridine were used in the radical polymerization and the selected photoinitiator was 2,2-dimethoxy-2-phenyl acetophenone (DMPA) (Irgacure 651). All chemicals were used as received without further purification.

### Synthesis

The cyclohexene oxide end-functional macro monomer of polystyrene (CHO-PSt) and its polymer, (PCHO-PSt comb-shaped polymer) were synthesized by atom transfer radical polymerization according to our previous study [10]. Synthesis route is given in Scheme 1.



**Scheme 1.** Synthesis route of the PCHO-PSt comb-shaped polymer

Based on this, firstly the condensation of 3-cyclohexene-1-methanol with 2-bromopropanoyl bromide was carried out for the synthesis of the 3-cyclohexenylmethyl-2-bromopropanoate. Subsequently, to obtain the epoxy end-functional initiator as used in ATRP, epoxidation of the obtained 3-cyclohexenylmethyl-2-bromopropanoate was performed using 3-chloroperoxybenzoic acid. The macro monomer of polystyrene with an epoxy end group was obtained by means of this initiator in conjunction with the cuprous complex  $\text{Cu(I)Br/bipyridine}$  with styrene (St) in bulk at  $110^{\circ}\text{C}$ . The obtained CHO end-functional macro monomers were used as precursors in the photoinitiated cationic polymerization.

### TG-DTA experiments

The thermal characteristics of PCHO-PSt comb-shaped polymer decomposition were recorded on a DTG-60H Simultaneous DTA-TG apparatus (SHIMADZU Scientific Instruments Incorporated,

Kyoto, Japan). The sample was weighed in the range of 4-5 mg in a platinum pan including alumina ( $\alpha$ -alumina ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) powder for DTA Standard Material). TGA experiments were performed in the range of 30 °C-600 °C at the heating rates of 3, 5, 7 and 10 °C min<sup>-1</sup>, atmosphere conditions were a flow rate of 20 mL min<sup>-1</sup> of the nitrogen gas. In DSC tests a method consisting of heating or cooling the polymer was applied in inert gas media at a certain flow rate and at a certain heating/cooling rate based on ASTM D:3417-99 and ASTM D:3418-03. In the DSC test the amount of used compound was 10-11 mg, heating program was from 20 °C to 280 °C for 1<sup>st</sup> heating and holding at 280 °C for 5 min, cooling from 280 °C to -100 °C and holding at -100 °C for 5 min, then from -100 °C to 280 °C for 2<sup>nd</sup> heating. Heating rate was 10 °C min<sup>-1</sup> at a flow rate of 50 mL min<sup>-1</sup> of nitrogen gas.

## RESULTS AND DISCUSSION

In the TGA stage, 3, 5, 7, and 10 °C min<sup>-1</sup> as heating rates were selected and TG curves were obtained in the range of 30-650 °C. Derivative thermogravimetric (DTG) curves were formed by taking the derivation of TG curves. The TGA and DTG curves of PCHO-PSt comb-shaped polymer decomposition are shown in Fig. 1.

As is seen, the initial mass loss temperature was shifted from 316.07 °C at 3 °C min<sup>-1</sup> to 343.71 °C at 10 °C min<sup>-1</sup> (Fig. 1a). It was thought that the mass loss ended up at 409.11 °C and 452.92 °C for 3 °C

min<sup>-1</sup> and 10 °C min<sup>-1</sup>, respectively. During the decomposition, the uniform peak observed in Fig. 1 b, illustrated the DTG curve. The maximum mass loss rate was shifted to higher temperature. So, the temperature was 398.45 °C for 10 °C min<sup>-1</sup>, while it was 370.74 °C for 3 °C min<sup>-1</sup>. The thermal decomposition of the PCHO-PSt comb-shaped polymer started at a higher temperature, as heating rate was increased. This phenomenon can be attributed to the distribution of the heat in the polymer, which may decrease by the higher heating rate.

To see the phase transitions of PCHO-PSt comb-shaped polymer, DTA was performed at different heating rates within the range of 30-650 °C. Fig. 2a illustrates the obtained DTA curves at related heating rates.

According to graphs an endothermic peak was observed at 88 °C, which belonged to the glassy transition. This transition was clearly confirmed from the DSC graph (Fig. 2b). On the DTA graph in the range of 161 °C - 243 °C a change in endothermic energy was observed. This thermal change may be described as the melting transition due to no considerable mass loss in this temperature range of the TGA curve (Fig. 1a), referring to the reported melting point ( $T_m$ ) range of polystyrene (PSt) [11]. The  $T_g$  and  $T_m$  values were shifted to lower values due to the epoxy group presence in the polymer chain and the comb shape of the polymer.

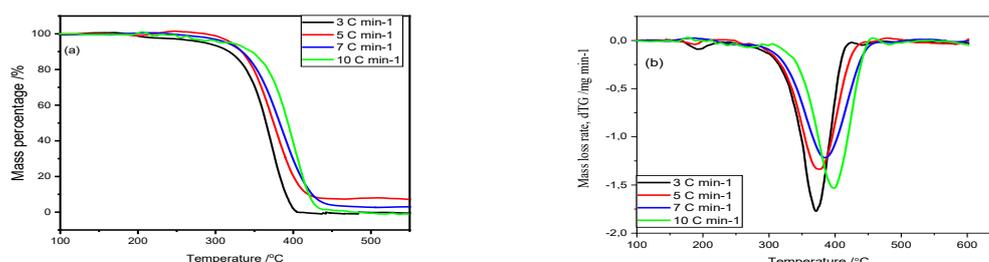


Fig. 1. TGA (a) and DTG (b) curves of the PCHO-PSt comb-shaped polymer at 3, 5, 7, and 10 C min<sup>-1</sup>

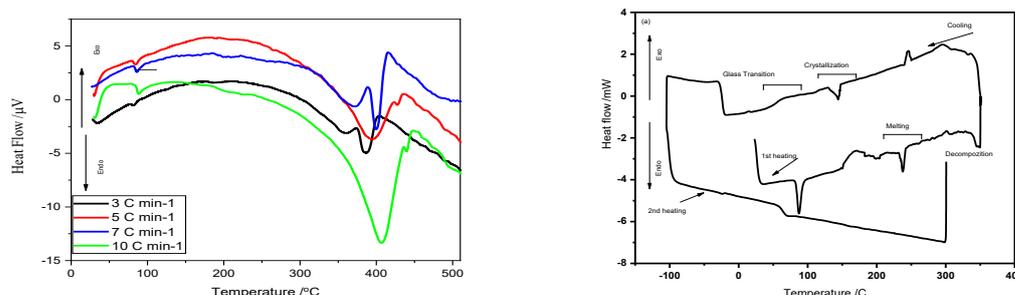


Fig. 2. Graphs of (a) DTA curves, (b) DSC curves of the PCHO-PSt comb-shaped polymer (amount: 10 mg; temperature: 350/-100 °C; gas flow rate: 50 mL min<sup>-1</sup> and heating/cooling rate: 10 °C min<sup>-1</sup>)

In the DTA curves observed exothermic and endothermic physical transitions took place due to the thermal history of the polymer, which are attributed to crystallization and melting, respectively. For the determination of the net values of these transitions it is necessary to evaluate the DSC cooling curve because the polymer was present at steady and pure situation after the 1<sup>st</sup> heating.

Fig. 2b illustrates the DSC curves of the polymer during 1<sup>st</sup> heating, cooling, and 2<sup>nd</sup> heating processes. The 1<sup>st</sup> heating was important as showing the thermal history of the polymer. So, glassy transition (T<sub>g</sub>) region was seen at the range of 78-90 °C. The region was seen at lower temperature, compared with literature [2]. This may be caused by the effect of other units in the polymer chain on the PSt unit as a plasticizer.

From the graph an exothermic change is observed from 173.62 °C to at 199.73 °C. From the TG curve this change was identified as crystallization because of lack of mass loss in the temperature range. so, the area under this range, that is crystallization enthalpy, was calculated as 9.7 J g<sup>-1</sup> and a DSC peak was read as 184.95 °C. This value conformed with the literature for thermal crystallization [12]

The melting started at 217 °C and ended at 250.62 °C. The area under this range, that is fusion enthalpy, was calculated as 16.29 J g<sup>-1</sup> by the DSC software. And the polymer was decomposed at 321.65 °C. During this phenomenon the absorbed heat from the medium was calculated as 532.86 J g<sup>-1</sup>.

The glass transition peak can be observed in both TG and DSC curve. Crystallization and melting peaks were monitored in TG and DTA and DSC. In addition to glass transition, crystallization and melting, starting of decomposition can be seen from the graph as about 320-350 °C from the curves.

*Kinetic parameters calculation of PCHO-PSt comb-shaped polymer decomposition.*

To use the kinetic equation, the solution of Eqn. 5 integration is primarily necessary [13]:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = g(\alpha) = A\beta^{-1} \int_0^T \exp\left(-\frac{E}{RT}\right) dT \quad (5)$$

The Doyle [14] approximation was one of the used approaches for the solution of the integration. The Ozawa-Flynn-Wall (OFW) [15, 16] method was derived by applying Doyle approaches for the temperature integral in Eqn. 5, respectively. For the OFW method:

$$g(\alpha) = \left(\frac{A}{\beta}\right) 0.00484 \exp\left(-1.052 \frac{E}{RT}\right) \quad (6)$$

Eqn. (7) is obtained by rearranging the natural logarithmic Eqn. (6):

$$\ln(\beta) = \ln\left(\frac{AE}{Rg(\alpha)}\right) - 5.331 - 1.052 \frac{E}{RT} \quad (7)$$

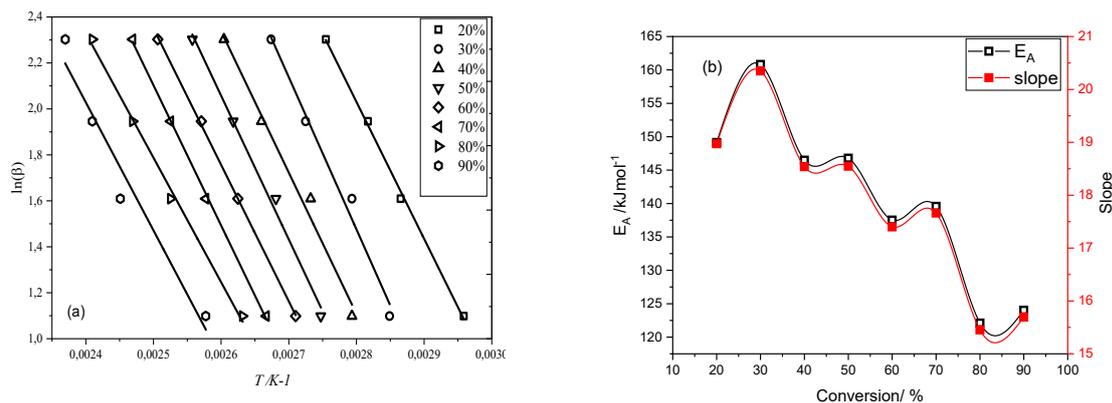
To obtain the activation energy (E) by using this method, firstly, the graphs including regression lines of ln(β) versus T<sup>-1</sup> were formed at different heating rates and different conversions, separately. Then, the energy values were calculated from the slope of each regression line. In our study, to determine the kinetic parameters of PCHO-PSt comb-shaped polymer decomposition, Ozawa-Flynn-Wall methods (OFW) was selected as isoconversional method. To draw the related graphs eight conversions from 20% to 90% with an increment of 10 were used for kinetic calculation. Related temperature for each conversion was read from the TGA curve. Thus, the formed regression lines according to this information are presented in Fig. 3a. According to the graph the parallel lines were attributed to a single decomposition mechanism or a combination of many reactions.

The correlation coefficient (R) referring to the accuracy of data and the activating energy (E<sub>A</sub>) were calculated from the slope of the related regression line for each conversion. The graph of the calculated activation energy values and the slope of the lines versus conversion is given in Fig. 3b, R is listed with other values in Table 1.

As seen from the figure, the highest activating energy is at 30% conversion as 160.82 kJmol<sup>-1</sup>. Then, the change in activation energy with conversion was trending a decrease as conversion was increasing. The cause of this might be the decreasing at molecule count to react. This result conformed with literature [5].

**Table 1.** Slope, R and E values calculated by the OFW method

α (%)	Slope	R	E (kJ mol <sup>-1</sup> )
20	18.972	0.9985	149.14
30	20.349	0.9841	160.82
40	18.538	0.9854	146.50
50	18.547	0.9921	146.79
60	17.401	0.9991	137.52
70	17.662	0.9995	139.58
80	15.451	0.9974	122.11
90	15.694	0.9611	124.03



**Fig. 3.** (a) Regression lines to the decomposition of PCHO-PSt comb-shaped polymer based on OFW method at 3, 5, 7 and 10 C min<sup>-1</sup> and (b) Activation energy changing with conversion calculated by the OFW method.

### CONCLUSIONS

In this study, the thermal characteristics and activation energy calculation of PCHO-PSt comb-shaped polymer decomposition were evaluated through TGA. The initial mass loss temperatures were observed in the higher temperature region as the the heating rate, as well as the maximum value of the mass loss rate increased. In the DTA curves the temperature range of the glass transition, crystallization and melting of the polymer were determined. So, the polymer started freezing at 245 °C (melting region during heating) and crystallized at 149-132 °C. The glass transition was shifted to 67-70 °C due to cooling. These results conformed with TG.

From the graph an exothermic change was observed from 173.62 °C to 199.73 °C. From the TG curve this change was identified as crystallization because of lack of mass loss in the temperature range. The melting started at 217 °C and ended at 250.62 °C. The area under this range, that is fusion enthalpy, was calculated to be 16.29 J g<sup>-1</sup> by DSC software. The polymer was decomposed at 321.65 °C. During this phenomenon the absorbed heat from the medium was calculated as 532.86 J g<sup>-1</sup>. To calculate the activation energy, the OFW method was selected and the value of the average activation energy deducted from the method was 140.81 kJ mol<sup>-1</sup>. The maximum activation energy achieved was 160.82 kJ mol<sup>-1</sup> at 30% conversion.

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