Non-isothermal Kinetics of Free Radical Polymerization of 2-Phenylethyl (Meth)acrylate

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ABSTRACT

Bulk polymerization kinetic of 2-phenylethyl acrylate (PEA) and 2-phenylethyl methacrylate (PEMA) was determined by non-isothermal differential scanning calorimetry. Kinetic parameters of polymerization for monomers were investigated by DSC in the non-isothermal mode in the presence of 2,2’-azobisisobutyronitrile (AIBN) as an initiator. The polymerization was investigated at temperatures range from 40 to 180 °C with varying ramp rate at four different initiator concentrations of initiator. Kissinger and Ozawa methods were applied to determine the activation energy (Eₐ) and the reaction order of free-radical polymerization. The average heat of polymerization (ΔHₚ) was also determined. These findings reveals that differential scanning calorimetry is a useful method for studying the kinetics of polymerization.

Keywords: Non-isothermal kinetics, 2-phenylethyl acrylate (PEA), 2-phenylethyl methacrylate (PEMA), activation energy.

INTRODUCTION

2-Phenylethyl acrylate and 2-phenylethyl methacrylate are widely used in specialty coatings, adhesives and for various optical applications.¹ Inspite of having such versatility in applications, not much literature is available about the thermodynamic properties of these (meth)acrylates, especially about their kinetic behavior in case of bulk polymerization. Due to their fast and highly exothermic nature of polymerization, most methods of studying
polymerization kinetics (e.g., dilatometry or monitoring of unreacted monomer concentration) are not suitable for studying bulk polymerization.²

Various types of thermal analysis have been applied in almost all fields of material research. The thermoanalytical method, in which the properties of a sample heated at a constant rate of heating and observed continuously, is an effective method when the thermal response time is large. Compared with rate, considerable change occurs during the period of heating the sample up to the desired temperature in an isothermal measurement.

A thermal analysis technique such as thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) provides the kinetic parameters during not only physical but also chemical changes. DSC provides both qualitative and quantitative information about material transitions. For some of these transitions, DSC can provide not only the temperature at which the transition (reaction) occurs and how much total heat is involved, but can also provide valuable information about the rate (kinetics) of reaction.

Differential scanning calorimetry (DSC) is a powerful tool for evaluating miscibility of crystalline/amorphous polymer blends and the direct measurement of the rate of an exothermic polymerization. DSC has been used with success to follow the course of free-radical polymerization with bulk monomer using either an isothermal or scanning method.³⁻⁷

DSC is used to measure the amount of energy to be supplied or removed to keep the temperature difference \(\Delta T = 0\) between the sample and the reference with respect to time or temperature as the two specimen are heated at a controlled heating rate. The DSC technique has been widely employed to determine the physical transitions such as glass transition temperature \(T_g\), crystallization \(T_c\) and melting temperature \(T_m\) of the polymers and to study the varieties of reactions such as polymerization, decomposition, oxidation, vulcanisation and curing reactions.¹⁰⁻¹⁶

### Non-Isothermal Techniques

In theory, a non-isothermal DSC trace should contain all the kinetic information normally embodied in a series of isothermal experiments.¹⁷ This makes the nonisothermal approach highly attractive. This technique is fairly rapid and works reasonably well for simple reactions. On the other hand this technique is not applicable in any of the following cases.¹⁸⁻²⁰

a. Overlapping reaction peaks
b. Decomposition occurs during reaction

### Kinetic parameters

The kinetic analysis of free-radical polymerization curves involves the search for the kinetic parameters such as activation energy \(E_a\) and rates of reactions associated with the process. It was assumed that the dynamic heat obtained as the area between the DSC curve and the baseline was a good approximation for the total reaction heat of polymerization.

### Kissinger method

Murray and White showed that the temperature of maximum deflection is defined by the kinetic constants of the material and the heating rate.²¹ The assumption that the peak
temperature occurs when the reaction rate is a maximum is supported by the experimental work. It should then be possible to calculate the kinetic constants directly from DSC data by making a number of patterns at different heating rates.

For the first order thermal decomposition at constant temperature,

\[
\frac{\partial x}{\partial t} = k_T(1-x)
\]

Where \( x \) is the fraction of material decomposed. The magnitude of the rate constant, \( k_T \), is determined by the temperature and is given by the Arrhenius equation:

\[
k_T = Ae^{\frac{E_a}{RT}}
\]

Where \( R \) is the gas constant, \( T \) is the Kelvin temperature, and \( A \) and \( E_a \) are constants that are properties of the material. The constant \( E_a \), called the activation energy, is often interpreted as the energy barrier opposing the reaction. The constant \( A \), most often called the frequency factor, is a measure of the probability that a molecule having energy \( E_a \) will participate in a reaction. When the temperature is changing with time, the reaction rate is:

\[
\frac{dx}{dt} = \left( \frac{\partial x}{\partial t} \right)_T + \left( \frac{\partial x}{\partial T} \right)_t \frac{dT}{dt}
\]

The rate of change of \( x \) with temperature, with the time coordinate fixed, \( \left( \frac{\partial x}{\partial t} \right)_t \), is zero, because fixing the time also fixes the number and position of the particles constituting the system. The only effect of an instantaneous change in temperature is in the velocity of thermal motion of the particles. The total rate of reaction may then be expressed as:

\[
\frac{dx}{dt} = A(1-x) e^{\frac{E_a}{RT}}
\]

The above expression 4 holds for any value of \( T \), whether constant or variable, as long as \( x \) and \( T \) are measured at the same instant. When the reaction rate is maximum, its derivative with respect to time is zero. Solving above equation for \( \left( \frac{\partial}{\partial t}\right)(\frac{\partial x}{\partial t}) \);

\[
\frac{d}{dt}\left( \frac{dx}{dt} \right) = \frac{dx}{dt} \left( \frac{E_a}{RT^2} \frac{dT}{dt} - Ae^{\frac{E_a}{RT}} \right)
\]

The maximum value of \( dx/dt \) occurs at temperature \( T_p \), defined by:

\[
Ae^{\frac{E_a}{RT_p}} = \frac{E_a}{RT_p^2} \frac{dT}{dt}
\]
Equation 6 derived by Murray and White.\textsuperscript{22} From above equation it is shown that:
\[
\frac{d}{d\left(\ln \frac{\phi}{T_p^2}\right)} = \frac{E_a}{R} \quad 7
\]

Where \( T_p \), \( \phi \), \( E_a \) and \( R \) is peak indicating temperature, heating rate, activation energy and the gas constant, respectively. According to equation 7 Kissinger\textsuperscript{23-24} derived the following equation;
\[
\ln \frac{\phi}{T_p^2} = -\frac{E_a}{RT_p} + C \quad 8
\]

The left term of the equation 8 was plotted vs. \( 1/T_p \), and then \( E_a \) can be evaluated from the slope.

\textbf{Ozawa method}

Ozawa method allows determining the activation energy \( E_a \) for \( n \)th order reactions.\textsuperscript{25} It is based on the variation of peak temperature of exothermic DSC curve with heating rate. Assuming that the extent of reaction at the peak temperature is constant and independent of heating rate, Ozawa derived the following expression;
\[
\ln \phi = \text{const} - 1.052 \frac{E_a}{RT_p} \quad 9
\]

This expression shows a linear dependence of the reciprocal absolute peak temperature \( T_p \) on the logarithm of heating rate. The activation energy \( E_a \) is calculated from the slope of the straight line obtained by Ozawa plot.

\textbf{EXPERIMENTAL}

2-phenylethyl acrylate and 2-phenylethyl methacrylate are prepared by reacting 2-phenylethanol with acryloyl and methacryloyl chloride, respectively. Synthesized monomers were purified by distillation under reduced pressure. 2,2'-azobisisobutyronitrile (AIBN) was recrystallized twice from methanol. DSC Q 100 (TA Instruments, USA) differential scanning calorimeter connected to Q Series PCA was used for online monitoring of the bulk polymerization process, using a TA 2920 analyzer and RCS DA cooler. Temperature calibration of the calorimeter was performed with pure indium metal as standard. All samples were run against an aluminium reference in crimped hermetic aluminium pans.

Samples of mixture (monomer + initiator) were prepared in glass vials of 5 mL capacity and degassed by \( N_2 \) at 0 °C. The mol ratios of the compositions (monomer: initiator) were:

\[
\text{[PEA]}: \ [\text{AIBN}] = 50.41:1, \ 76.34:1, \ 100.45:1, \ 124.45:1 \\
\text{[PEMA]}: \ [\text{AIBN}] = 51.52:1, \ 76.01:1, \ 100.58:1, \ 126.71:1
\]
The measurements were performed under nitrogen gas purge of 50 mL/min, in aluminum pans filled with 10 mg of the sample for each polymerization experiment. Heating rates of 2, 5, 7, 10, and 15 °C min\(^{-1}\) were used in case of 2-phenylethyl acrylate while 5, 7, 10, 15 and 18 °C min\(^{-1}\) were used in case of 2-phenylethyl methacrylate. Each sample was placed in the sample holder assembly of DSC at 40 °C and scanned up to 180 °C.

**RESULTS AND DISCUSSION**

The kinetic analysis of free-radical polymerization curves involves the search for Ea associated with the process. It was assumed that the dynamic heat obtained as the area between the DSC curve and the baseline was a good approximation for the total heat of polymerization. Figure 1 (a-d) and Figure 2 (a-d) shows DSC thermograms for the polymerization of PEA and PEMA obtained at different scan rates for various concentrations respectively.

It is observed from these curves that peak maximum temperature of polymerization exotherm increases with increase in heating rate and initiator concentration. Maximum of the curves shifted to higher temperature with increasing heating rate due to the dependence of monomer conversion on time and temperature. Similar results have been found in all samples with different molar ratios of \([\text{PEA}]:[\text{AIBN}]\) and \([\text{PEMA}]:[\text{AIBN}]\). Table 1 and 2 gathers the exothermic DSC peak temperatures and heat of polymerization of every sample at different heating rates for PEA and PEMA respectively. In case of PEA heat of polymerization ranges from 71.82 to 85.67 kJ/mol whereas for PMMA it ranges from 61.04 to 65.44 kJ/mol.

![DSC curves of the samples with concentration [PEA:AIBN] (a) 50.41:1, (b) 76.34:1, (c) 100.45:1 and (d) 124.45:1](image-url)
Table 1: DSC peak temperature and Heat of polymerization for various concentrations of PEA:AIBN at different heating rates

<table>
<thead>
<tr>
<th>φ (°C)</th>
<th>PEA:AIBN (mol:mol)</th>
<th>50.41:1</th>
<th>76.34:1</th>
<th>100.45:1</th>
<th>124.45:1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T_p (°C)</td>
<td>ΔH (kJ/mol)</td>
<td>T_p (°C)</td>
<td>ΔH (kJ/mol)</td>
<td>T_p (°C)</td>
</tr>
<tr>
<td>2</td>
<td>88.68</td>
<td>71.34</td>
<td>92.7</td>
<td>78.31</td>
<td>97.56</td>
</tr>
<tr>
<td>5</td>
<td>96.32</td>
<td>81.12</td>
<td>97.51</td>
<td>78.45</td>
<td>100.06</td>
</tr>
<tr>
<td>7</td>
<td>96.97</td>
<td>82.97</td>
<td>101.23</td>
<td>81.9</td>
<td>102.94</td>
</tr>
<tr>
<td>10</td>
<td>99.18</td>
<td>82.03</td>
<td>103.13</td>
<td>81.96</td>
<td>104.12</td>
</tr>
<tr>
<td>15</td>
<td>104.22</td>
<td>75.47</td>
<td>107.34</td>
<td>76.43</td>
<td>108.77</td>
</tr>
</tbody>
</table>

Figure 2: DSC curves of the samples with concentration [PEMA:AIBN] (a) 51.52:1, (b) 76.01:1, (c) 100.58:1 and (d) 126.71:1

Table 2: DSC peak temperatures and Heat of polymerization for various concentrations of PEMA:AIBN at different heating rates

<table>
<thead>
<tr>
<th>φ (°C)</th>
<th>PEMA:AIBN (mol:mol)</th>
<th>51.52:1</th>
<th>76.01:1</th>
<th>100.58:1</th>
<th>126.71:1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T_p (°C)</td>
<td>ΔH (kJ/mol)</td>
<td>T_p (°C)</td>
<td>ΔH (kJ/mol)</td>
<td>T_p (°C)</td>
</tr>
<tr>
<td>5</td>
<td>106.57</td>
<td>63.11</td>
<td>111.98</td>
<td>63.69</td>
<td>114.65</td>
</tr>
<tr>
<td>7</td>
<td>113.51</td>
<td>64.34</td>
<td>112.70</td>
<td>62.54</td>
<td>117.63</td>
</tr>
<tr>
<td>10</td>
<td>115.86</td>
<td>64.86</td>
<td>117.81</td>
<td>63.21</td>
<td>120.65</td>
</tr>
<tr>
<td>15</td>
<td>121.25</td>
<td>64.35</td>
<td>121.88</td>
<td>61.04</td>
<td>124.70</td>
</tr>
<tr>
<td>18</td>
<td>123.06</td>
<td>65.44</td>
<td>125.35</td>
<td>61.10</td>
<td>125.72</td>
</tr>
</tbody>
</table>
Kinetic parameters

Since the peak corresponding to polymerization reaction is well resolved, non-isothermal methods are employed for kinetic analyses. Variable heating rates, which depend on peak maxima in DSC curve, are employed for the purpose, where the apparent variations in activation parameters caused by heating rates are taken care of. Moreover, the method does not invoke reaction order or fractional conversion in deriving the kinetic parameters. The Kissinger’s and Ozawa’s methods, based on variable heating rate were used for finding the activation parameters and their dependency on structure of the monomers.

According to Kissinger equation 8, \( \ln(\phi/T_p^2) \) was plotted vs \( 1/T_p \) (Figure 3), and then \( E_a \) values for both monomers were evaluated from the slope. The obtained \( E_a \) values are listed in Table 1, mean \( E_a \) values for PEA and PEMA are 159.24 and 107.75 kJ/mol, respectively. Also \( E_a \) values were determined applying Ozawa equation (9) by plotting \( \ln(\phi) \) vs. \( 1/T_p \) (Figure 4). According to Ozawa mean \( E_a \) values for PEA and PEMA are 174.16 and 120.19 kJ/mol, respectively.

![Figure 3 (a-b): Determination of activation parameters by Kissinger’s method for polymerization reaction of (a) PEA and (b) PEMA at various concentrations](image1)

![Figure 4 (a-b): Determination of activation parameters by Ozawa’s method for polymerization reaction of (a) PEA and (b) PEMA at various concentrations](image2)
The polymerization kinetics of (meth)acrylates ester initiated with AIBN is considered by a mechanism of free-radical polymerization, which consists of a sequence of three steps: initiation, propagation and termination. The mean $E_a$ obtained by Kissinger method and Ozawa method is overall activation energy, which is the result of combining three separate Arrhenius-type equations for each process (initiation, propagation and termination).

Activation energies were calculated for the polymerization reaction by Kissinger and Ozawa methods. The $E_a$ values are compiled in Table 3. The lowest $E_a$ value for the monomer implies a kinetically facile polymerization reaction. It is found that the $E_a$ value for PEMA is less than that of PEA.

### Table 3: Activation energies for PEA and PEMA

<table>
<thead>
<tr>
<th></th>
<th>Energy of Activation $E_a$ (kJ/mol) for PEA</th>
<th>Energy of Activation $E_a$ (kJ/mol) for PEMA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_a$ (kJ/mol) for PEA</td>
<td>$E_a$ (kJ/mol) for PEMA</td>
</tr>
<tr>
<td>PEA:AIBN; 50:41</td>
<td>145.69</td>
<td>51.52</td>
</tr>
<tr>
<td>PEA:AIBN; 76.34</td>
<td>159.72</td>
<td>92.74</td>
</tr>
<tr>
<td>PEA:AIBN; 100.45</td>
<td>159.72</td>
<td>92.74</td>
</tr>
<tr>
<td>PEA:AIBN; 124.45</td>
<td>159.72</td>
<td>92.74</td>
</tr>
<tr>
<td>Average</td>
<td>159.24</td>
<td>107.75</td>
</tr>
</tbody>
</table>

### Activation parameters

The pre-exponential factor $A$ is the pre-exponential constant in Arrhenius equation, an empirical relationship between temperature and rate coefficient also $A$ depends on probability $P$ and number of collisions $\langle \rho \rangle$. It is usually designated by $A$ when determined from the experiment. $A$ can be found from the relation 10;

$$A = \phi \cdot \frac{E_a e^{E_a/RT}}{RT^2}$$

The activation parameters are determined for concentration [monomer: initiator; 100:1] in case of both monomers and presented in Table 4.

### Table 4: Activation parameters determined by Kissinger and Ozawa methods

<table>
<thead>
<tr>
<th>Conc. (mol/mol)</th>
<th>Kissinger $A$ (s$^{-1}$)</th>
<th>Ozawa $A$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEA:AIBN; 100:1</td>
<td>$7.34 \cdot 10^{19}$</td>
<td>$2.15 \cdot 10^{20}$</td>
</tr>
<tr>
<td>PEMA:AIBN; 100:1</td>
<td>$2.07 \cdot 10^{16}$</td>
<td>$1.54 \cdot 10^{18}$</td>
</tr>
</tbody>
</table>

The lowest $E_a$ value for the monomer implies a kinetically facile polymerization reaction. Since rate constant depends on both $A$ and $E_a$ by the Arrhenius relationship;

$$k = Ae^{-E_a/RT}$$

The value of $E_a$ alone does not give a correct idea about the facile nature of the reaction. Therefore, the rate constants were computed using $E_a$ and $A$ values for various temperatures and plotted in Figure 5.

It was found that the rate of reaction is less in case of PEMA than PEA. Under heating conditions, the acryloyl groups polymerize by free radical process. Acryloyl double bonds are sluggish in radical polymerization for two reasons. The double bonds are not activated due to the initiator concentration. Secondly, the steric factor around the acryloyl double bonds retards the polymerization. In present case, same initiator concentration was used for polymerization. Hence, the difference in polymerizability came from the difference in steric hindrance around the acryloyl double bonds. For PEA, smaller steric hindrance was expected to be favorable for free radical polymerization. However, in case of PEMA, α-methyl group on the double bond and 2-phenylethyl on ester group have influenced the process of free-radical polymerization. As the steric hindrance in PEMA is more than PEA, the polymerizability of the monomers was expected to be in the reverse order, viz. PEA> PEMA and the kinetic study confirmed this order of estimation.

![Figure 5: Temperature dependency of rate constants in case of (a) Kissinger and (b) Ozawa](image)

CONCLUSION

Free radical bulk polymerization kinetics of 2-phenylethyl (meth)acrylate was studied by non-isothermal differential scanning calorimetry. Kinetics of free radical polymerization of the monomers in the presence of 2,2’-azobisisobutyronitrile (AIBN) as initiator were investigated by differential scanning calorimetry in the non-isothermal mode. The polymerization was investigated with varying ramp rates, at different initiator concentrations. Based upon the peak temperature dependence on heating rates, the energy of activation ($E_a$) was evaluated by Kissinger and Ozawa methods. It was found that the rate of reaction is lower in case of PEMA than PEA.

REFERENCES