Estimation of Activation Energy for the Free Radical Polymerization by Using Isoconversional Analysis

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등전환 분석(Isoconversional Analysis)을 이용한 자유라디칼 중합의 활성화 에너지 계산

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ABSTRACT : In this paper, the simple way to evaluate the value of the activation energy for the overall rate of free radical polymerization by using DSC thermograms was studied using free radical polymerization of butylacrylate as a model. Activation ehergies were determined at heating rates of 1, 2, 5, and 10℃/min by applying the multiple scanning-rate methods of Kissinger, Osawa, and half-width methods as well as the single rate method of Barrett. The value of the overall activation energy measured was closely matched with the values calculated from individual data. This work also demonstrated that the use of the isoconversional method was a simple and effective way to estimate the activation energy for the overall free radical polymerization

요 약 : 이 연구는 열분석법을 이용하여 간단하게 자유 라디칼 중합의 활성화 에너지를 결정하는 방법을 부틸 아크릴레이트을 모델로 하여 구했다. 활성화 에너지는 Kissinger, Osawa 및 half-width법인 다수의 주사 속도법 (multiple scanning-rate method)을 이용하여 1 ℃/min, 2 ℃/min, 5 ℃/min, 그리고 10 ℃/min로 측정하였으며 단수 주사 속도법인 Barret 법을 이용하여 구하였다. 열분석법에 의해 구해진 중합반응의 활성화 에너지는 개시반응, 성장반응 및 종결반응의 각각의 활성화 에너지에서 계산된 전체 중합반응에서의 활성화 에너지와 가깝게 접근하였다.

Keywords : activation energy, free radical polymerization, butylacrylate, isoconversional analysis

I. Introduction

Differential scanning calorimetry (DSC) is a convenient tool to study the kinetic behavior of polymerization. DSC is used for characterizing crosslinking kinetics of thermosetting systems such as epoxy and unsaturated polyester. We can analyze the actual overall rate of reaction from DSC data because heat flow from the reaction system considered all the contributions of reactions. Kinetic analysis of the reaction is usually based on a single kinetic equation.[1]

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

(1)

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where t is the reaction time, T is the temperature, α is the extent of conversion, and f(α) is the reaction model. The explicit temperature dependence of the rate constant, k, is introduced by replacing k(T) with the Arrhenius equation, which gives

$$\frac{d\alpha}{dt} = A \exp(\frac{-E}{RT}) f(\alpha) \tag{2}$$

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

From the practical point of view, nonisothermal kinetics has found widespread use due mainly to the convenience of rapid access to kinetic parameters. In nonisothermal conditions, when the temperature varies with time according to a constant heating rate, β=dT/dt, the kinetics of thermal transformations are represented by :

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp(\frac{-E}{RT}) f(\alpha) \tag{3}$$

To evaluate the parameters A and E by equations (2) and (3), the experimental data are fitted to reaction model. When applied to non-isothermal data, model fitting methods tend to produce highly unreliable values of Arrhenius parameters.[2] These problems can be resolved by using model free methods that allow the activation energy to be evaluated without assuming any reaction model.[3] To use these methods one has to perform a series of experiments at different heating rates.

The effective activation energy determined from the overall rate measurements should be a function of both temperature and extent of reaction. If changes in the overall reaction rate are associated with changes in the activation energy, they can be detected by using the model-free isoconversional methods.[4] These methods are based on the isoconversional principle that the reaction rate at a constant extent of conversion is only a function of the temperature.

$$\left[\frac{d\ln(d\alpha/dt)}{dT^{-1}}\right]_\alpha = \frac{-E_\alpha}{R} \tag{4}$$

Henceforth the subscript α indicates the value related to a given extent of conversion. This equation shows the E_α varies with α, which gives insight the change of reaction behavior during overall reaction rate.

In the free radical polymerization, there are numbers of reaction rates for characterizing the overall process of reactions, such as rate of decomposition of initiator, rate of propagation, and rate of termination. But practically, we are mainly interested in the overall rate of polymerization which is not need to separate each of rate of component reactions. The overall rate of polymerization, R_p, is represented by[5]:

$$R_p = k_p \left(\frac{f k_d [I]}{k_t}\right)^{\frac{1}{2}} [M] \tag{5}$$

where k_p is the rate of propagation, f is the initiator efficiency, k_d is the rate of decomposition of initiator, k_t is the rate of termination, [I] is the concentration of the initiator and [M] is the concentration of monomers.

If we neglect the temperature dependence of f, the temperature dependence of overall rate of polymerization is given by following relation :

$$R_p = C \exp\left(-\frac{E_p + \frac{E_d}{2} - \frac{E_t}{2}}{RT}\right) \tag{6}$$

where all the temperature-independent quantities are involved into a single constant C.

From above equation, the value of (E_p+Ed/2-Et/2) is important for characterizing the temperature dependence of the overall rate of polymerization.

In this experiment, the simple way to evaluate the value of (E_p+Ed/2-Et/2) by using DSC thermogram

was studied by using free radical polymerization of butylacrylate as a model. This work also demonstrated that the use of the isoconversional method was a simple and effective way to estimate the activation energy for overall free radical polymerization. The approach for isoconversional kinetic analysis that offers the effective activation energy at a given conversion helps not only to disclose the complexity of a process but also to identify its kinetic scheme.

II. Experimental

Butylacrylate was washed three times with 10 percent sodium hydroxide solution to remove inhibitors, washed six times with distilled water, dried with calcium hydroxide, and fractionally distilled under reduced pressure prior to use. Azo-bis (isobutyronitrile) (AIBN) was recrystallized from methanol and dried under vacuum prior to use. Differential scanning calorimetry(DSC, TA Instrument) was used to monitor the reaction kinetics. The DSC enthalpy was calibrated using a high purity indium sample; a high purity Tin sample was also used to calibrate the temperature scale. Initial kinetic studies were performed in the scanning mode with the butylacrylate and AIBN being scanned from room temperature to 250 ℃ at the rates of 1, 2, 5, and 10 ℃/min. Samples of approximately 10 mg were used in a sealed aluminum pan for all experiments to prevent evaporation of reactants. The carrier gas was nitrogen at a flow rate of 50 ml/min. The DSC thermograms were analyzed based on the following assumptions : (1) the area under the curves is proportional to the extent of reaction and (2) the heat released at any time (or temperature) is proportional to the number of moles reacted at that time.

To perform isoconversional analysis, the original DSC data were transformed into the form α (conversion) vs. T_α (temperature at conversion α) for heating rates, β.

The effective activation energies at certain conversion were calculated from the slope of the plot of $\ln (\beta / T_\alpha^2)$ vs. $T_\alpha^{-1.4}$

III. Results and Discussion

The activation energy of the free radical polymerization of butylacrylate in the presence of AIBN as an initiator was determined by applying the multiple scanning-rate methods[1] of Kissinger, Osawa, and half-width methods as well as the single rate method of Barrett. The basic equations of each rate method are collected in Table 1.

Figure 1 shows the DSC thermogram for free radical polymerization of butylacrylate in the presence of 0.01 mol% of AIBN as an initiator at heating rates of 1, 2, 5, and 10 ℃/min. Heat is evolved during the polymerization, and the exothermic peaks shown in Figure 1 are characterized by a maximum temperature T_{max}. It was observed that the values of T_{max} increased with the scanning rate.

Table 1. Differential Methods Used in Non-isothermal Kinetic Analysis (linear plots : y = mx + c)

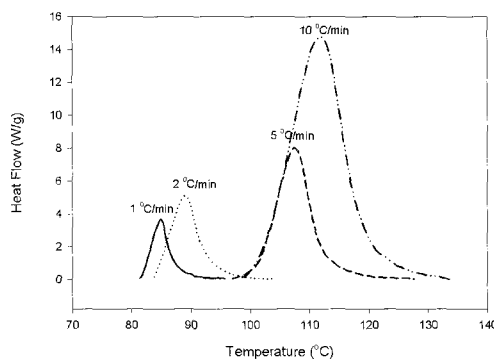| Method	y	x	Slope (m)
Kissinger	$\ln[\phi/(T_{max})^2]$	$1/T_{max}$	$-E/R$
Osawa	$\ln \phi$	$1/T_{max}$	$-E/R$
Half-width	$\ln t_{1/2}$	$1/T_{max}$	E/R
Barret	$\ln k^a$	$1/T$	$-E/R$

[a] $k(dH_t/dt)/(H_r - H_t)$

Figure 1. DSC thermograms for free radical polymerization of butylacrylate in the presence of AIBN as an initiator.

The Barrett method demonstrated a useful method to investigate the rate of reaction and kinetic parameters. In Barrett method, deviation from linearity in the plot of ln k versus 1/T provides additional information about reactions, such as diffusion process and gel effect.[1]

The conversions (α) of the polymerization at the polymerization time t was determined from the heat evolved up to that time, ΔH_t, by the expression :

$$\alpha = \frac{\Delta H_t}{\Delta H_r} \qquad (7)$$

where ΔH_t is the partial area under a DSC trace up to the time t and ΔH_r is the overall heat of reaction.

In this work, the activation energies were determined at all the temperature scanning rates. Table 2 shows the results. The Barrett method provided higher values than the others obtained by multiple scanning-rate methods. The value obtained from half-width method shows far below than those obtained from other methods.

In the reference,[6] the values of the activation energies for the of decomposition of AIBN, propa-gation, and termination were 52.3, 125, and 73.7 kJ/mol, respectively. From above values, we can calculate the overall activation energy by applying the following equation ($E_p+Ed/2-Et/2$). The value of

the overall activation energy was about 78.0 kJ/mol which was closely matched with the values measured from thermogram of DSC, especially by the Kissinger method.

Figure 2 shows the relationship between reaction rate and temperature. The reaction system demonstrated similar behavior with increasing the scanning rate. A shift of the ln k values to higher temperatures (lower 1/T values) is observed.

At the region of low and high temperatures, the rate of polymerization was increased sharply. But in the region of middle temperature, the rates of polymerizations were increased slowly.

The similar behavior is obtained in Figure 3, which shows the shift of ln k as a function of yield. Initial sharp increase of polymerization was shown from 0.05 until about 0.2 extent of reaction. Second stage shows the slow increase of reaction afterward. Third stage shows a sharp increase.

Figure 4 shows the dependence of the activation energy characterized by isoconversional method on the extent of conversion for the free radical polymerization of butylacrylate in the presence of AIBN as an initiator.

Activation energies characterized by isoconversional method were ranged from about 90.0 to 70.0 kJ/mol which closely matched with experimental values. Activation energies in the range of $0.4 < \alpha < 0.8$ were approximately constant with
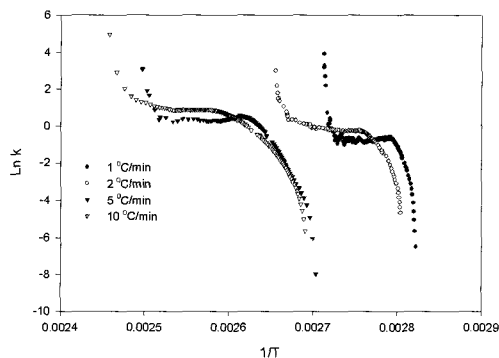
Table 2. Energies of Activation for the Free Radical Polymerization of Butylacrylate in the Presence of AIBN as Initiator

Method	Energy of activation (kJ/mol)			
	1 ℃/min	2 ℃/min	5 ℃/min	10 ℃/min
Barrett*	85	89	108	116
Kissinger	76			
Osawa	84			
Half width	47			
Literature**	78			

* For Barrett method, calculations were performed for the linear part of the plot.
** Energy of activation (kJ/mol) obtained by the result of calculation of ($E_p+Ed/2-Et/2$). The value of Ep, Ed, and Et are 52.3 kJ/mol, 125 kJ/mol, and 73.7 kJ/mol, respectively.

Figure 2. Plot of ln k versus T^{-1} (K^{-1}) for the free radical polymerization of butylacrylate.
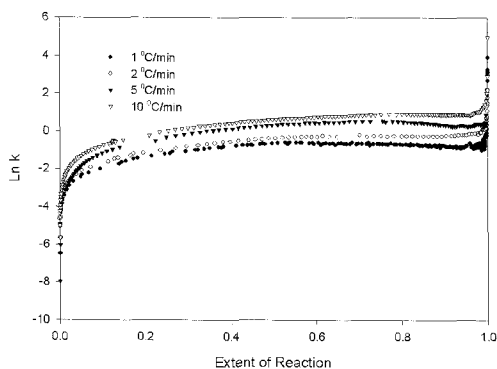
Figure 3. Plot of ln k versus extent of conversion for the free radical polymerization of butylacrylate.
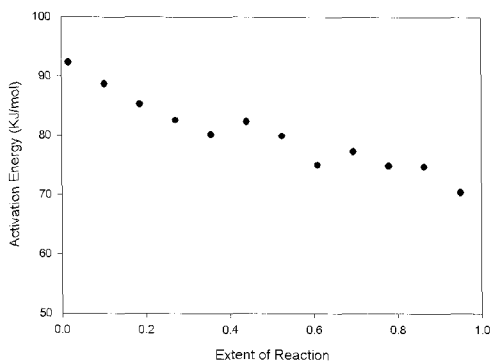

Figure 4. Dependence of the activation energy characterized by isoconversional method on the extent of conversion for the free radical polymerization of butylacrylate.

a mean value of 78 kJ/mol. On the other hand the values of activation energy at initial stage and final stage were found to be deviated from the value of 78 kJ/mol, probably due to the deviation from the equation of overall rate of polymerization.[7] The results clearly shows that the isoconversional kinetic analysis that offers the effective activation energy at a given conversion helps not only to disclose the complexity of a process but also to identify its kinetic scheme.

IV. Conclusion

Simple way to evaluate the values of the activation energy for the overall rate of free radical polymerization by using DSC thermograms was studied using free radical polymerization of butylacrylate as a model. The value of the overall activation energy was about 78.0 kJ/mol which was closely matched with the values measured from thermogram of DSC, especially Kissinger method. Activation energies characterized by isoconversional method were ranged from about 90.0 to 70.0 kJ/mol which closely matched with experimental values. Activation energies in the range of 0.4 < α < 0.8 were approximately constant with a mean value of 78 kJ/mol. On the other hand the values of activation energy at initial stage and final stage were found to be deviated from the value of 78 kJ/mol, probably due to the deviation from the equation of overall rate of polymerization.

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