NON-ISOTHERMAL KINETICS OF FREE-RADICAL POLYMERIZATION OF 2,2-DINITRO-1-BUTYL ACRYLATE

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The free-radical bulk polymerization of 2,2-dinitro-1-butyl-acrylate (DNBA) in the presence of 2,2'-azobisisobutyronitrile (AIBN) as the initiator was investigated by DSC in the non-isothermal mode. Kissinger and Ozawa methods were applied to determine the activation energy (E_a) and the reaction order of free-radical polymerization. The results showed that the temperature of exothermic polymerization peaks increased with increasing the heating rate. The reaction order of non-isothermal polymerization of DNBA in the presence of AIBN is approximately 1. The average activation energy (92.91 ± 1.88 kJ mol^{-1}) obtained was smaller slightly than the value of E_a=96.82 kJ mol^{-1} found with the Barrett method.

Introduction

Thermal analysis techniques such as thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) provide the physical quantities during not only physical but also chemical changes. The kinetics of physical or chemical changes and the mixed state of polymer blends are evaluated from TG and DSC data [1–4]. DSC is a convenient tool to observe the reaction as endothermic or exothermic heat flow. The kinetics of chemical reaction is available from DSC exothermal peak obtained from either isothermal or non-isothermal measurements [5, 6].

Geminal dinitro polymers are interesting material in the field of explosives, because it is stable and suits the binders of plastic bonded explosive (PBX). Among them, some geminal dinitro polymers have been found application in the production of energetic materials [7]. The preparation of nitroalkyl acrylates have been reported [8]. The heat of polymerization of nitropropyl (meth)acrylates monomers has been studied by DSC in dynamic and isothermal modes [9]. However, the kinetic studies on free radical polymerization of gem-dinitroalkyl acrylate monomer are scarcely reported.

In this work, 2,2-dinitro-1-butyl-acrylate (DNBA) was prepared by esterification of acrylic acid with 2,2-dinitrobutanol in an excess of acrylic acid [9], the free-radical bulk polymerization of DNBA in the presence of AIBN as the initiator was investigated by DSC in the non-isothermal mode. Kissinger [10] and

Ozawa [11] methods were applied to determine the E_a and reaction order of free-radical polymerization.

Experimental

Materials

2,2'-azobisisobutyronitrile (AIBN) was recrystallized twice from ethanol solution. DNBA was prepared by esterification of acrylic acid with 2,2-dinitrobutanol. The esterification was carried out in the presence polymeric phosphoric acid and hydroquinone in ethylene dichloride solution. The DNBA was further purified by distillation under a reduced pressure. It was characterized by FTIR and NMR.

DNBA, IR(KBr): 3436 cm^{-1} (=CH), 2971 cm^{-1} (=CH$_2$), 1746 cm^{-1} (C=O), 1631 cm^{-1} (C=C), 1562 and 1325 cm^{-1} (NO$_2$), 1168 cm^{-1} (C–O–C). ^{1}H NMR (CD$_3$Cl, 400 MHz): δ6.42 (t, 1H, =CH–), δ5.96–6.13 (m, 2H, =CH$_2$), δ5.00 (s, 2H, OCH$_2$), δ2.58–2.63 (q, 2H, CH$_2$), δ1.04–1.07 (t, 3H, CH$_3$).

Methods

DSC measurements

DSC experiments were performed at varying scan speeds using a Seiko Differential Scanning Calorimeter (DSC6200) connected to a Seiko thermal analysis system.

Samples of mixture (monomer+initiator) were prepared in conical flasks of 25 mL and degassed by
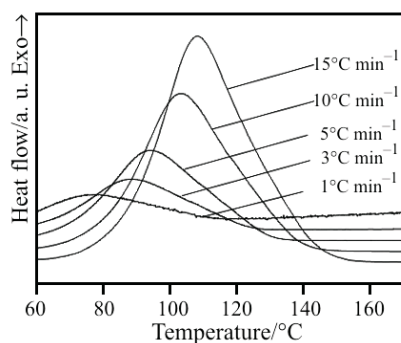
N$_2$ at 0°C. The compositions of the samples were: [monomer]/[AIBN]=46.41, 77.13, 119.15, 187.74, 224.09 mol mol^{-1}, respectively. The measurements were performed under nitrogen in aluminum pans filled with 25 mg of the sample for each polymerization experiment. Heating rates of 1, 3, 5, 10 and 15°C min^{-1} were used. Each sample was placed in the sample holder assembly of the DSC at 40°C and scanned up to 190°C. Temperature calibration of the calorimeter was performed with pure indium metal of melting point 156.6°C.

Results and discussion

Figure 1 shows five thermograms for the DNBA polymerization obtained at scan speed of 1, 3, 5, 10 and 15°C min^{-1}, respectively. The maximum of the curves shifted to higher temperature with increasing heating rate due to the dependence of monomer conversion on time and temperature. The similar results have been found in other four samples with different molar ratios of [DNBA]/[AIBN]. Table 1 gathers the exothermic DSC peak temperatures of every sample at different heating rates.

Kinetic parameters

The kinetic analysis of free-radical polymerization curves involves the search for the kinetic parameters reaction order (*n*) and the E_a associated with the pro-

Fig. 1 DSC curve of the sample with [DNBA]/[AIBN]=46.41 at different heating rates

cess. 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.

Activation energy

Kissinger method

As it is known, the method allows the calculation of the activation energy of the reactive process by using an equation that relates and temperature and scan speed. Kissinger method was proposed to permit the kinetic analysis of DTA curves. It was proved that the method was used for DSC date [12]. Kissinger equation can be described as [10]:

$$\frac{d \ln \frac{\phi}{T_p^2}}{d \frac{1}{T_p}} = -\frac{E_a}{R} \qquad (1)$$

where T_p, ϕ, E_a and R is peak indicating temperature, heating rate, activation energy and the gas constant, respectively. According to Eq. (1), we obtain the following equation.

$$\ln \frac{\phi}{T_p^2} = -\frac{E_a}{R}\frac{1}{T_p} + C \qquad (2)$$

The left term of the above equation was plotted *vs.* $1/T_p$, and then E_a was evaluated from the slope. The obtained E_a values were listed in Table 3, the mean E_a value was 91.05 kJ mol^{-1}.

Ozawa method

Ozawa method allows us to determine the activation energy E_a for n^{th}-order reactions [5]. It is based on the variation of peak exotherm temperature with heating rate. Assuming that the extent of reaction at the peak temperature is constant and independent of heating rate, Ozawa [11] derived the following expression:

$$\ln \phi = \text{const} - 1.052 \frac{E_a}{RT_p} \qquad (3)$$

Table 1 DSC peak temperature of DNBA/AIBN samples at different heating rates

ϕ/°C min^{-1}	T_p/K				
	[DNBA]/[AIBN]				
	46.41	77.13	119.15	187.74	224.09
1	350.85	355.85	357.67	359.85	363.15
3	362.15	366.45	373.35	374.15	374.45
5	367.45	371.55	378.15	379.35	381.25
10	376.95	380.85	383.35	390.15	390.85
15	381.55	386.55	392.05	392.85	394.95

Table 2 Activation energies for DNBA non-isothermal polymerization

[DNBA]/[AIBN]	Kissinger method		Ozawa method	
	E_a/kJ mol^{-1}	r	E_a/kJ mol^{-1}	r
46.41	91.12	0.9987	94.73	0.9991
77.13	94.46	0.9972	98.06	0.9976
119.15	89.23	0.9884	93.01	0.9898
187.74	87.60	0.9965	91.46	0.9969
224.09	92.85	0.9986	96.62	0.9988
mean	91.05		94.78	

Table 3 Non-isothermal polyreaction orders of DNBA/AIBN samples with different molar ratios at different heating rates

ϕ/°C min^{-1}	n				
	[DNBA]/[AIBN]				
	46.41	77.13	119.15	187.74	224.09
1	1.02	1.04	1.12	1.14	1.10
3	1.09	1.12	1.16	1.06	1.09
5	1.08	1.11	1.12	1.14	1.07
10	1.06	1.10	1.12	1.07	1.02
15	1.01	1.10	1.14	1.12	1.08
mean	1.05	1.09	1.13	1.11	1.07

This expression shows a linear dependence of the reciprocal absolute peak temperature T_p on the logarithm of heating rate ϕ. The activation energy E_a is calculated from the slope of the straight line obtained by Ozawa plot. A good fit was observed with the linear regression coefficients of r=0.99. From values tabulated in Table 2, a mean value of E_a=94.78 kJ mol^{-1} was obtained, which agreed reasonably well with that evaluated by Kissinger method.

The polymerization kinetics of an acrylic ester initiated with AIBN is considered by a mechanism of free-radical polymerization. This consists of a sequence of steps: initiation, propagation and termination. The mean E_a obtained by Kissinger equation 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).

Reaction order

Kissinger [10] indicated that the reaction order (n) could be determined form the shape of endothermic differential thermal analysis peak. The n is given by:

$$n=1.26S^{0.5} \qquad (4)$$

where S is the shape index, S=a/b. The value of a and b is obtained as shown in Fig. 2. A series of S values were obtained from DSC curves for the sample at different heating rate. The corresponding non-isother-

mal polymerization orders were calculated from Eq. (4), the values of n were given in Table 3. From Table 3 the mean reaction order was 1.09±0.4, which was a very close approximation to 1. The result indicated that the free-radical bulk polymerization of DNBA was 1st-order reaction in the range of molar ratios [DNBA]/[AIBN] shown in Table 3.

Barrett method

If it is assumed that the heat evolved is proportional to the number of moles reacted, and as the polymerization is first order, the rate constant (k) of polyreaction is estimated from variation of monomer conversion (α) vs. time (t), using Barrett's relation [13], as follows:

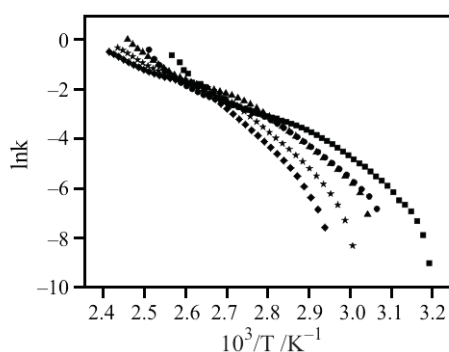$$k = \frac{d\alpha\ /\ dt}{A-a} = \frac{dH\ /\ dt}{A-a} \qquad (5)$$

where A is the total area of the DSC peak, α is the partial area at a particular temperature, dH/dt is the heat
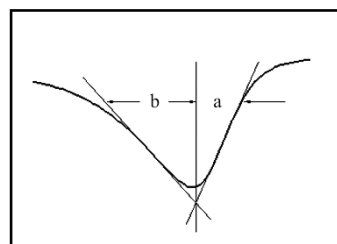
Fig. 2 Shape index of the DSC curve

Table 4 E_a of [DNBA]/[AIBN] samples at different heating rates

$\phi/°C\ min^{-1}$	[DNBA]/[AIBN]											
	46.41		77.13		119.15		187.74		224.09			
	$E_a/kJ\ mol^{-1}$	T-intervals/K	$E_a/kJ\ mol^{-1}$	T-intervals/K	$E_a/kJ\ mol^{-1}$	T-intervals/K	$E_a/kJ\ mol^{-1}$	T-intervals/K	$E_a/kJ\ mol^{-1}$	T-intervals/K		
1	89.68	324–350	74.87	339–375	73.10	344–380	78.13	339–375	80.44	339–375		
3	98.20	332–360	83.55	338–374	94.15	354–390	91.66	344–380	114.38	340–376		
5	99.97	337–367	92.10	341–377	100.37	355–391	93.26	356–392	98.12	351–387		
10	106.12	345–381	97.06	353–389	100.3	351–387	104.50	367–403	105.96	356–392		
15	123.34	346–382	99.32	360–396	104.46	366–402	103.21	369–405	114.15	367–402		
mean	103.46		89.38		94.48		94.15		102.61			
Overall mean E_a					96.82							

Fig. 3 Arrhenius plots of the sample ([DNPA]/[AIBN]=46.41) in different heating rates. Heating rate: ■ – 1, ● – 3, ▲ – 5, ★ – 10 and ◆ – 15°C min^{-1}

flow (J min^{-1}). The Barrett method assumes that the temperature dependence of the reaction rate follows Arrhenius type relationship:

$$k = Ze^{-E_a/RT} \qquad (6)$$

This expression can be written in the logarithmic form:

$$\ln k = \ln \frac{dH/dt}{A-a} = \ln A - \frac{E_a}{RT} \qquad (7)$$

In Fig. 3 Arrhenius plots for the polymerization of the sample with [DNBA]/[AIBN]=46.41 at five heating rates are shown. Each curve consists of 3 parts. The non-linear part of the curve at low temperature is ascribed to errors introduced by small heat generations, the non-linear part at high temperature is caused by yet unknown factors [14]. The E_a values were calculated from the intermediate linear part. Table 4 gives the E_a values of the different molar ratio sample obtained in temperature intervals for each heating rate considering Eq. (7). In general, the kinetic parameters are not constant and show a dependence upon the heating rate. As shown in Table 4, the E_a value of the every sample increased with increasing heating rate. In the range of experimental heating rate and [DNPA]/[AIBN] molar ratio, overall average activation energy was 96.82 kJ mol^{-1}, which was slightly higher than the mean E_a (92.91±1.88 kJ mol^{-1}) evaluated by Kissinger and Ozawa method.

Conclusions

- The polymerization of DNBA in the presence of AIBN as the initiator was studied by means of DSC with various heating rates. Exothermic peak temperature on the DSC curve increased with the heating rate increased, the starting temperature of DNBA polymerization shifted to higher with decreasing AIBN amount at a fixed heating rate.
- Based upon the peak temperature dependence on heating rates, the energy of activation was evaluated by Kissinger and Ozawa methods. The mean value of E_a=92.91±1.88 kJ mol^{-1} obtained is smaller slightly than the value of E_a=96.82 kJ mol^{-1} found with the Barrett method.
- By applying the Kissinger method, the non-isothermal polymerization of DNBA in the presence of AIBN as the initiator was the first order reaction.

Acknowledgements

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