

DIFFERENTIAL SCANNING CALORIMETRIC STUDY ON FREE-RADICAL POLYMERIZATION OF *gem*-DINITROALKYL ACRYLATES AND METHACRYLATE

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2,2-dinitropropyl acrylate (DNPA), 2,2-dinitrobutyl acrylate (DNBA) and 2,2-dinitrobutyl methacrylate (DNBMA) were synthesized and the kinetics of their free-radical polymerization in the presence of 2,2'-azobisisobutyronitrile (AIBN) were investigated by DSC in the non-isothermal mode. The kinetics of the free-radical polymerization as estimated by the Kissinger and Ozawa methods showed that the reaction is disfavoured by increasing steric hindrance around the acrylyl double bond. The rate constants calculated from the activation parameters showed the structural dependency. The polymerization kinetics revealed that the polymerizability of three monomers decreased due to the presence of substituent methyl groups on the acrylyl double bond and 2,2-dinitrobutyl on ester group. Thus, the polymerization tendency increased in the order DNPA>DNBA>DNBMA.

Keywords: DSC, free-radical polymerization, *gem*-dinitroalkyl acrylate, kinetics

Introduction

Nitroalkyl acrylate polymers have been studied as the energetic binder in the field of propellants and explosives [1, 2]. Among them, 2,2-dinitropropyl acrylate (DNPA) and 2,2-dinitrobutyl acrylate (DNBA) polymer has been applied to the plastic bonded explosive (PBX) [3]. However, kinetic studies on free radical polymerization of *gem*-dinitroalkyl acrylate monomer are scarce.

Differential scanning calorimetry (DSC) is a powerful method for not only evaluating miscibility of crystalline/crystalline polymer blends [4], but also 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 [5–7]. Because of its advantages such as small sample size, handiness of manipulation, rapidity of performance and versatility, DSC seemed to be attractive for studying *gem*-dinitroalkyl acrylate polymerization system. The heat of polymerization of nitropropyl(meth)acrylate monomers has been studied by DSC in dynamic and isothermal modes [3]. We have recently investigated the free-radical bulk polymerization of (DNPA) in the presence of 2,2'-azobisisobutyronitrile (AIBN) by DSC in the non-isothermal mode and determined the activation energy (E_a) and reaction order of free-radical polymerization [8]. In the present paper, we report the kinetics of free-radical polymerization of three

gem-dinitroalkyl (meth)acrylate monomer by DSC and examine the structural dependency.

Experimental

Materials

AIBN was recrystallized twice from ethanol solution. DNPA, DNBA and 2,2-dinitrobutyl methacrylate (DNBMA) were prepared by esterification of (meth)acrylic acid with 2,2-dinitropropanol or 2,2-dinitrobutanol in an excess of (meth)acrylic acid [3]. The esterification was carried out in the presence polymeric phosphoric acid and hydroquinone in ethylene dichloride solution. The DNPA, DNBA and DNBMA were further purified by distillation under a reduced pressure. They were characterized by FTIR and NMR.

DNPA, IR(KBr): 3014(=CH), 2971(=CH₂), 1744(C=O), 1635(C=C), 1575 and 1326(NO₂), 1254 and 1175(C–O–C). ¹H NMR(CD₃Cl, 400 MHz): δ6.45–6.51(d, 1H, CH₂=), δ6.09–6.17(t, 1H, =CH), δ5.98–6.02(d, 1H, CH₂=), δ5.01(s, 2H, CH₂), δ2.22(s, 3H, CH₃).

DNBA, IR(KBr): 3436(=CH), 2971(=CH₂), 1746(C=O), 1631(C=C), 1562 and 1325(NO₂), 1168(C–O–C). ¹H NMR(CD₃Cl, 400 MHz): δ6.42(t, 1H, =CH–), δ5.96–6.13(m, 2H, =CH₂), δ5.00(s, 2H, OCH₂), δ2.58–2.63(q, 2H, CH₂), δ1.04–1.07(t, 3H, CH₃).

DNBMA, IR(KBr): 2984(=CH₂), 1738(C=O), 1638(C=C), 1574 and 1324(NO₂), 1153(C–O–C).

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^1H NMR(CD_3Cl , 400 MHz): δ 6.09(d, 1H, =CH₂), δ 5.65(d, 1H, =CH₂), δ 4.96 (s, 2H, OCH₂), δ 2.60–2.63(q, 2H, CH₂), δ 1.92(s, 3H, =CCH₃), δ 1.06–1.08(t, 3H, CH₃).

DSC measurements

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

Reaction mixture was prepared in conical flasks of 25 mL and degassed by N₂ at 0°C. The composition of the polymerization reaction mixtures was: [monomer]/[AIBN]=229±5 mol mol⁻¹. The measurements were performed under nitrogen in aluminum pans filled with 25 mg of the reaction mixture 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 25°C and scanned up to 180°C. Temperature calibration of the calorimeter was performed with pure indium metal of melting point 156.6°C.

Results and discussion

DSC analyses

Three monomers of gem-dinitroalkyl (meth)acrylate, DNPA, DNBA and DNBMA, were synthesised and were characterized by IR and NMR, both conforming to the expected structure. The AIBN-initiated bulk polymerization of gem-dinitroalkyl (meth)acrylate was measurable by DSC under the non-isothermal condition. Figure 1 showed the dynamic DSC for three monomers polymerization obtained at a heating rate of 10°C min⁻¹. The maximum of the curves shifts to higher temperature in the order of DNPA, DNBA and DNBMA. All curves showed an exotherm and the results of the DSC peak maxima of the exotherm of the monomers, obtained at five heating rates are given

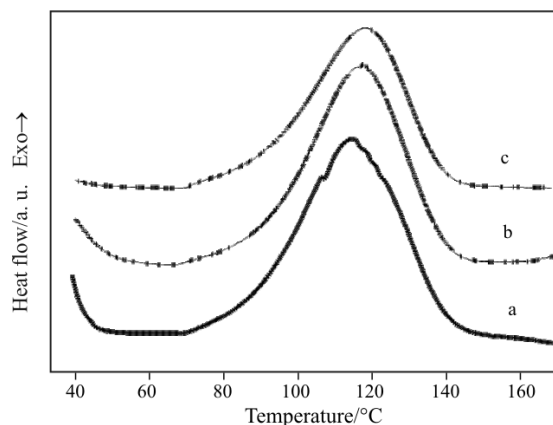


Fig. 1 DSC curves of a – DNPA, b – DNBA and c – DNBMA. Heating rate 10°C min⁻¹

Table 1 DSC peak maxima (in °C) for DNPA, DNBA and DNBMA

Heating rate/ °C min ⁻¹	DNPA	DNBA	DNBMA
	T_p	T_p	T_p
1	91.8	90.0	89.7
3	101.1	101.3	105.5
5	108.8	108.1	111.7
10	115.7	117.7	118.2
15	123.6	121.8	124.5

in Table 1. The peak temperatures increase systematically with increasing heating rates due to the dependence of monomer conversion on time and temperature [7].

Kinetic analysis

It was interested to study the kinetics of the polymerization reaction from the DSC. Since the peak corresponding to the polymerization reaction was well resolved, the non-isothermal methods were employed for the kinetic analyses. Variable heating rates, which depend on peak maxima in DSC were employed for the purpose, where the apparent variations in activation parameters caused by heating rates are taken care of. Moreover, the method do not invoke reaction order or fractional conversion in deriving the kinetic parameters [9]. 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.

Kissinger's method [10] makes use of the Eq. (1)

$$\frac{d[\log(\phi/T_p^2)]}{d(1/T_p)} = -\frac{0.434E}{R} \quad (1)$$

where T_p is the temperature corresponding to the maximum in the DSC exotherm at a heating rate, ϕ .

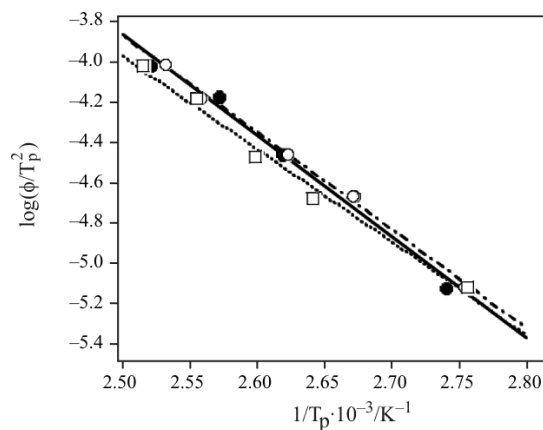


Fig. 2 Determination of activation parameters by Kissinger's method for polymerization reaction of ● – DNPA, ○ – DNBA and □ – DNBMA

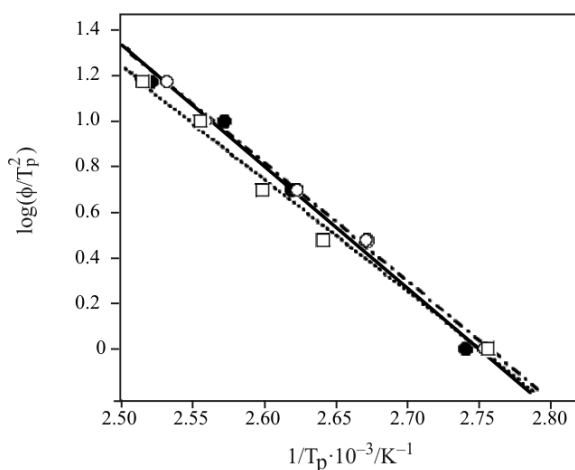


Fig. 3 Determination of activation parameters by Ozawa's method for polymerization reaction of ● – DNPA, ○ – DNBA and □ – DNBMA

The slope of the linear plot of $\log(\phi/T_p^2)$ vs. $1/T_p$ give E .

Ozawa's method [11] uses a similar equation as

$$d \log(\phi) = -0.465 \frac{E}{R} d \frac{1}{T_p} \quad (2)$$

E is obtained from the slope of the plot of $\log \phi$ vs. $1/T_p$. Typical kinetic plots by Kissinger's and Ozawa's methods are shown in Figs 2 and 3, respectively.

A was found from the relation

$$A = \frac{\phi E e^{E/RT_p}}{RT_p^2} \quad (3)$$

The activation parameters are given in Table 2 for all the three monomers for the polymerization reaction. Both the methods give nearly identical values for the reaction.

Kinetics of free-radical polymerization

DSC results indicated free-radical polymerization. The kinetic constants were calculated for the polymerization reaction by the Kissinger and Ozawa methods. The A and E values are compiled in Table 2. The lowest E value for the monomer implies a kinetically facile polymerization reaction. Since rate constant depends on both A and E by the Arrhenius relationship,

Table 2 Polymerization kinetic parameters determined by Kissinger and Ozawa methods

Monomer	Kissinger		Ozawa	
	$E/\text{kJ mol}^{-1}$	A/s^{-1}	$E/\text{kJ mol}^{-1}$	A/s^{-1}
DNPA	96.3	$9.98 \cdot 10^{10}$	95.8	$8.46 \cdot 10^{10}$
DNBA	92.9	$3.42 \cdot 10^{10}$	92.6	$3.13 \cdot 10^{10}$
DNBMA	88.5	$6.82 \cdot 10^9$	88.5	$6.82 \cdot 10^9$

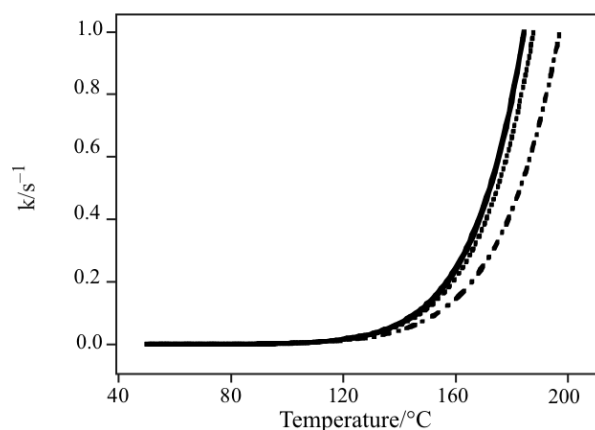


Fig. 4 Temperature dependency of rate constants for polymerization for — – DNPA, --- – DNBA and -.-.- – DNBMA

$k = Ae^{-E/RT}$, the value of E alone does not give a correct idea about the facile nature of the reaction. Therefore, the rate constants were computed using the E and A values for various temperatures and plotted in Fig. 4. It was found that the rate of reaction decreased in this order: DNPA > DNBA > DNBMA.

Under heating conditions, the acrylyl groups polymerize by free radical process. Acrylyl 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 acrylyl double bonds retards the polymerization. In the present cases, the initiator concentration was the same for reaction mixtures. Hence, the difference in polymerizability came from the difference in the steric hindrance around the acrylyl double bonds. For DNPA, the smaller steric hindrance was expected to be favorable for free radical polymerization. However, in the case of DNBMA, α -methyl group on the double bond and 2,2-dinitrobutyl on ester group have influenced the process of free-radical polymerization. As the steric hindrance of monomers increased in the order of DNBMA > DNBA > DNPA, the polymerizability of the monomers was expected to be in the reverse order, viz. DNPA > DNBA > DNBMA and the kinetic study confirmed this order or estimation.

Conclusions

The polymerization process of three monomers of *gem*-dinitroalkyl (meth)acrylate initiated with AIBN was studied by DSC at different heating rates. The kinetic analysis was performed by the Kissinger and Ozawa methods. The results showed a good agreement between two methods. The kinetics of free-radical polymerization as studied by dynamic DSC showed that the small steric hindrance around the acrylyl double bonds was favorable for this reaction. The rate

constants calculated from the activation parameters evidenced it. The polymerization kinetics revealed that the polymerizability decreased by the presence of substituent methyl groups on the acrylyl double bond and 2,2-dinitrobutyl on ester group.

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