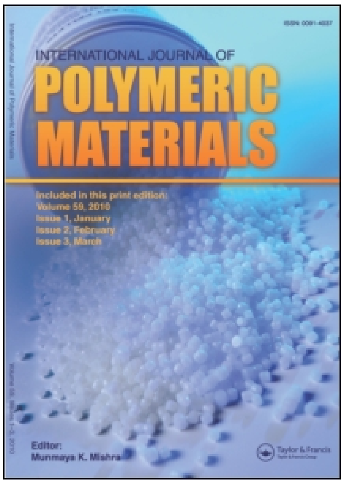

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Kinetic of 8-quinolinyl Methacrylate Polymerization by Differential Scanning Calorimetry

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The kinetic of 8-quinolinyl methacrylate (8-QMA) polymerization was studied using 2,2′-azobisisobutyronitrile (AIBN) as a free radical initiator by differential scanning calorimetry (DSC) under two different experimental variables *viz.*, heating rate and initiator concentration. Borchardt – Daniel (B – D) kinetic method was applied to estimate the various kinetic parameters for the free radical polymerization of 8-QMA. The effect of initiator concentration and heating rate on the rate of polymerization was discussed. The importance of isothermal and isoconversion predictive curves in optimizing the polymerization process parameters has also been discussed.

Keywords: 8-quinolinyl methacrylate; differential scanning calorimetry; Borchardt – Daniel kinetic; isothermal; isoconversion

INTRODUCTION

Differential scanning calorimetry 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 transition such as glass transition temperature (Tg) and melting temperature (Tm) of the polymers and to study the varieties of

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reactions such as crystallization, polymerization, decomposition, oxidation, vulcanization and curing reactions [1–7] Patel *et al.* [8] empolyed DSC to study the comparative curing profile of liquid epoxy resin using hydroxy terminated aryl-ether sulfone oligomers, 4,4′-diaminodiphenyl sulfone (DDS) and phthalic anhydride (PA) as a curing agents. Feliu *et al.* [9] studied the kinetic of bulk polymerization of methyl methacrylate with and without using AIBN by DSC technique.

The present work describes the kinetic study on the free radical bulk polymerization of 8-QMA by DSC technique.

EXPERIMENTAL

Materials

Methacrylic acid, Benzoyl chloride, 8-hydroxyquinoline and AIBN used were of analytical grade reagents.

Synthesis of 8-quinolinyl Methacrylate

The 8-quinolinyl methacrylate monomer was synthesized as per the reported process [10].

Kinetic of 8-QMA Polymerization by DSC

Du-pont-910 DSC attached with 9900 thermal analyzer data acquisition and processing system was used for the present study. Three separate samples, each containing about 5 mg of 8-QMA thoroughly mixed with 1% w/w AIBN, were sealed in the DSC aluminium sample pans. DSC thermogram were recorded using these three samples at 5°, 10°, and 15°C/min heating rate in nitrogen atmosphere from room temperature to 250°C. Similar experiments were performed with 8-QMA containing 2% and 3% w/w AIBN. Thermal data from these experiment were processed further to evaluate various kinetic parameters by B–D DSC kinetic method.

Borchardt and Daniels [11] proposed a technique to study the reaction kinetics by application of differential thermal analysis (DTA). This technique has been refined significantly by subsequent researchers in the thermal analysis field to make it applicable in conjunction with the DSC system [12, 13].

The B–D method assumes that the reaction follows *n*th order kinetics, *i.e.*, obeys the relationship:

$$\frac{d\alpha}{dt} = k_{(T)}(1-\alpha)^n$$

Where

α = fractional conversion (dimensionless)
$k_{(T)}$ = specific rate constant at temperature T (sec^{-1})
n = reaction order (dimensionless)

The method also assumes that the temperature dependence of the reaction rate follows the Arrhenius expression:

$$k_{(T)} = Ze^{-E/RT}$$

Where

Z = pre-exponential factor (sec^{-1})
E = activation energy (J mol^{-1})
R = gas constant (8.314 J mol$^{-1}\cdot$K)
T = absolute temperature (°K)

DSC is used to measure heat flow into or out of a sample as it is exposed to a controlled thermal profile. With the development of computer-aided data analyses in the thermal techniques, kinetic methods to study the polymerization reactions have become more widely used. B–D DSC kinetic data analysis software (DuPont-V 1.0 G) used in the present study in conjunction with DuPont-910 DSC system provide a rapid automatic calculation of reaction order (n), activation energy (E), pre-exponential factor (Z) and heat of reaction (ΔH). These values are then used in the data analysis programme to provide a series of predictive thermal curves to assess the polymerization process in terms of conversion, time and temperature. These data are of particular interest in process development for predicting optimum polymerization conditions as well as in the process control for optimization of the conversion.

RESULTS AND DISCUSSION

Table I shows various kinetic parameters of free radical polymerization of 8-QMA evaluated by B – D DSC kinetic method using different initiator concentration and at different heating rates. The values of activation energy (*Ea*) ranges from 265 to 518, 230 to 321 and 121 to 265 kJ mole^{-1} for 1%, 2% and 3% AIBN concentration respectively. It is observed that, excluding few exception in some practical reading, with increase in rate of heating, activation energy decreases as it is expected in case of free radical polymerization of vinyl monomers. The heat of fusion (ΔH_f) ranges from 64 to 96, 50 to 75 and 152 to 215 kJ mole^{-1} whereas heat of polymerization ranges from 104 to 118, 64 to 97 and 193 to 273 J g^{-1} for 1%, 2% and 3% AIBN concentration respectively. The order of reaction (*n*) varied from 1 to 3 and decreasing with increase in heating rate whereas value of pre-exponential factor (log Z) ranges from 17 to 80 min^{-1} and decreases with increase in, both, initiator concentration and rate of heating.

Figures 1(a) – (c) shows comparative DSC exotherm of 8-QMA polymerization initiated respectively by 1%, 2% and 3% w/w AIBN at three different heating rates. It is observed from these curves that peak maximum temperature of polymerization exotherm increases with increase in, both, heating rate and initiator concentration. Figure 2 shows an illustrative raw data curve for the DSC kinetic study of the 8-QMA polymerization at 5°C/min heating rate using 1% AIBN

TABLE I B – D DSC kinetic parameters for free radical polymerization of 8-QMA

Sample	*Heating rate* ($°C/min$)	*Sample weight* (mg)	*Energy of activation* Ea ($kJ \cdot mol^{-1}$)	*Heat of fusion* ΔH_f ($kJ \cdot mol^{-1}$)	*Heat of reaction* (Jg^{-1})	*Order of reaction* n	*Log Z* (min^{-1})
8-QMA + AIBN (1% w/w)	5	5.10	518	83	104	3	80
	10	4.45	274	64	112	2	41
	15	4.76	265	96	118	1	40
8-QMA + AIBN (2% w/w)	5	3.80	321	50	64	3	49
	10	6.30	340	75	97	2	51
	15	3.15	230	58	75	2	34
8-QMA + AIBN (3% w/w)	5	4.30	265	152	193	3	40
	10	2.30	121	215	273	2	17
	15	3.33	122	186	233	1	17

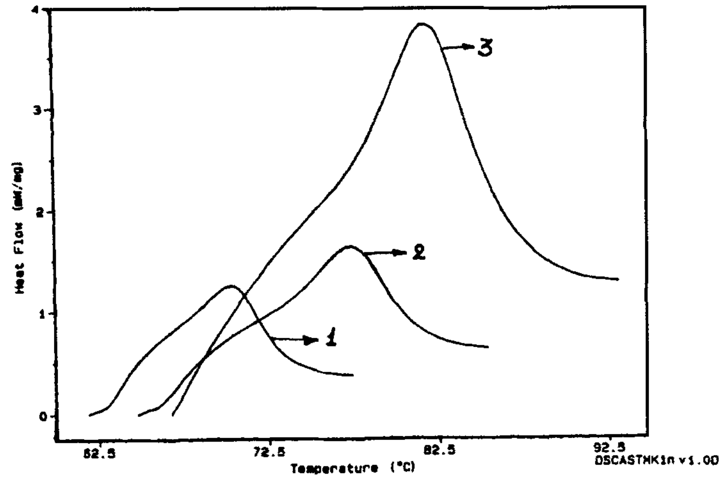

FIGURE 1(a) DSC exotherm of 8-QMA + 1% w/w AIBN Polymerization at (1) 5°, (2) 10°, (3) 15°C/min.

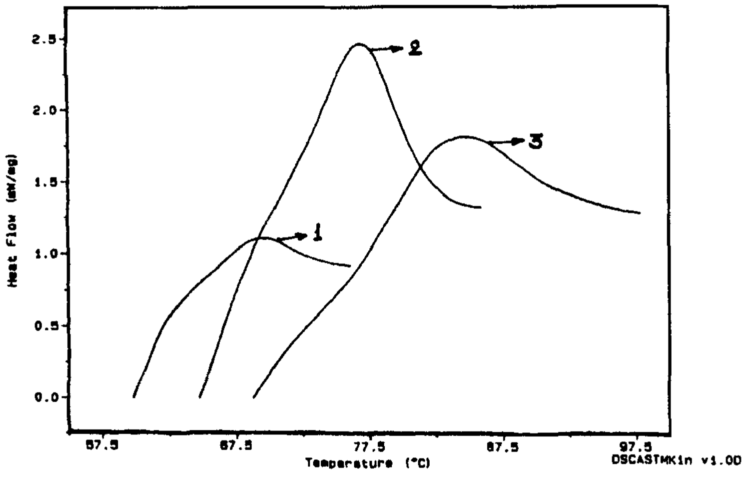

FIGURE 1(b) DSC exotherm of 8-QMA + 2% w/w AIBN Polymerization at (1) 5°, (2) 10°, (3) 15°C/min.

initiator. Two types of data presentation are helpful for comparative studies of polymerization profiles. The isothermal polymerization predictive curves (Fig. 3), consisting of a series of isothermal plots, are

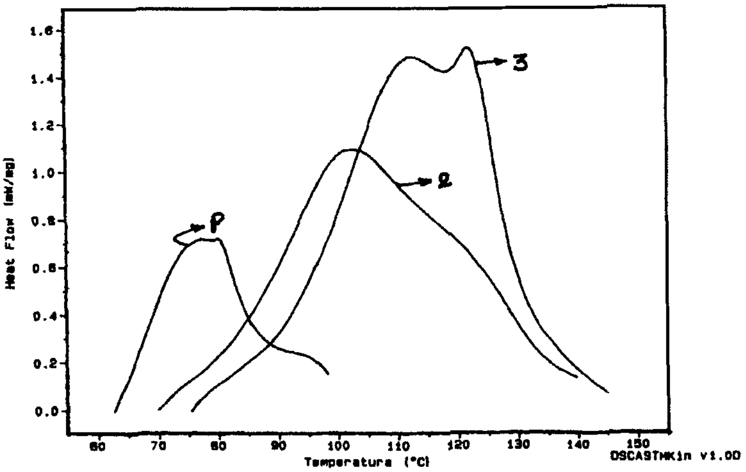

FIGURE 1(c) DSC exotherm of **8-QMA + 3% w/w AIBN** Polymerization at (1) 5°, (2) 10°, (3) 15°C/min.

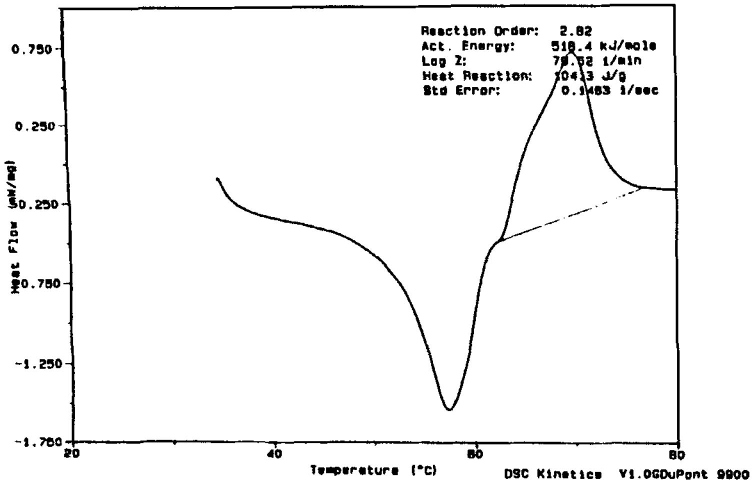

FIGURE 2 An illustrative raw data curve for the DSC kinetic study of 8-QMA polymerization.

most useful in setting of polymerization cycles for a novel systems. It is observed from these curves that as the temperature of polymerization increases, the time required to achieve a particular degree of conversion

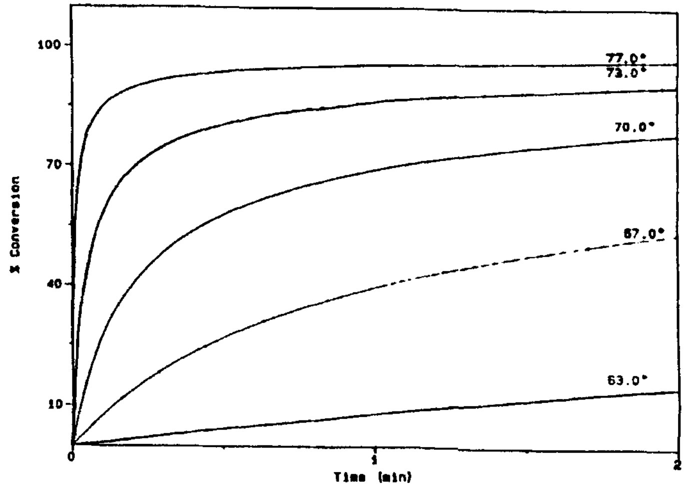

FIGURE 3 An illustrative **isothermal** predictive polymerization curves for 8-QMA.

decreases to the considerable extent. Moreover, at lower polymerization temperature, the relation between percentage conversion and time is linear as it is shown in Figure 3 for 63°C temperature, whereas at higher temperature, the rate of % conversion in the initial stage increases rapidly as it is shown for 67, 70 73 and 77°C in the isothermal curves. These predictive curves may provide the way to select optimum temperature of polymerization to achieve optimum rate of % conversion with respect to time thereby to synthesized the polymers with required properties because polymerization temperature and rate of conversion are observed to effect many important properties of polymers such as glass transition temperature, melting range, molecular weight and its distribution and thermal degradation profile.

Figure 4 shows an alternative report option described as an isoconversion predictive polymerization curves. This series curves can be use to provide time and temperature profiles for selection of optimum polymerization time required to achieve a specific degree of conversion. In practice the use of such predictive curves make the process development work much faster and easier.

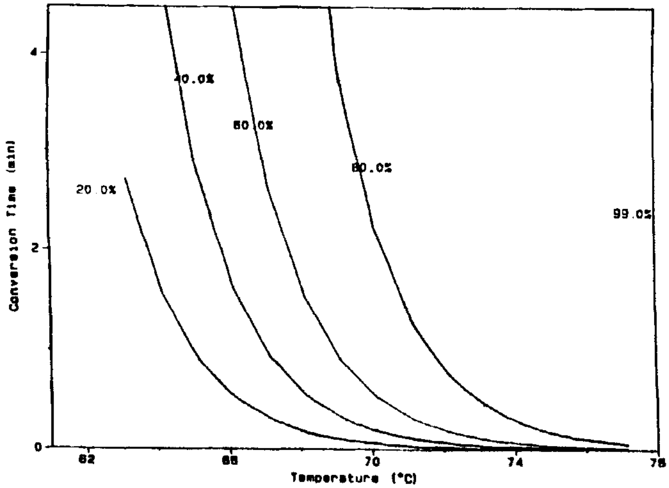

FIGURE 4 An illustrative **isoconversion** predictive polymerization curves for 8-QMA.

CONCLUSION

DSC has been proved an excellent method for the kinetic study of varieties of reaction. The DSC techniques used in the present study has provided a rapid and detailed analysis of 8-QMA polymerization kinetics in terms of effect of experimental variables on the rate of reaction and % conversion with respect to time and temperature. It is also possible to utilize the predictive experimental data in setting-up of process parameters of large scale polymerization.

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