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BULK POLYMERIZATION KINETICS OF METHACRYLIC DIMETHYL AMINO ETHYL ESTER ACID BY DTA

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ABSTRACT

The kinetics of methacrylic dimethyl amino ethyl ester acid bulk polymerization in the temperature range 428–438 K were determined by differential thermal analysis (DTA). The polymerization reaction of this compound was found to be of first order with respect to the monomer. The values of overall activation energy, E_A, as well as the pre-exponential factor, B, were calculated.

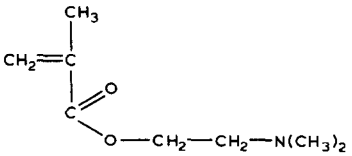
INTRODUCTION

During the last 10 years or so, differential thermal analysis (DTA) and differential scanning calorimetry (DSC), which are equivalent techniques, have been shown to be two experimental methods which easily allow the study of solid-state polymer properties, the determination of the glass transition temperature, T_G, crystallinity, fusion, etc. [1–7]. These techniques offer important advantages, such as the small quantity of monomer sample necessary for the experiment (a few milligrams), handiness of manipulation, rapidity of performance, versatility and precision of temperature control. Because of their advantages they are very useful in the study of physicochemical processes, such as the determination of the polymerization kinetics, due to the fact that these type of reactions are exothermic and so they can be easily followed isothermally and dynamically by DTA and DSC. These kind of studies have been carried out in liquid monomers, in bulk polymerizations for styrene [8], methyl methacrylate [9,10] and its derivatives [11], *N*-vinylcarbazole [12] and acenaphthylene [13]. They have also been employed in the study of copolymerization kinetics [14,15].

In the following paper, the methacrylic dimethyl amino ethyl ester acid bulk polymerization kinetics in the liquid state, in the temperature range 428–438 K by DTA, will be discussed.

EXPERIMENTAL

Methacrylic dimethyl amino ethyl ester acid (FLUKA) (see below) was purified by distillation at reduced pressure, and its purity was checked by IR spectroscopy and liquid chromatography. Calorimetric measurements, dynamic as well as isothermal, were made using a Mettler TA 2000 differential



thermal analyzer (DTA) instrument, equipped with a scanning auto-zero device for obtaining a straight baseline, which was calibrated using the heat of fusion of indium (28.0 J g^{-1}).

The polymerization kinetics were studied over the temperature range 428–438 K. The absolute temperature was calculated by the equation

$$T_{S1} = T_{P1} - \tau(dT_P/dt) + \Delta U_1/S \qquad (1)$$

where T_S is the sample temperature at point T_1, T_P the program temperature at point T_1 (°C), τ an intrinsic DTA constant (0.5), dT_P/dt the heating rate, ΔU_1 the signal at point T_1 (μV) and S the sensitivity of the thermocouple.

Measurements were made in aluminium crucibles, filled with monomer quantities of approximately 8–17 mg, for every experiment. Attempts to measure rates of polymerization in the absence of added initiators have often

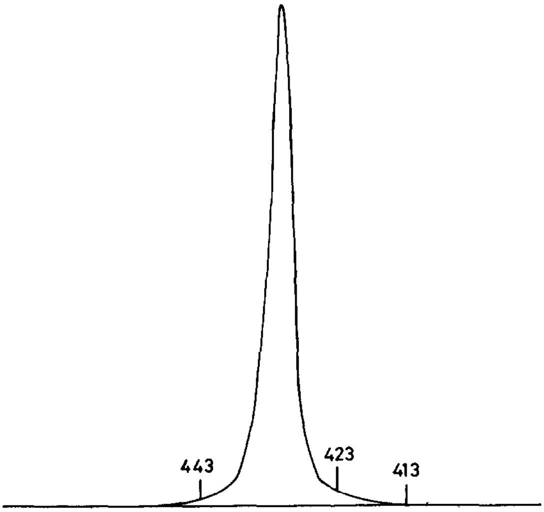


Fig. 1. Thermal behaviour of methacrylic dimethyl amino ethyl ester acid.

yielded conflicting results. For this reason, DTA measurements were run at least in triplicate. In all cases we found similar results.

When no more reaction was indicated by the recorder, a heating program of 10°C min^{-1} up to 200°C was applied in order to determine the amount of residual monomer. The samples were weighed using a 0.000005-g precision Mettler balance.

Isothermal polymerizations were carried out by placing the aluminium crucibles with the monomer in the furnace previously heated to the desired temperature. For all measurements an empty reference crucible was used as a reference. The IR spectra of all polymerized samples indicate that we have effectively obtained poly(dimethyl amino ethyl methacrylate).

The partial and total areas of the different thermograms were calculated by two different methods: using a Commodore CBM-64 computer and weighing the areas at different times. In both cases we have found similar results.

In order to obtain the reaction order, we have supposed that the reaction heat, H, is proportional to the number of monomer moles, n, converted to polymer at every moment, i.e.

$$\mathrm{d}H = \mathrm{d}n \Delta H_{\mathrm{SP}} \tag{2}$$

where ΔH_{SP} is the specific reaction enthalpy. This equation can be written in the form

$$\mathrm{d}n/\mathrm{d}t = (\mathrm{d}H/\mathrm{d}t)(1/\Delta H_{\mathrm{SP}}) \tag{3}$$

where $\mathrm{d}n/\mathrm{d}t$ can be determined from the DTA curve.

RESULTS AND DISCUSSION

Figure 1 shows the thermal behaviour of methacrylic dimethyl amino ethyl ester acid. As can be seen between 413 and 443 K there is an exothermic reaction in the system which probably corresponds to a polymerization process. The determination of molecular weights of the samples obtained indicates that the methacrylic dimethyl amino ethyl ester acid has effectively suffered a polymerization reaction.

Figure 2 shows three typical isothermal thermograms for the bulk polymerization of monomer in the temperature range 428–438 K. As it was expected, the reaction rate increased with temperature. We have obtained different thermograms with a temperature interval of 5° in order to obtain convenient reaction rates.

From these thermograms we have calculated the conversion rate at different times; from the data obtained at low conversions we have determined that the reaction is first-order kinetic. However, at high conversion we can see in Fig. 3 a change in the reaction mechanism probably due to an

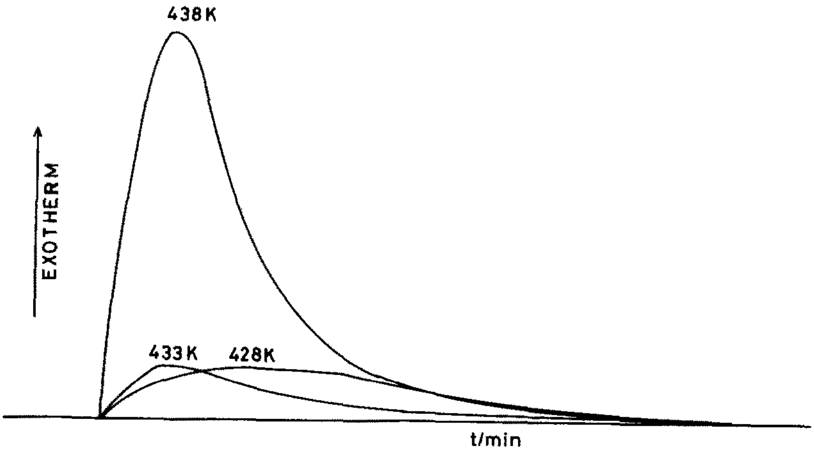


Fig. 2. Typical DTA thermograms of the bulk polymerization of methacrylic dimethyl amino ethyl ester acid at 428, 433 and 438 K.

autoacceleration in the rate of polymerization [16]. The autoacceleration may lead to a large rise in temperature [17] and, hence, in the rate of polymerization, if, under the conditions used, dissipation of the heat of polymerization is inadequate.

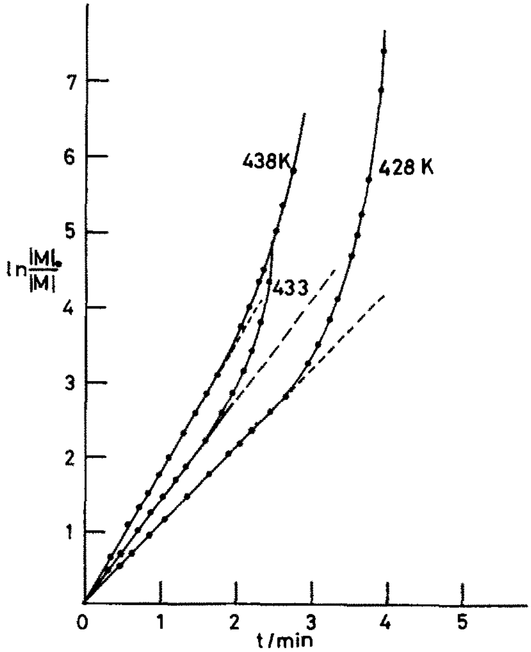


Fig. 3. Conversion against time curves for the bulk polymerization of methacrylic dimethyl amino ethyl ester acid.

TABLE 1

Overall rate constant, k_{OV} (min^{-1}) of poly(dimethyl amino ethyl methacrylate) at different temperatures

T (K)	From slopes	From eqn. (4)
428	1.05	1.06
433	1.35	1.37
438	1.80	1.81

The kinetic parameters and, hence, the rate constants, have been obtained from the initial slopes of plots of $\ln(|M|_0/|M|)$ against time, for each temperature.

Another way to calculate the overall rate constant, k_{OV}, is through the equation [18]

$$k_{\mathrm{OV}} = \frac{(AV/n_0)^{x-1}(\mathrm{d}H/\mathrm{d}t)}{(A-a)^x} \tag{4}$$

where A (mJ) is the total area under the DTA curve on a time axis, a (mJ) the area corresponding to the heat evolved up to any time, $\mathrm{d}H/\mathrm{d}t$ (mJ s^{-1}) the rate of heat evolution at time t, n_0/V the initial concentration of monomer (mol l^{-1}) and x the order of the reaction. As the polymerization is of first order, eqn. (4) reduces to

$$k_{\mathrm{OV}} = (\mathrm{d}H/\mathrm{d}t)/(A-a) \tag{5}$$

In Table 1 we can see the overall rate constant, k_{OV}, calculated using both methods in the temperature range 428–438 K. As it is seen, the values obtained are very coincident at all temperatures.

Finally, it has to be borne in mind that the overall kinetic rate constants depend greatly on temperature, according to the Arrhenius equation

$$k = B \exp(-E_{\mathrm{A}}/RT)$$

where B is a constant called the pre-exponential factor, E_{A} the activation

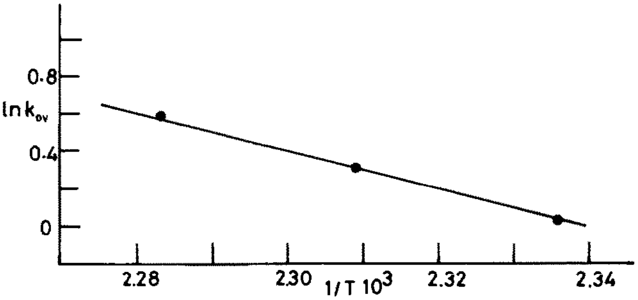


Fig. 4. Arrhenius plot for methacrylic dimethyl amino ethyl ester bulk polymerization.

energy (kJ mol^{-1}), R the gas constant and T the absolute temperature. By plotting ln k_{OV} against $1/T$ in the customary fashion, E_{A} and B may be determined from the slope of the straight line obtained. In Fig. 4 we can see the Arrhenius plot for our system. The calculated value is 83.2 kJ mol^{-1}. Burnett [19] reported the value 96.2 kJ mol^{-1} for styrene, and Burnett and Melville [20] found 80.2 kJ mol^{-1} for vinyl acetate, in satisfactory agreement with the value given above.

The value obtained for the pre-exponential factor, B, is 4.2×10^{7}. This value is higher than that obtained for other methacrylic monomers [21]. Baxendale and Evans [22] considered that this can be attributed to an increase in the degree of freedom of the monomer in the activated state with respect to its previous situation as an independent molecule in the liquid state.

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