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FREE-RADICAL BULK POLYMERIZATION KINETICS OF 1-VINYL-IMIDAZOLE AT TOTAL CONVERSION BY DTA

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ABSTRACT

The free-radical polymerization of 1-vinyl-imidazole at total conversion in the temperature range 363 to 433 K has been studied by differential thermal calorimetry (DTA). From the experimental data the kinetic order has been calculated and a change in the order has been found in the temperature interval 363–393 K. At higher temperatures the kinetic order remains constant. In order to explain this change we have proposed a kinetic scheme. Finally, the activation energy, E_A, and the pre-exponential factor, A, are calculated using the Arrhenius equation.

INTRODUCTION

The free radical-initiated bulk polymerization of vinyl monomers is probably one of the most extensively studied subjects in polymer chemistry. In this paper the monomer to polymer conversion has been followed by differential thermal calorimetry (DTA). This technique has proved to be a very useful tool for studying the kinetics of polymerization of several vinyl monomers [1–8]. In general, deviations from simple kinetics at ultrahigh conversions have been observed in the temperature range 363–433 K.

In this paper we have studied the bulk polymerization kinetics of 1-vinyl-imidazole at total conversion using 1,2-azobisisobutyronitrile (AIBN) as initiator.

EXPERIMENTAL

To obtain the monomer, inhibitor was removed from 1-vinyl-imidazole (Fluka) (Fig. 1) by distillation under reduced pressure and a middle fraction selected (refractive index $n_D = 1.5298 \pm 0.0005$). The boiling point of 1-vinyl-imidazole was determined by differential calorimetry and was found to be 461 K. The purity of the monomer was checked by IR spectroscopy.

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A weighed amount of 1,2-azobisisobutyronitrile (AIBN) (ranging between 0.03 and 0.05 mg) was dissolved in purified monomer (4–12 mg) and the mixture was placed in an aluminium standard crucible. The cells were sealed and weighed using a Mettler balance with a precision of 0.000005 g before being placed in the DTA furnace.

The kinetics of polymerization were studied in the temperature range 363–433 K using a Mettler TA 2000 differential thermal analyzer system, equipped with a scanning auto-zero device for obtaining a straight baseline. The instrument was previously calibrated using the fusion heat of indium as reference (28.5 J g^{-1}). Temperature calibration was performed with the International Confederation for Thermal Analysis certified reference material indium ($T_m = 429.7$ K).

The absolute sample temperature was calculated using the following expression

$$T_{s_1} = T_{p_1} - \tau(\mathrm{d}T_p/\mathrm{d}T) + \Delta U_1/S \qquad (1)$$

where T_{s_1} is the sample temperature at point T_1, T_{p_1} is the program temperature at point T_1 (°C), τ is an intrinsic DTA constant (0.408), $\mathrm{d}T_P/\mathrm{d}T$ is the heating rate, ΔU_1 is the signal at point T_1 (μV) and S is the sensitivity of the thermocouple.

The isothermal polymerizations were carried out by placing the aluminium crucibles with the monomer and initiator in the furnace previously heated to the desired temperature. Before carrying out the isothermal polymerizations a dynamical calorimetric determination of the sample was made in order to determine the temperature range in which the 1-vinyl-imidazole monomer undergoes the polymerization process. For all measurements an empty reference crucible was used as a reference. DTA measurements were run in triplicate at least. In all cases similar results were obtained.

For calculation of the monomer reaction rate, it has been assumed that the reaction heat was always proportional to the conversion from monomer to polymer

$$\mathrm{d}H = \mathrm{d}n\Delta H_{sp} \qquad (2)$$

where ΔH_{sp} is the specific reaction enthalpy. Equation (2) can be expressed as

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

Therefore, the reaction rate is directly proportional to the enthalpy change with time, i.e., to the signal obtained on the thermogram.

When no further reaction was indicated by the recorder, a heating program of 10°C min^{-1} up to 525 K was applied in order to determin the amount of residual monomer.

The determination of the conversion degree and the kinetic order was carried out using a BASIC program written for a Commodore CBM-64 personal computer. The program calculates the partial and total areas of the different thermograms by means of a trapezoidal method.

Assuming total monomer to polymer conversion the conversion degree is obtained as the ratio of the partial to total thermogram area. The kinetic order is calculated by integration of the equation

$$-(\mathrm{d}|M|/\mathrm{d}t) = k|M|^x$$

The BASIC program allowed us to plot the integrated equation corresponding to the different kinetic orders of reaction in order to select the best. The program also calculates the intercept and the slope of the straight line and the correlation coefficient obtained from the experimental data fitting. The constant rate is calculated from the slope. The listing of the BASIC program is available upon request.

RESULTS AND DISCUSSION

Figure 2 shows the thermal behaviour of 1-vinyl-imidazole in the temperature range 363–433 K. The boiling temperature is 461 K, which agrees with reported values [9]. The observed exothermal peak which begins at 363 K corresponds to the temperature range over which the monomer polymerizes. The enthalpy of boiling for this compound is found to be 96.47 ± 0.05 kJ mol^{-1}. The polymerization enthalpy was -88.74 ± 0.05 kJ mol^{-1}.

In Fig. 3 the isothermal thermograms corresponding to the different temperatures of polymerization taken at intervals of ten degrees from 363 to 433 K are shown. From the partial and total areas under the thermograms as a function of time the kinetics of polymerization can be studied. The areas were calculated using a BASIC program able to integrate the experimental peak areas with a precision higher than 1%.

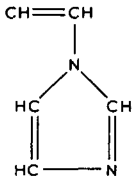

Fig. 1. Chemical structure of 1-vinyl-imidazole.

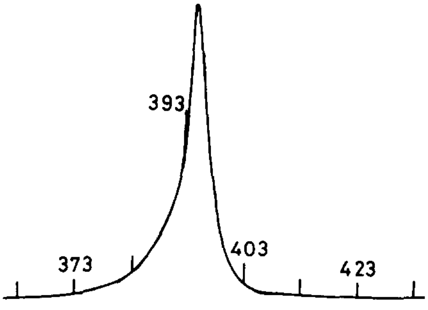

Fig. 2. Thermal behaviour of 1-vinyl-imidazole in the temperature range 363–433 K.

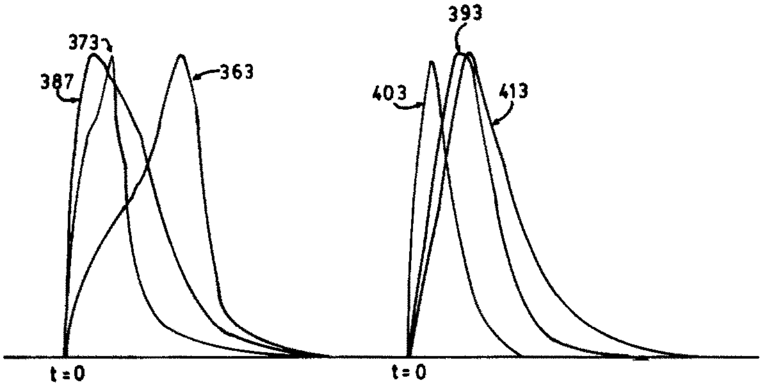

Fig. 3. Thermograms for the isothermal polymerization of 1-vinyl-imidazole at several temperatures.

As can be seen in Fig. 4 there is an order change in the kinetics of polymerization of 1-vinyl-imidazole for conversions no higher than 5%. In this conversion interval the reaction is monomer zero order kinetics. At higher conversion monomer first order kinetics are obtained.

The change in the kinetic order was only observed in the temperature range 363–393 K. Figure 5 shows an example of this behaviour at 363 K. Figure 5(a) shows the monomer first order kinetics and Fig. 5(b) the monomer zero order kinetics using the same experimental data. For this temperature interval we have calculated both overall kinetic constants (Table 1).

To obtain a kinetic equation which could reproduce the kinetic data, it is necessary to integrate the equation

$$-(\mathrm{d}\,|M|/\mathrm{d}t) = k_0 + k_1\,|M|$$

where k_0 and k_1 are the overall constants for the zero and first orders,

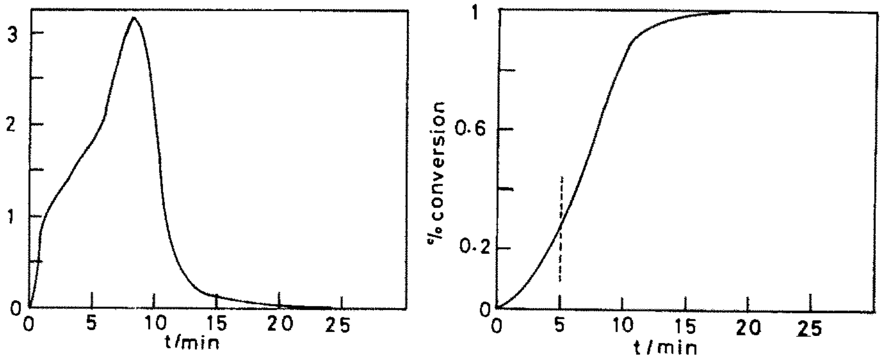

Fig. 4. Thermogram and conversion curves at 363 K obtained using the BASIC program.

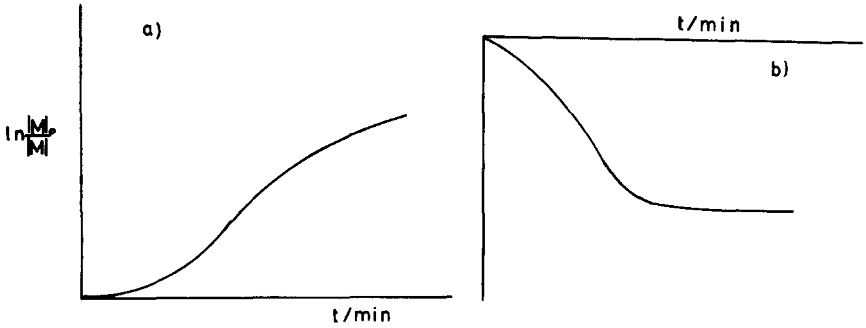

Fig. 5. Kinetic order: (a) first order kinetics and (b) zero order kinetics.

respectively. The integrated equation is

$$(1/k_1)\ln(k_0 + k_1 |M|)\Big]_{|M|_0}^{|M|} = t_1 - t_0$$

This equation is in good agreement with the experimental data over the whole time interval.

In order to explain the experimental results the following kinetics are suggested

$$\left.\begin{array}{l} \mathrm{I} \overset{k_d}{\rightarrow} 2\mathrm{R}^{\bullet} \\ \mathrm{R}^{\bullet} + \mathrm{M} \overset{k_i}{\rightarrow} \mathrm{RM}^{\bullet} \end{array}\right\}\text{initiation}$$

$$\left.\begin{array}{l} \mathrm{RM}^{\bullet} + \mathrm{M} \overset{k_p}{\rightarrow} \mathrm{RM}_2^{\bullet} \\ \quad\vdots \qquad\qquad\quad \vdots \\ \mathrm{RM}_n^{\bullet} + \mathrm{M} \overset{k_p}{\rightarrow} \mathrm{R{-}M}_{n+1}^{\bullet} \end{array}\right\}\text{propagation}$$

$$\left.\begin{array}{l} \mathrm{RM}_x^{\bullet} + \mathrm{RM}_y^{\bullet} \overset{k_{tc}}{\rightarrow} \mathrm{RM}_x\text{-}\mathrm{M}_y\text{-}\mathrm{R} \\ \mathrm{RM}_x^{\bullet} + \mathrm{RM}_y^{\bullet} \overset{k_{td}}{\rightarrow} \mathrm{RM}_x + \mathrm{RM}_y \end{array}\right\}\text{termination}$$

$$\mathrm{RM}_x^{\bullet} + \mathrm{M} \overset{k_{tr}}{\rightarrow} \mathrm{RM}_x + \mathrm{M}^{\bullet} \quad \text{chain transfer to monomer}$$

where I is the initiator, M the monomer and RM$^{\bullet}$ the radical. At first $k_{tr} \gg k_t$ and the kinetic order is zero with respect to monomer; when the conversion reaches a value higher than 5% k_{tr} becomes less important than k_t, and a change in the order of reaction is observed. This has been confirmed by measuring the molecular weight as a function of polymerization time. We have found that during the time the polymerization follows

TABLE 1

Rate constants for 1-vinyl-imidazole for zero and first order

T (K)	$k_0 \times 10^2$	k_1	T (K)	k_1
363	7.3	2.23×10^{-1}	403	2.01
373	21.7	3.05×10^{-1}	413	2.93
383	29.7	5.72×10^{-1}	423	4.78
393	58.0	1.17	433	8.28

TABLE 2

Enthalpy of polymerization, ΔH_p (kJ mol^{-1}) for 1-vinyl-imidazole in the temperature range 363–433 K

T (K)	363	373	383	393	403	413	423	433
$-\Delta H_p$ (kJ mol^{-1})	69.7	50.0	36.9	46.7	29.7	16.3	12.7	0.80

first order kinetics the molecular weight average remains constant. However, when zero order kinetics are followed the molecular weight changes constantly. Figure 4 shows the thermogram obtained at 363 K and its corresponding conversion curve obtained using the BASIC program.

Table 2 gives the values of the polymerization enthalpy, ΔH_p, in the temperature range 363–433 K. As generally observed [10] polymerization enthalpy, ΔH_p, changes with temperature and ranges between -69.7 and

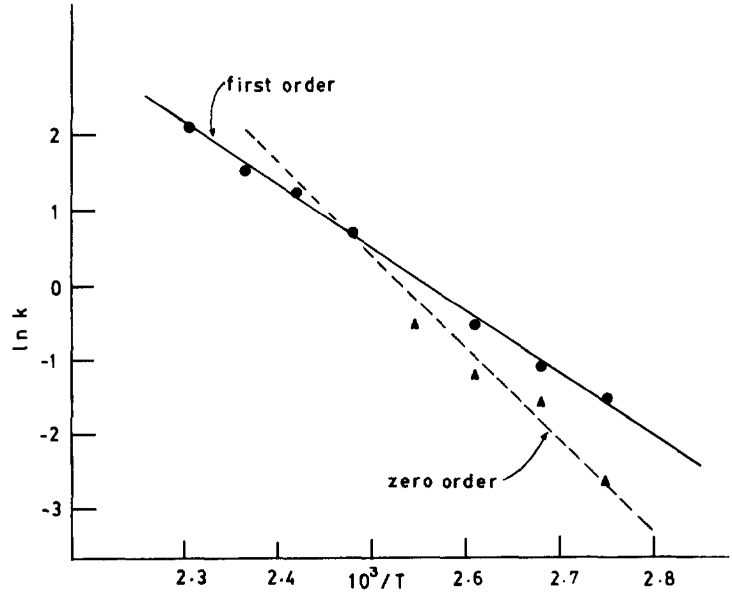

Fig. 6. Arrhenius plot in the temperature interval 363–433 K for zero and first order kinetics.

-0.8 kJ mol^{-1}. These values are comparable with those reported for N-vinylcarbazole [11], N-vinyl succinimide [12] and acenaphthylene [13].

By applying the Arrhenius equation

$$k = A \exp(-E_A/RT)$$

the activation energy E_A (kJ mol^{-1}) and the pre-exponential factor A can be evaluated. Figure 6 shows the Arrhenius plot in the temperature interval 363–433 K. In this system we obtain two different values for activation energy. For first order kinetics the slope gives the value $E_A^1 = 71.5$ kJ mol^{-1}, while for zero order kinetics, $E_A^0 = 104.4$ kJ mol^{-1}. These differences between activation energies indicate that the reaction of chain transfer to monomer has approximately the same probability of occurring as the reaction of termination by combination or dismutation. At higher temperatures than 393 K the latter process is most probable. This may be due to an increased diffusion rate of the monomer to the active centres.

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