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# DTA DETERMINATION OF BULK KINETICS POLYMERIZATION OF *N*-VINYLCARBAZOLE IN THE SOLID STATE

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## ABSTRACT

The bulk polymerization of *N*-vinylcarbazole by differential thermal analysis was studied in the temperature range 200–250°C. The reaction order with respect to monomer at different conversions as well as the kinetic rate constants and the process activation energy were calculated.

## INTRODUCTION

In recent years it has been shown that differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are techniques which allow, in a relatively easy way, the determination of the kinetics of polymerization and copolymerization [1–7]. In a previous paper we studied the bulk polymerization kinetics of acenaphthylene in the temperature range 140–200°C [8]. In this paper, the results obtained for the vinylcarbazole bulk polymerization in the range 200–250°C are given. The results obtained show that both the monomers follow different mechanisms of polymerization, which implies that the kinetics are also different, the one studied in the present work being more complex.

## EXPERIMENTAL

Vinylcarbazole (Fluka puriss) was purified by successive crystallizations in methanol, and its purity was checked by IR and DTA. The calorimetric measurements were carried out in a Mettler TA 2000 differential thermal analyzer system. The data were calibrated in absolute units by comparing with the specific heat of a sample of indium.

The kinetics of polymerization were studied in the temperature interval 200–250°C. The absolute temperature was calculated by the equation

$$T_{s_1} = T_{p_1} - \tau \mathrm{d}T_p/\mathrm{d}t + \Delta U_1/S$$

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where $T_s$ is the sample temperature at point $T_l$, $T_p$ is the program temperature at point $T_l$(°C), $\tau$ is an intrinsic DTA constant (0.5), $dT_p/dt$ is the heating rate, $\Delta U_l$ is the signal at point $T_l$($\mu$V) and $S$ is the sensitivity of the thermocouple.

All measurements were made using aluminium crucibles, and monomer samples ranged between 8 and 12 mg. The samples were weighed using a Mettler balance with a precision of 0.000005 g. The isothermic polymerizations were carried out by introducing the aluminium crucibles with the monomer in the furnace previously heated at the desired temperature.

The partial and total areas of the different thermograms were obtained by weight and the given results are the mean value from several experiments. The IR spectra of all samples indicate that the obtained product corresponds to polyvinylcarbazole [9]. In order to calculate the reaction order, we have supposed that the reaction heat is proportional to the conversion from monomer to polymer at every moment, i.e.

$$dH = dn\Delta H_{sp} \tag{1}$$

where $\Delta H_{sp}$ is the specific reaction enthalpy. Equation (1) can be written in the form

$$dn/dt = (dH/dt)(1/\Delta H_{sp}) \tag{2}$$

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

## RESULTS AND DISCUSSION

The thermal behaviour of PNVC as a function of temperature is shown in Fig. 1. As can be seen, the monomer fusion is produced at 65°C (endother-

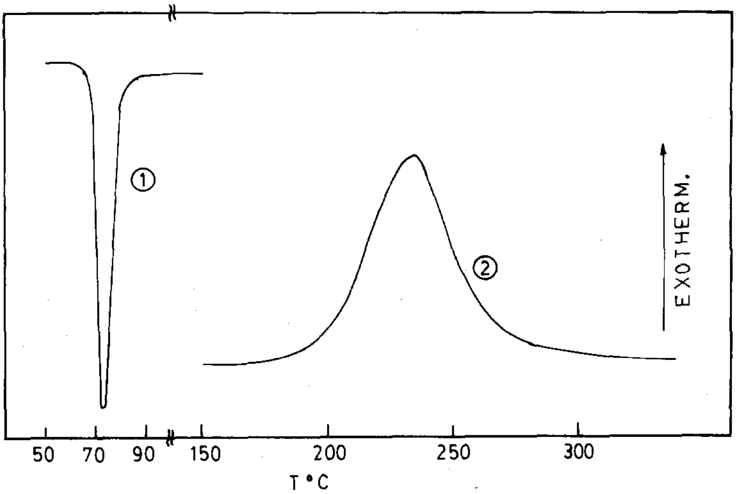

Fig. 1. Fusion thermogram of vinylcarbazole (1), and thermal behaviour of vinylcarbazole (2).

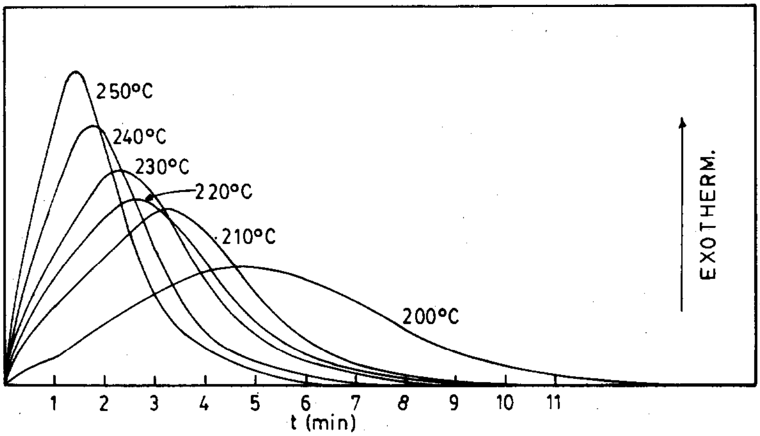

Fig. 2. Thermograms for the isothermic polymerizations of vinylcarbazole in the temperature range 200–250°C.

mic peak). The monomer fusion enthalpy was calculated as 17.66 kJ mole$^{-1}$. Likewise, an exothermic peak is observed beginning at 180°C. At this point, the PNVC begins to polymerize thermally. To obtain convenient reaction rates, measurements were taken at 20° intervals up to this temperature.

The thermograms obtained in the temperature range 200–250°C are shown in Fig. 2. As expected, the reaction rate increases with temperature. The treatment of experimental data indicates, as shown in Fig. 3, that for small conversions we have second order kinetics with respect to the monomer, while for higher conversions the order is 3/2. The variation of the reaction order implies that a change in the reaction mechanism has been produced. Additional experiments are at present under way in order to

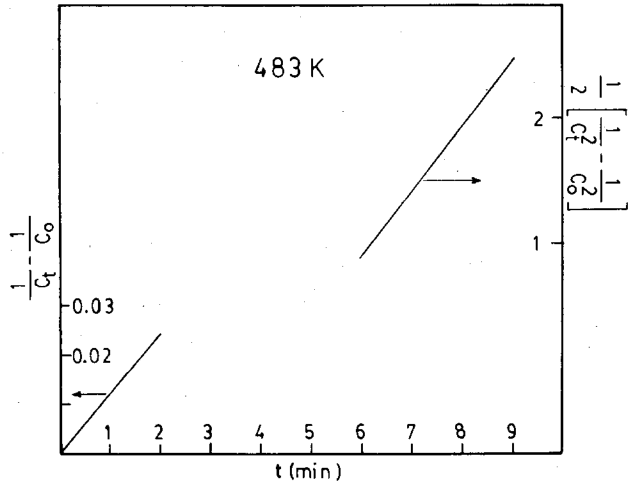

Fig. 3. Kinetic equation plot in the whole interval of conversion.

TABLE 1

Rate constants for *N*-vinylcarbazole for 2 and 3/2 order

| $T$(K) | $K_2$ | $K_{3/2}$ |
|---|---|---|
| 473 | 0.0071 | 0.4885 |
| 483 | 0.0123 | 0.5253 |
| 493 | 0.0136 | 0.5734 |
| 503 | 0.0215 | 0.6037 |
| 513 | 0.0244 | 0.6999 |
| 523 | 0.0368 | 0.7367 |

determine the causes which produce this change of order.

The rate constants can be determined from the slopes of the straight lines obtained for each temperature. The obtained values are given in Table 1. In order to find a kinetic equation which could reproduce the kinetic data, it is necessary to begin with a differential equation as follows

$$-\mathrm{d}|M|/\mathrm{d}t = K_2|M|^2 + K_{3/2}|M|^{3/2}$$

where $K_2$ and $K_{3/2}$ are the global rate constants for the second and 3/2 orders, respectively. If this equation is integrated we obtain

$$\frac{2}{k_{3/2}^2}\left| \frac{k_{3/2}}{|M|^{1/2}} - \frac{k_{3/2}}{|M_0|^{1/2}} + k_2 \ln\left(\frac{|M|}{|M_0|}\right)^{1/2} - k_2 \ln \frac{k_{3/2}+k_2|M|^{1/2}}{k_{3/2}+k_2|M_0|^{1/2}} \right| = t$$

This equation is in good agreement with the experimental data obtained in the temperature range studied. Using the global rate constants, we have calculated the activation enthalpy for both processes (Fig. 4). Their values are 64.2 kJ mole$^{-1}$ and 17.7 kJ mole$^{-1}$ for the second and 3/2 orders,

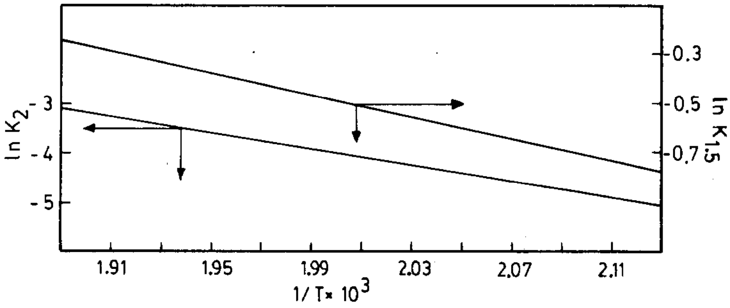

Fig. 4. Arrhenius plot of polymerization rate constants against $1/T$.

TABLE 2

Reaction enthalpies

| $T$(K) | 473 | 483 | 493 | 503 | 513 | 523 |
|---|---|---|---|---|---|---|
| $\Delta H_R$ (kJ mole$^{-1}$) | 61.7 | 63.6 | 62.8 | 66.1 | 67.4 | 69 |

respectively. These values confirm that the reaction mechanism changes for high conversions ($>35\%$). Also, for each temperature, the reaction enthalpies using the overall area of the thermogram have been calculated. The results (Table 2) agree with the well-known fact that the reaction heat changes with temperature (Kirchoff law).

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