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DSC STUDY OF THE BULK POLYMERISATION OF *N*-VINYLSUCCINIMIDE

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ABSTRACT

The kinetics of the bulk polymerization of *N*-vinylsuccinimide were studied by differential scanning calorimetry. The polymerization process was found to be second-order, with respect to the monomer, with a polymerization enthalpy ranging from -55 to -60 kJ mol^{-1}.

INTRODUCTION

In recent years, differential scanning calorimetry (DSC) and other thermal analysis techniques have proved to be very useful tools for studying the kinetics of polymerization of various monomers. In early works, experiments were carried out on the polymerization [1–3] or copolymerization [4,5] of liquid monomers. More recently, the thermal polymerization of solid samples has also been successfully investigated [6,7].

This paper reports the results of a DSC study of the polymerization of *N*-vinylsuccinimide in the temperature range 290–420 K.

EXPERIMENTAL

Sample

N-Vinylsuccinimide (NVS) was prepared from succinimide and vinyl acetate according to the procedure of Bayer et al. [8]. About 4 g of succinimide were added under stirring to 60 ml of vinyl acetate containing 100 mg of Na_2PdCl_4. The resulting mixture was heated at 75 °C for 24 h. After filtration, the solution was vacuum dried and the resulting solid extracted with 100 ml of ethyl ether. After distillation of ether, NVS was recrystallized from benzene (m.p., 47 °C).

The purity of the sample was checked by IR spectroscopy.

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Measurements

The calorimetric data were obtained from a Setaram model DSC 101 differential scanning calorimeter. The instrument was calibrated by the determination of the heats of fusion of indium and tin.

The corrected sample temperature, T_c, was calculated from the equation

$$T_c = T_p - \alpha R_H + \Delta P/S \quad (1)$$

where T_p is the program temperature read from the recorded thermogram, R_H is the heating rate, α is a constant of the apparatus ($\alpha = 0.501$), ΔP is the heat flow, and S is the sensitivity of the thermocouple at temperature T. Measurements were made using aluminium crucibles, with samples ranging between 5 and 10 mg. For isothermal polymerizations, the crucibles were introduced into the sample compartment, which was previously heated to the desired temperature. For calculations it was assumed that the reaction heat is always proportional to the extent of the polymerization. Partial and total areas under the thermograms were determined with an OTT planimeter.

Thermograms recorded with crucibles containing a previously polymerized sample indicated no fusion peak of residual monomer.

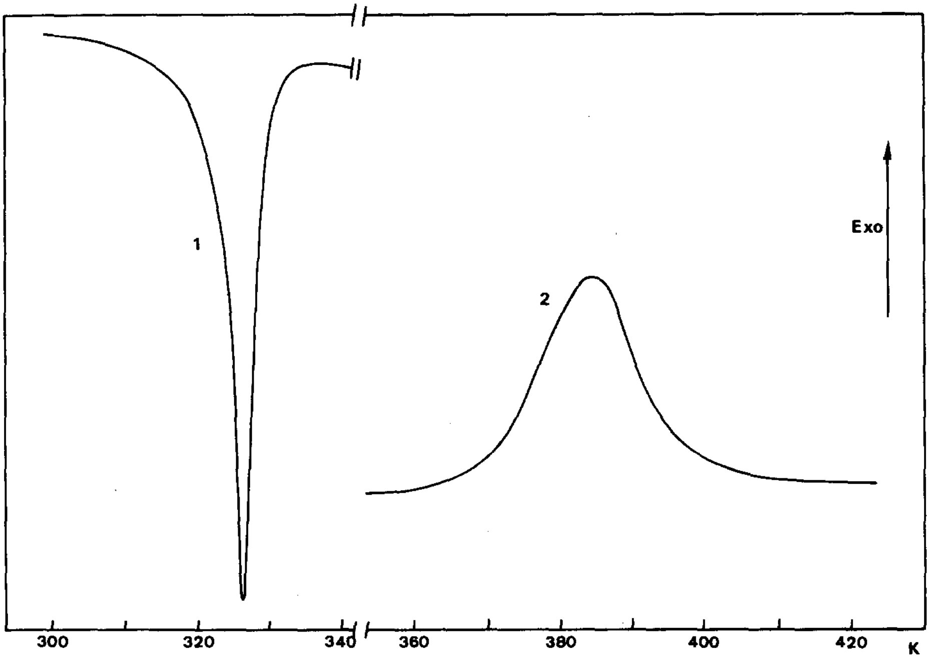

Fig. 1. Thermal behaviour of *N*-vinylsuccinimide: (1) sensitivity, $s = 250$ μV mW^{-1}; (2) sensitivity, $s = 1$ mV mW^{-1}.

RESULTS AND DISCUSSION

Figure 1 shows the thermal behaviour of NVS in the temperature range 290–420 K. The fusion of NVS is observed at 323 K ($T_c = 47\,°C$) as an endothermic peak. The enthalpy of fusion was calculated to be $+12.84 \mp 0.2$ kJ mol^{-1} (average of five experiments) which may be compared to 17.66 kJ mol^{-1} found for *N*-vinylcarbazole [7]. At higher temperatures, an exothermic peak is observed beginning at 370 K ($T_c = 88\,°C$) which corresponds to the polymerization of the sample ($\Delta H_p = -58.6$ kJ mol^{-1}). Figure 2 shows the different thermograms obtained during the isothermal polymerization of

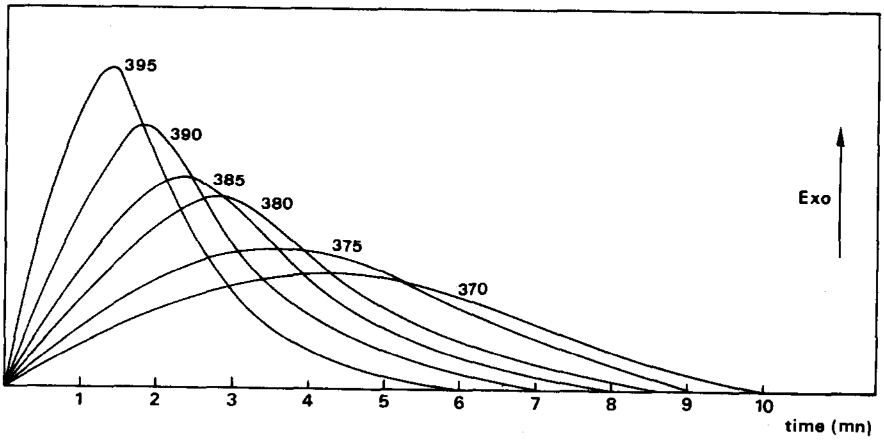

Fig. 2. Isothermal polymerization of *N*-vinylsuccinimide at different temperatures.

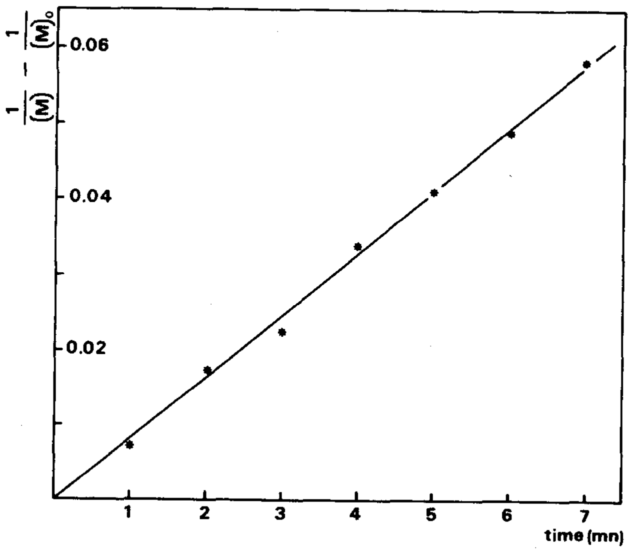

Fig. 3. Second-order kinetic plot at 375 K.

TABLE 1

Rate constant, K_2 ($\mathrm{mol^{-1}\ l\ min^{-1}}$), for the second-order polymerization of *N*-vinylsuccinimide

T(K)	370	375	380	385	390	395
K_2	0.0067	0.0083	0.0109	0.0134	0.0165	0.0211

TABLE 2

Enthalpy of polymerization, ΔH_p ($\mathrm{kJ\ mol^{-1}}$), for *N*-vinylsuccinimide

T(K)	370	375	380	385	390	395
ΔH_p	−54.7	−56.9	−57.7	−58.6	−59.1	−59.6

NVS at different temperatures. From the partial areas under the thermograms as a function of time, the kinetics of polymerization can be studied.

Experimental results indicate (as shown in Fig. 3 for $T = 375$ K) second-order kinetics with respect to NVS in the majority of the polymerization process.

Rate constants, K_2 (Table 1), were obtained from the slopes of the straight lines $1/[M] - 1/[M]_0 = f(t)$ at different temperatures.

Using these values, the activation enthalpy for the polymerization of NVS can be calculated. The value found is 55.7 kJ $\mathrm{mol^{-1}}$.

For acenaphthylene, which is a bulky and strained monomer, the activation enthalpy is 81 kJ $\mathrm{mol^{-1}}$ for a zero-order reaction [6]. For 9-vinylcarbazole, the activation enthalpy is 64 kJ $\mathrm{mol^{-1}}$ for a second-order (low conversion) and 17 kJ $\mathrm{mol^{-1}}$ for a 3/2-order reaction at high conversions [7]. Thus, our results are rather close to those of 9-vinylcarbazole at low conversions.

Table 2 gives the values of the polymerization enthalpy, ΔH_p, at different temperatures. As generally observed [6,7], ΔH_p changes with temperature, and ranges between −55 and −60 kJ $\mathrm{mol^{-1}}$. These values are close to those reported for the polymerization of various liquid [9] and solid monomers [6,7].

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