Thermochimica Acta, 223 (1993) 251–257
Elsevier Science Publishers B.V., Amsterdam

Differential scanning calorimetry of the solid-state thermal polymerization of *N-tert*-butylacrylamide–$ZnCl_2$ complex

Andrzej Kaim * and Dariusz Odzeniak

University of Warsaw, Faculty of Chemistry, ul. Pasteura 1, 02-093 Warsaw (Poland)

(Received 13 November 1992; accepted 11 December 1992)

Abstract

The application of differential scanning calorimetry and thermogravimetry to the study of the solid-state polymerization of *N-tert*-butylacrylamide complexed with $ZnCl_2$ has been studied. The scanning rate has a pronounced effect on the calculated endotherm and exotherm enthalpies. The polymerization enthalpy of the amide complexed with $ZnCl_2$ was calculated as 18.4 kJ mol^{-1}, using an extrapolation of the scanning rate to zero. It is shown that the higher the heating rate, the smaller the influence of the decomposition reaction of the complex on the total endothermic effect. For higher heating rates, the total endothermic value, due almost entirely to the melting process of the complex, is estimated as 28.2 kJ mol^{-1}.

INTRODUCTION

Thermal analysis methods are widely used in the determination of different kinetic parameters for many reactions, assuming that the rate of heat released is proportional to the rate of the reaction.

It is known that thermal analytical methods are also useful for investigation of polymerization reactions. Calorimetry can be a particularly powerful method for the investigation of solid-state polymerization reactions which are not easily followed by normal physical and kinetic methods. In many cases, however, the polymerization reaction is accompanied by changes in some physical property, e.g. a simultaneous melting or diffusion-controlled reaction, and/or by simultaneous reactions, e.g. thermal destruction or cross-linking reactions, which can make kinetic analysis difficult. The application of thermal analysis methods to the solid-state polymerization of complexed reagents is often affected by such inconveniences [1]. Therefore, it is clearly of practical and fundamental interest

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* Corresponding author.

to clarify the capabilities and limitations of thermal analysis when applied to such polymerizations.

The main purpose of this work was to study the thermal behavior of the solid-state polymerizable *N-tert*-butylacrylamide–$ZnCl_2$ complex by means of differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). Using a simple derivatograph, some thermal properties of the *N-tert*-butylacrylamide–$ZnCl_2$ complex have already been studied in our laboratory, over the temperature range 20–600°C, and compared with other zinc and cadmium halide complexes [2].

In some earlier publications, it was shown that *N-tert*-alkylacrylamides can undergo radiation-induced solid-state polymerization [3] as well as thermal solid-state and solution polymerization when complexed with Lewis acids [4, 5].

EXPERIMENTAL

Materials

N-tert-Butylacrylamide was synthesized from acrylonitrile and *tert*-butyl alcohol by the Plaut and Ritter method [6]. The solid amide was purified by repeated crystallization from methanol (m.p. 128.8°C).

The preparation of *N-tert*-butylacrylamide–$ZnCl_2$ complex was performed with a amide: $ZnCl_2$ molar ratio of 2:1, using a method previously described [5]. The resulting complex had a m.p. of 143°C as measured with a Bethius apparatus.

Apparatus and procedures

All data were obtained with either a Du Pont differential scanning calorimeter (model 910) or a Du Pont thermogravimetric analyzer (model 951). Both devices were plug-in modules used with the Du Pont 9900 computer/thermal analyzer, which controlled and recorded the progress of the experiments and was then used for data analysis. The DSC model was equipped with a cell that allowed experiments to be carried out in atmospheres of air, oxygen or argon. The same atmospheres were used for the DTG measurements. In both the DSC and DTG experiments, the investigated samples were heated at rates in the range 0.5–65 K min^{-1}. Because the sample size can be a source of anomalies in DSC experiments [7], approximately constant weights (9 mg) were used. They were scanned over the temperature interval from 100 to 200°C in aluminum pans without covers.

The DSC apparatus was automatically adjusted with both pans empty; the baseline scan was a straight line. With material in the sample pan, except for the heating rate range of 9–15 K min^{-1}, the DSC curves did not show any substantial drift, even after completion of the polymerization. The initial baseline did not coincide with the final one. It is known that for many reactions the two lines do not coincide because the specific heat capacity of the material changes during the scan [8, 9]. For the computer/thermal analyzer calculations, the baseline was approximated automatically by a horizontal sigmoidal line drawn independently for the endothermic and exothermic effects between assumed initial and final points of the event.

The time–conversion experiments were carried out in sealed glass ampoules. The polymerized complex was dissolved in methanol, precipitated with an equal amount of water, and filtered after 48 h of coagulation. The precipitate was washed with a methanol–water mixture (1:1 by volume) and dried under vacuum to constant weight.

RESULTS AND DISCUSSION

The thermal behavior of *N-tert*-butylacrylamide–$ZnCl_2$ complex in the temperature range 100–200°C was followed by means of DSC. As shown in Fig. 1, two different regions of the DSC curve, see for example curve A, can

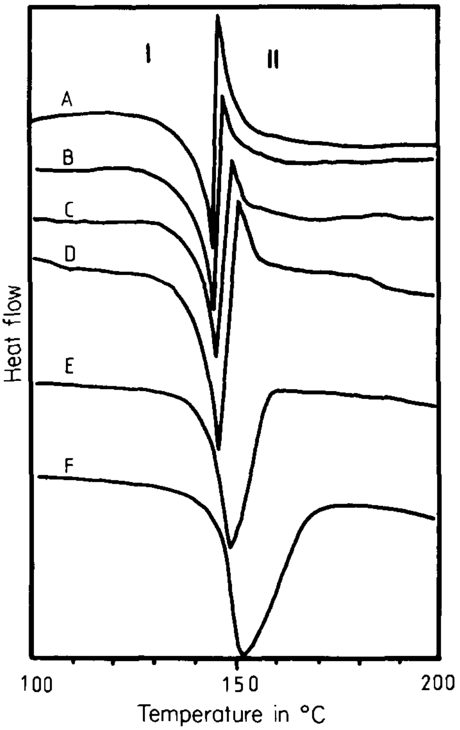

Fig. 1. DSC scans with different heating rates (K min^{-1}): A, 2; B, 5; C, 9; D, 20; E, 40; F, 65. I and II, endothermic and exothermic regions, respectively.

be distinguished, i.e. regions I and II, for the endothermic and exothermic effects, respectively. A very strong relationship between scanning speed and the shape of the DSC curve of this complex has previously been observed [2]. This is not unexpected because the heat of the endothermic and exothermic reactions, calculated by area measurement, depends on the reaction time as well as on the reaction temperature. For less complicated transformations, however, the area measurement error and peak temperature shifts can be even negligible [9]. The total endothermic and exothermic effects as functions of the heating rate, are presented in Fig. 2.

In the range of 15–20 K min^{-1}, the calculated values for the exothermic region are uncertain, because the shape of the DSC curves does not allow the final point of the event (Fig. 1, curves C and D) to be determined precisely. For these heating rates, an additional exothermic effect, probably due to the extended polymerization in the temperature range 150–190°C can also be taken into consideration (the broken lines in Fig. 2a). An

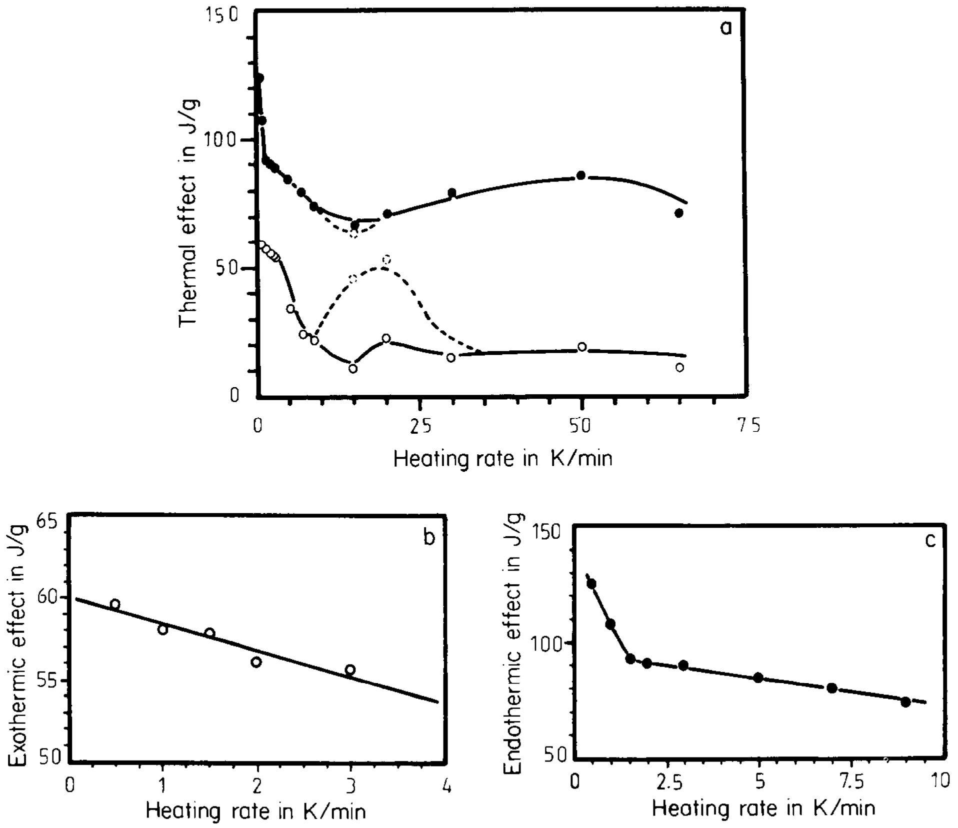

Fig. 2. (a) Thermal effect vs. heating rate: ●, endothermic effect; ○, exothermic effect; – – –, corresponds to the probable extended polymerization reaction over the temperature range 150–190°C. (b) Exothermic effects vs. heating rate. (c) Endothermic effects vs. heating rate.

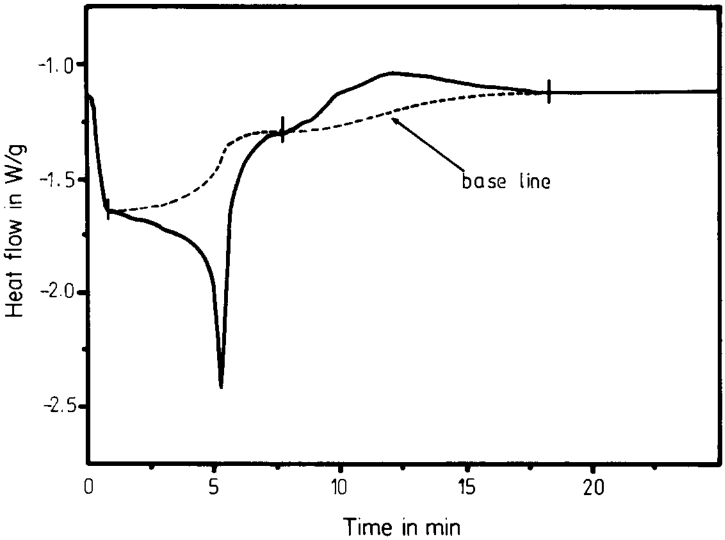

Fig. 3. Isothermal DSC scan of the complex at 140°C.

oxidative process cannot be responsible for this effect because the shape of the DSC curves was the same for experiments performed in air, oxygen or argon.

Nevertheless, the total exothermic value calculated using a linear extrapolation of the heating rate to zero (Fig. 2b), corresponding to the maximal accomplished polymerization reaction, was calculated as 60.0 ± 0.4 J g^{-1}. The polymerization heat measured at isothermal conditions at 140°C (Fig. 3) was calculated as 54.6 J per g of complex. Because these values are close (to within 10%) it may be concluded that under both dynamic (with extrapolation of the heating rate to zero) and isothermal conditions, almost the same degree of conversion was obtained. Taking into account that the 64 wt.% conversion of the complexed monomer attained after about 45 min of reaction in glass ampoules at 140°C (Fig. 4) does not change significantly with time, together with the polymerization heat calculated above, the solid-state polymerization enthalpy of *N-tert*-butylacrylamide complexed with $ZnCl_2$ can be estimated to 4.4 kcal mol^{-1}.

Region I, the total endothermic process, comprises decomposition and melting of the complex. Detailed TGA investigations showed that a very slow decomposition of the complex, accompanied by liberation of some percentage of amide molecules (resublimated amide could have been collected at the gas outlet of the measuring cell to confirm this), starts to be measurable at temperatures above 120°C (Fig. 3).

The endothermic effect of the decomposition reaction has only a small influence on the total endothermic value of region I. This can be corroborated by integration of the isothermal DSC curve corresponding to

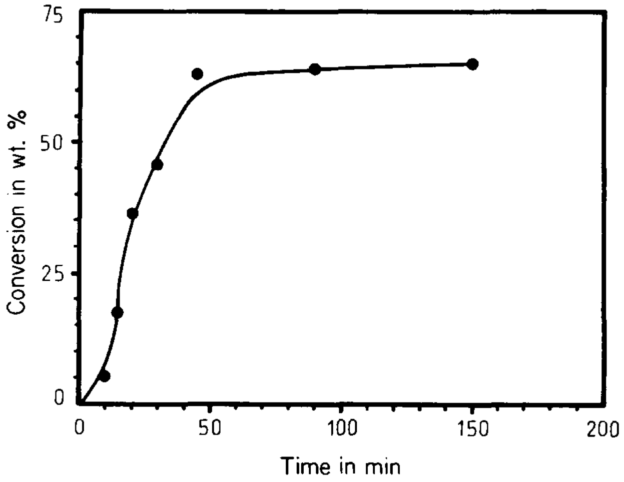

Fig. 4. Solid-state polymerization curve of *N-tert*-butylacrylamide complexed with $ZnCl_2$ at 140°C in pure N_2.

the decomposition of the complex at 130°C (Fig. 5) which for 200 min of reaction time and an 8.9000 mg sample, gives an endothermic value of 720.9×10^{-3} J. From the TGA curve, it was calculated that after 200 min at 130°C, 22.45 wt.% of the complex had decomposed. This leads to a molar decomposition enthalpy for the *N-tert*-butylacrylamide–$ZnCl_2$ complex of 70.9 kJ mol^{-1}, which is very high when compared to the total endothermic value of 28.2 kJ mol^{-1} calculated from the isothermal scan at 140°C (Fig. 3). The participation of the decomposition reaction in the total endothermic

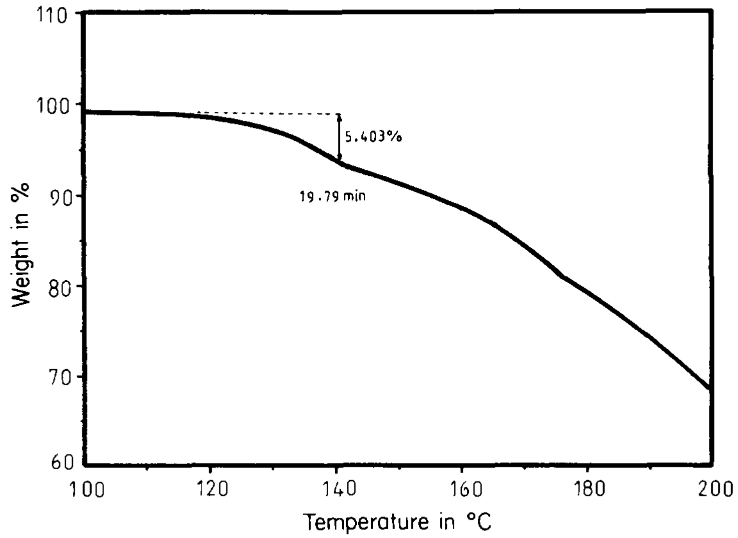

Fig. 5. TGA curve of *N-tert*-butylamide–$ZnCl_2$ complex in argon. Heating rate, 5 K min^{-1}.

effect becomes much more pronounced with very low heating rates (see Fig. 2c). Thus, it can be concluded that for an approximate calculation of the endothermic effect, a dynamic DSC scan with a higher scanning rate is preferred.

Finally, the order of appearance of the thermal effects (endothermic and then exothermic) during the DSC scan seems to confirm that the thermal solid-state polymerization of the *N-tert*-butylacrylamide–$ZnCl_2$ complex is preceded by destruction of the crystalline structure of the complex (melting and/or decomposition of the complex).

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