

## KINETICS OF ACENAPHTHYLENE BULK POLYMERIZATION BY DTA

I. KATIME, L.C. CESTEROS and J.R. OCHOA

*Grupo de Propiedades Termodinámicas de Macromoléculas en Disolución, Facultad de Ciencias, Departamento de Química Física, Universidad del País Vasco, Bilbao (Spain)*

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### ABSTRACT

The kinetics of acenaphthylene bulk polymerization in the temperature range 413–473 K were determined by DTA. The polymerization reaction of this compound was found to be zero order with respect to the monomer.

### INTRODUCTION

In recent years, differential thermal analysis (DTA) and differential scanning calorimetry (DSC), both equivalent techniques, have become increasingly important in the study of macromolecular chemistry. They have been applied in particular to the study of solid state polymer properties, the determination of  $T_g$ , crystallinity, fusion, etc. [1–7].

These techniques have very important advantages, such as the small amount of sample required (a few mg) and the precision of the temperature control. These characteristics make them especially useful for the study of the kinetics of polymerization because its exothermic character can be easily followed by DTA or DSC, isothermally as well as dynamically.

Early works of this type were carried out in liquid monomers, in block polymerizations for styrene [8], as well as methylmethacrylate [9,10] and its derivatives [11]. They are applicable in the study of copolymerizations [12,13].

This paper reports a study of the kinetics of the polymerization of acenaphthylene in the solid state in the temperature range 413–473 K using DTA.

### EXPERIMENTAL

Acenaphthylene (Fluka) was purified by successive crystallizations in methanol, and its purity was verified by IR spectroscopy. The calorimetric

measurements, dynamic as well as isothermal were carried out using a Mettler TA 2000 differential thermal analysis (DTA) instrument, calibrated by the determination of the heat of fusion of indium. The experiments were done in aluminium standard cells with the tops perforated in order to facilitate contact with the atmosphere. The monomer quantities used were approximately 10 mg for each experiment.

The isothermal polymerizations were carried out by placing the cells with the monomer in the furnace previously heated at the desired temperature. The area of the thermogram corresponding to the polymerization process was obtained by extrapolation of the base line obtained at the end of the process. The partial and total areas of the different thermograms were obtained by weighing; the data provided are the means of several experiments. The IR spectrum was obtained for all the samples, and was found to correspond to that of polyacenaphthylene [14].

## RESULTS AND DISCUSSION

Figure 1 shows the thermal behaviour of acenaphthylene. The monomer fusion at 346 K (endothermic peak) is observed, and an exothermic peak begins at approximately 393 K, corresponding to the fused monomer polymerization process.

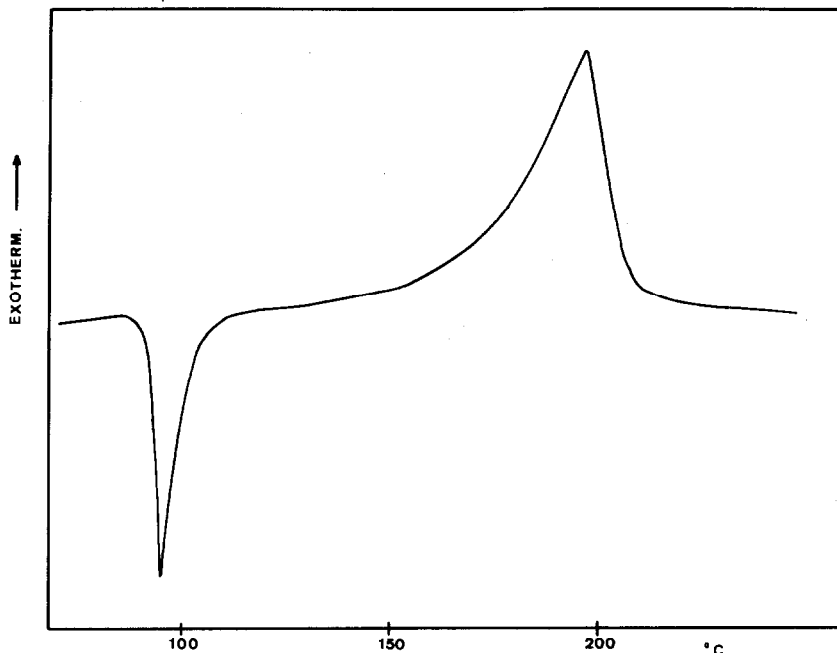


Fig. 1. Thermal behaviour of acenaphthylene in the temperature range 80–220°C.

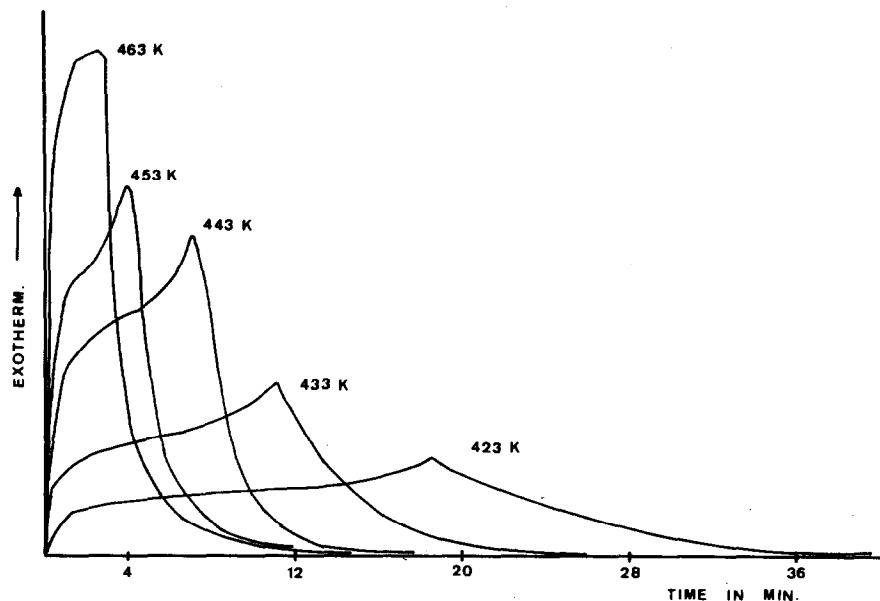


Fig. 2. Thermograms for the isothermal polymerizations of acenaphthylene in the 413–473 K temperature range.

Figure 2 shows the thermograms for the isothermal block polymerization of acenaphthylene in the temperature range 413–473 K. From these thermograms, the reaction order in relation to the monomer was determined, and was found to be zero order for conversions no higher than 35%. After this initial conversion, a pronounced gel effect appears, and it is all the more important as the polymerization temperature increases. This effect has already been observed in other monomers [15–17] and seems to be characteristic of the radical-type polymerizations at high temperatures. Burnett and Duncan [18] have explained the auto-acceleration effect of the polymeriza-

TABLE I

Polymerization temperature and polymerization heat of acenaphthylene at several temperatures

Polymerization temperature (K)	Heat of polymerization (kJ mole <sup>-1</sup> )
413	-58.2
423	-57.7
433	-57.3
443	-56.9
453	-56.1
463	-54.8
473	-53.9

TABLE 2

Rate constant values at different temperatures for acenaphthylene bulk polymerization

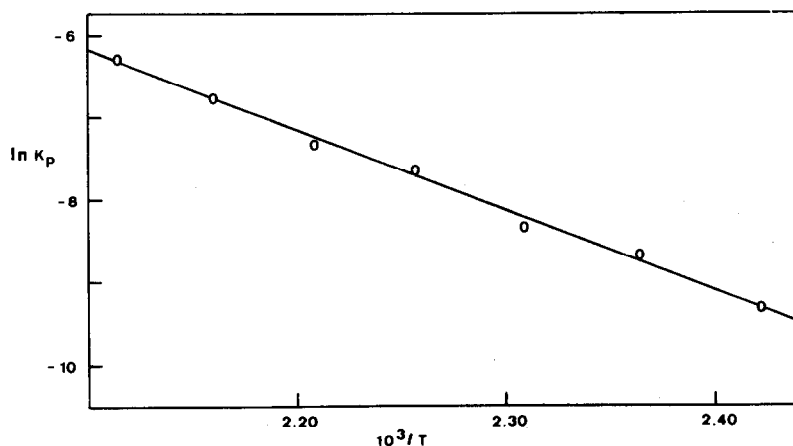
$T$ (K)	$k_p \times 10^5$ (mole s <sup>-1</sup> )
413	9.21
423	17.11
433	23.95
443	47.57
453	65.79
463	116.58
473	189.61

tion rate as a radical accumulation phenomenon. As can be expected, when the temperature becomes higher, the polymerization time decreases; also, the fused state polymerization of this monomer seems to be a total inversion, because when the thermogram is later obtained in the cell containing the thermally obtained polymer, no fusion peak corresponding to the residual monomer is observed.

Using the thermogram areas obtained at different temperatures, the heat of polymerization of acenaphthylene was calculated and is seen to decrease with increase in temperature (Table 1).

In order to calculate the reaction order, we have supposed that the reaction heat is proportional to the conversion from monomer to polymer at all times, i.e.

$$dH = dn\Delta H_{sp} \quad (1)$$

Fig. 3. Arrhenius plot of the polymerization rate constants against  $1/T$ .

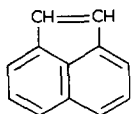


Fig. 4. Acenaphthylene.

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

$$\frac{dn}{dt} = \frac{dH/dt}{\Delta H_{sp}}$$

and, therefore, the reaction rate is then directly proportional to the enthalpy change with time. The data obtained for conversions under 35% adjust well with the zero order in relation with the monomer. The rate constant values for the different temperatures are shown in Table 2.

The activation energy for this reaction (Fig. 3) can be calculated from the rate constant values. The calculated value is  $80.9 \text{ kJ mole}^{-1}$ , which is in good agreement with that obtained for this monomer by other authors [19].

Although at first look, kinetics of zero order in relation with the monomer proves to be infrequent in the polymerization process, it seems to be adequate in our case. We must take into account that the acenaphthylene is a monomer with a very bulky side group (Fig. 4), and therefore the mobility of these molecules in the fused state must be difficult. All this leads us to think that transfer to the monomer is a fundamental process in this polymerization leading to a polymerization rate which is independent of the monomer concentration.

Finally, atmospheric oxygen was seen to have a significant influence on the polymerization rate. Experiments carried out in closed cells demonstrate a notable diminution in the process rate, which leads us to conclude that the oxygen plays a fundamental role in the initiation mechanism by the formation of peroxides which initiate the polymerization in a radical way.

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