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CALORIMETRIC STUDY OF THE KINETICS OF THE BULK POLYMERIZATION OF ETHYL ACRYLATE

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ABSTRACT

The bulk polymerization of ethyl acrylate using 1-1′-azobisisobutyronitrile as initiator at several temperatures has been studied by DTA. The order with respect to the monomer and the apparent activation energy of the polymerization process have been determined.

INTRODUCTION

The study of polymerization processes of vinyl monomers at high conversions has recently become of great importance [1–3]. This is of particular interest due to its industrial application. One of the objectives of this work is to determine whether changes in the reaction order are produced when the conversion increases.

Differential thermal analysis was used and, as in former works [4,5], its usefulness when working at high temperatures is demonstrated. In the present work, the polymerization of ethyl acrylate in 1-1′-azobisisobutyronitrile is studied at several temperatures (80, 83, 85, 87 and 90°C) for total conversion.

EXPERIMENTAL

Ethyl acrylate (Explosivos Rio Tinto) was purified under reduced pressure distillation. During the distillation, head and tail fractions were excluded. The monomer was found to be 99.9% pure [6] by vapour phase chromatography.

The polymerization conditions were chosen after making a sweep of one monomer sample with the initiator using a heating rate of 10°C min^{-1} (Fig. 1). As a consequence of that, the temperature range 80–90°C was chosen.

Figure 2 shows the thermograms obtained for each temperature studied.

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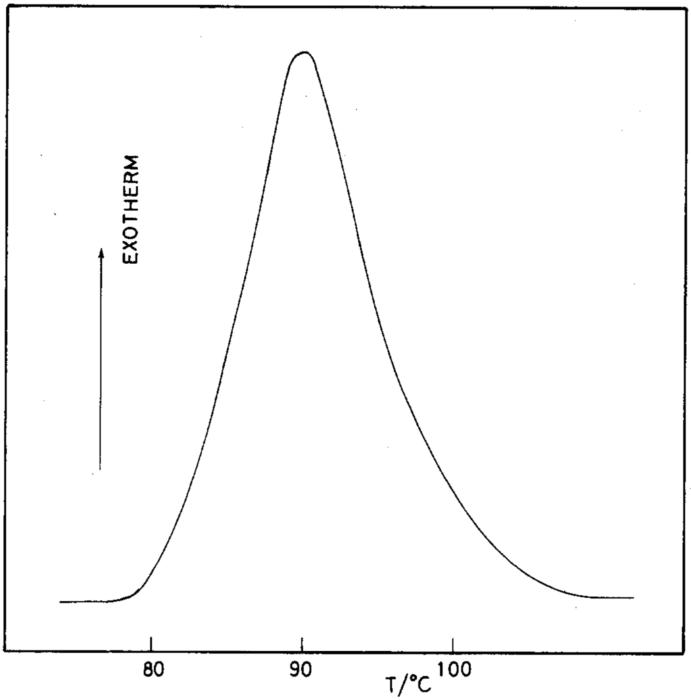

Fig. 1. The thermal behaviour of ethyl acrylate in the temperature range 80–100°C.

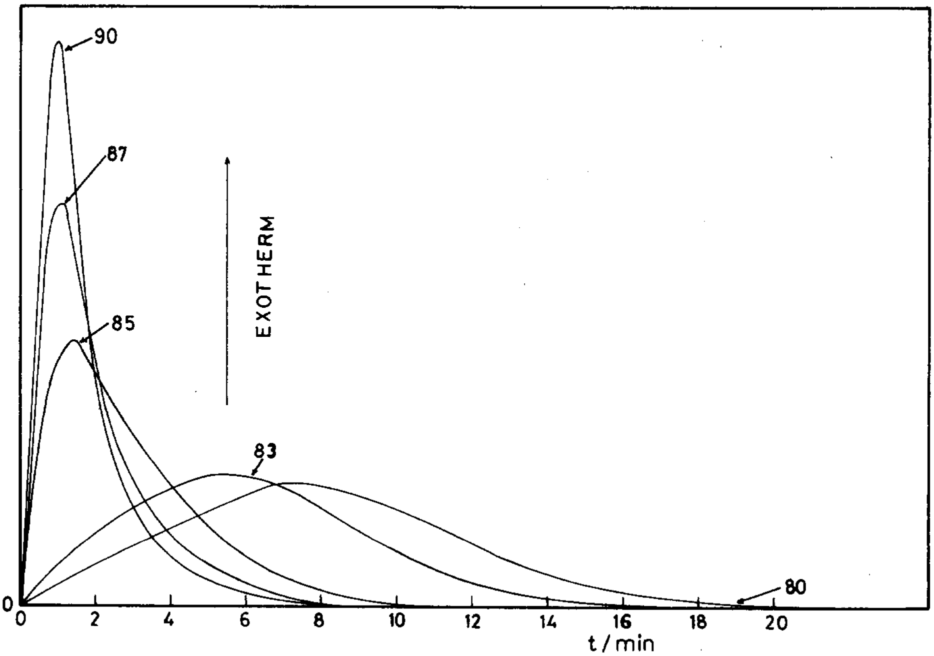

Fig. 2. Thermograms for the isothermal polymerizations of ethyl acrylate in the temperature range 80–90°C.

As expected, the rate of the polymerization process increases with temperature. The area under the curves is proportional to the heat of reaction of ethyl acrylate. Three polymerizations were made for each temperature, varying the initial quantities of the monomer and initiator.

The calorimetric measurements were carried out in a Mettler TA 2000 differential thermal analyzer system. The instrument was calibrated using a sample of indium as standard. The absolute temperature was calculated using the equation

$$T_s = T_p - \tau(\mathrm{d}T_p/\mathrm{d}t) + \Delta U/S \tag{1}$$

where T_s is the sample temperature at point T_1, T_p is the program temperature at point T_1 (°C), τ is an intrinsic constant of DTA whose value is 0.5, $\mathrm{d}T_p/\mathrm{d}t$ is the heating rate, ΔU is the signal at point T_1, and S is the sensitivity of the thermocouple.

All measurements were made using aluminium crucibles and monomer samples in the range 8–15 mg. Samples were weighed on a Mettler balance with a precision of 0.000005 g. The partial and total areas of the different thermograms were obtained by weight and the given results are the mean values from several experiments.

In order to calculate the reaction order, it was assumed that the heat of reaction is proportional to the conversion from monomer to polymer throughout, i.e.

$$\mathrm{d}H = \mathrm{d}n\, \Delta H_{sp} \tag{2}$$

where ΔH_{sp} is the specific reaction enthalpy. Equation (2) can be written in the form

$$\frac{\mathrm{d}n}{\mathrm{d}t} = \frac{\mathrm{d}H}{\mathrm{d}t}\frac{1}{\Delta H_{sp}} \tag{3}$$

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

RESULTS AND DISCUSSION

Using the thermograms obtained for each temperature (Fig. 2) it is possible, by integrating the curve several times, to obtain the variation of the weight of ethyl acrylate as a function of time. The results obtained for the different temperatures studied as a function of polymerization time are shown in Fig. 3, where only one of the three polymerizations made for each temperature is plotted.

Knowing the variation of weight of ethyl acrylate with time and bearing in mind that it is a bulk polymerization initiated by an initiator, the first-order

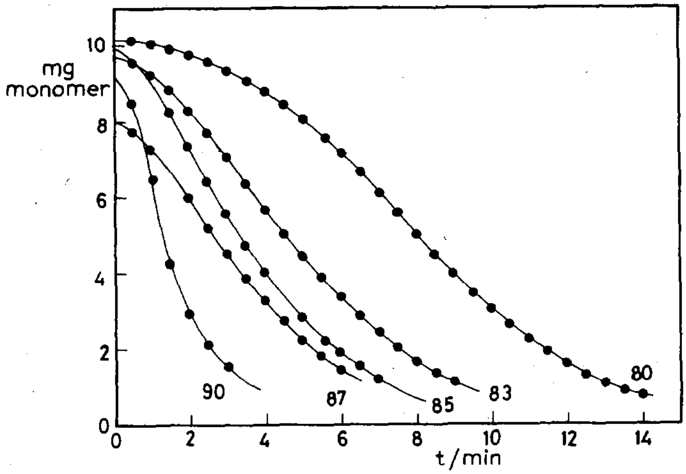

Fig. 3. Variation of the weight of ethyl acrylate as a function of time in the temperature range 80–90°C.

kinetics equation must be used

$$-\frac{\mathrm{d}|M|}{\mathrm{d}t}=\frac{k_\mathrm{p}}{\sqrt{k_\mathrm{t}}}(\mathrm{f}k_\mathrm{d}|I|)^{1/2}|M| \tag{4}$$

which on integration gives

$$\ln\frac{|M|_0}{|M|}=\frac{k_\mathrm{p}}{\sqrt{k_\mathrm{t}}}(\mathrm{f}k_\mathrm{d}|I|)^{1/2}t \tag{5}$$

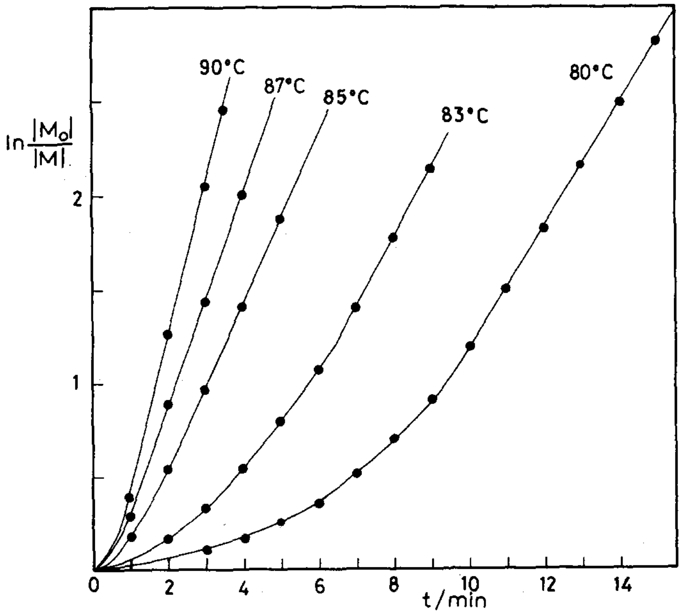

Fig. 4. The kinetic equation plot over the whole interval of conversion.

In Fig. 4, it can be seen that eqn. (5) is followed by the kinetics between 85 and 90°C. However, at lower temperatures, there is a definite deviation from first order with respect to the monomer at the start. This behaviour can be explained by supposing that at these temperatures both a polymerization with an initiator and a thermal polymerization take place simultaneously. Therefore, at the beginning, the equation must be taken as

$$-\frac{\mathrm{d}|M|}{\mathrm{d}t} = k_\mathrm{T}|M|^2 + k_\mathrm{R}|M| \tag{6}$$

where K_T and K_R are the global constants of the polymerization processes initiated thermally and radically, respectively. Integration of this differential equation gives [7]

$$\frac{1}{k_\mathrm{R}}\left(\ln\frac{|M|_0}{|M|} - \ln\left\{\frac{k_\mathrm{T}|M|_0 + k_\mathrm{R}}{k_\mathrm{T}|M| + k_\mathrm{R}}\right\}\right) = t \tag{7}$$

This equation can explain the curve observed initially. However, after a few moments, straight lines are observed for all temperatures because, as stated by Flory [8], the apparent constant of the thermal process is small ($K_\mathrm{i} = 4.2 \times 10^{-11}$ l s mole^{-1} for styrene at 100°C). The second term of the first member becomes constant and the reaction follows first-order kinetics with respect to the monomer. On the other hand, as

$$k_\mathrm{T} = \frac{k_\mathrm{P}\sqrt{k_\mathrm{i}}}{\sqrt{k_\mathrm{T}}} \quad \text{and} \quad k_\mathrm{R} = \frac{k_\mathrm{P}}{\sqrt{k_\mathrm{t}}}(\mathrm{f}k_\mathrm{d}|I|)^{1/2} \tag{8}$$

the second term of the first member can be written as

$$\ln\left\{\frac{k_\mathrm{T}|M|_0 + k_\mathrm{R}}{k_\mathrm{T}|M| + k_\mathrm{R}}\right\} = \ln\left\{\frac{1 + k_\mathrm{i}^{1/2}(\mathrm{f}k_\mathrm{d}|I|)^{-1/2}|M|_0}{1 + k_\mathrm{i}^{1/2}(\mathrm{f}k_\mathrm{d}|I|)^{-1/2}|M|}\right\} = \ln\left\{\frac{1 + A|M|_0}{1 + A|M|}\right\} \tag{9}$$

where

$$A = k_\mathrm{i}^{1/2}|M|_0(\mathrm{f}k_\mathrm{d}|I|)^{-1/2} \tag{10}$$

As $A|M|_0 \ll 1$, eqn. (9) becomes constant after the first few moments and eqn. (7) becomes

$$\ln\frac{|M|_0}{|M|} = k_\mathrm{R}t + \mathrm{cte} \tag{11}$$

which is in good agreement with that expected for vinyl monomers.

We have also calculated the apparent activation energy of the process starting from the thermal dependence of the global polymerization constant of the process, as can be seen in Fig. 5. The apparent activation energy obtained is 50 kJ mole^{-1}, in good agreement with that expected for vinyl monomers [9].

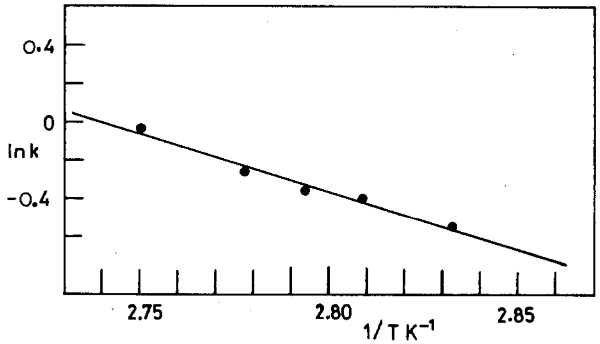

Fig. 5. The Arrhenius plot of polymerization rate constants vs. $1/T$.

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REFERENCES

1 I. Katime, R. López-Arbeloa, J. Suso, J. Peñafiel and C. de Dios, 5th Annual Meeting of the Portuguese Chemical Society, Porto, Portugal, 30 March 1982, Paper No. C30-57.
2 G. Luft, Chem. Ing. Tech., 51 (1979) 960.
3 T. Malasavic, I. Vizovisek, U. Osredkar and I. Anzur, J. Polym. Sci., Polym. Symp., 69 (1981) 73.
4 I. Katime, L.C. Cesteros and J.R. Ochoa, Thermochim. Acta, 59 (1982) 25.
5 I. Katime, J. Peñafiel, L.C. Cesteros and J. Veguillas, Thermochim. Acta, 59 (1982) 199.
6 J. Timmermans, Physico-chemical Constants of Pure Organic Compounds, Elsevier, Amsterdam, 1950.
7 J.A. Marin Tejerizo, Matemáticas para Técnicos, Saeta, Madrid, 1958.
8 P.J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, 1953.
9 G. Champetier and L. Monnerie, Introduction à la Chimie Macromoléculaire, Masson, Paris 1969. F.W. Billmeyer, Jr, Textbook of Polymer Science, Wiley-Interscience, New York, 1971.