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INVESTIGATION OF THE THERMAL DECOMPOSITION KINETICS OF POLYACRYLAMIDE USING A DYNAMIC TG TECHNIQUE

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ABSTRACT

In this study, the kinetic parameters for the thermal decomposition of polyacrylamide are established with the use of a dynamic TG technique. Kinetic parameters which involve activation energy, reaction order and pre-exponential factor are found to be 157.48 ∓ 1.66 kJ mol^{-1}, 1 and 6.46×10^{11} respectively.

INTRODUCTION

Polyacrylamide and its derivatives being extensively used in the textile, paper, petroleum recovery industry and waste treatment application exhibit an important thermal decomposition.

Firstly the loss of water which is non-stoichiometric will appear. Then subsequent ammonia loss and other gas products of reaction will occur partly from a polyacrylonitrile structure which forms during the decomposition of polyacrylamide and partly from the remaining polyacrylamide in the course of heating up to 600°C. Polyacrylamide does not give any acrylamide monomer while the thermal decomposition does [1,2].

The Ozawa Method [3,4] which is a dynamic analysis technique was used in this study. The derivation of the method is outlined in the original papers. Here, the use of the final operative equation is investigated. This takes the form

$$\log \beta = \log(AE/R) - 2.315 - 0.4567(E/RT) - \log g(\alpha) \quad (1)$$

where β is the heating rate (K min^{-1}), A is the pre-exponential factor (min^{-1}), R is the gas constant (8.314 J mol^{-1} K^{-1}) and

$$g(\alpha) = (AE/\beta R)P(x) \quad (2)$$

$$x = E/RT \quad (3)$$

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α is the fraction of decomposition

$$\alpha = (W_o - W_t)/(W_o - W_f) \tag{4}$$

where, W_o is the initial weight of polyacrylamide, W_t is the weight of polyacrylamide at temperature t and W_f is the final weight.

In the Ozawa Method, plots of log β against the reciprocal of absolute temperature give parallel lines for each α value. The slope of these lines gives the activation energy, as seen from eqn. (5)

$$\text{slope} = -0.4567(E/R) \tag{5}$$

The next step in the analysis is the determination of A and reaction order n. The theoretical curves of $(1-\alpha)$ against log $g(\alpha)$ have been determined before [3,5].

EXPERIMENTAL

Preparation of polyacrylamide. Acrylamide was recrystallized in benzene. A solution of acrylamide in water was polymerized under an atmosphere of nitrogen at 70–80°C. Peroxydisulphate was used as the initiator and isopropyl alcohol as chain transfer agent. Polymer samples were precipitated in methanol and then dried under 20 mmHg vacuum at 50°C.

The mean value of the molecular weight of polyacrylamide was calculated using the Staudinger equation

$$[\eta] = K_m \overline{M}_v a \tag{6}$$

The characteristic constants a and K_m are 0.66 and 6.8×10^{-4} for the polyacrylamide–water system, respectively.

Polyacrylamide was ground and sieved with 150 mesh sieving. DSC, TG and DTG traces were obtained using the Du Pont unit at various heating rates in a stream of nitrogen (5 cm^3 min^{-1}).

RESULTS

TG data were determined at three different heating rates, 5, 10 and 20°C min^{-1}. TG and DTG curves are shown in Fig. 1. The DSC curve is also seen in Fig. 2.

$(1-\alpha)$ values were found for each heating rate from these TG curves. Then $(1-\alpha)$ was plotted against $1/T$ (Fig. 3). The reciprocal of the absolute temperature was determined from these curves for each $(1-\alpha)$, in which there is a 0.05 difference between each one and the curves are plotted as log β versus $1/T$ (Fig. 4). The activation energies determined from the slope of log β versus $1/T$ are listed in Table 1. It was found that the mean value of the activation energies was 157.48 ∓ 1.66 kJ mol^{-1}.

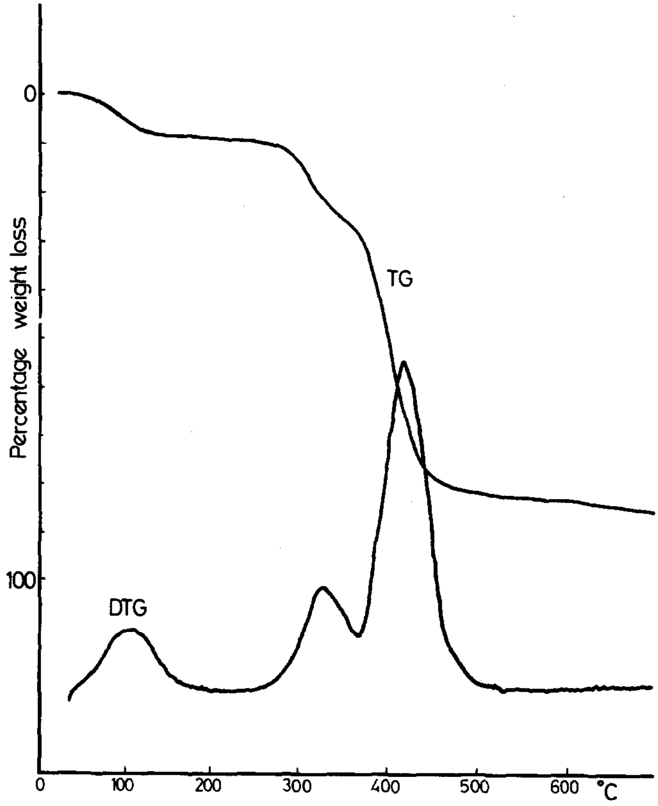

Fig. 1. TG and DTG curves of polyacrylamide.

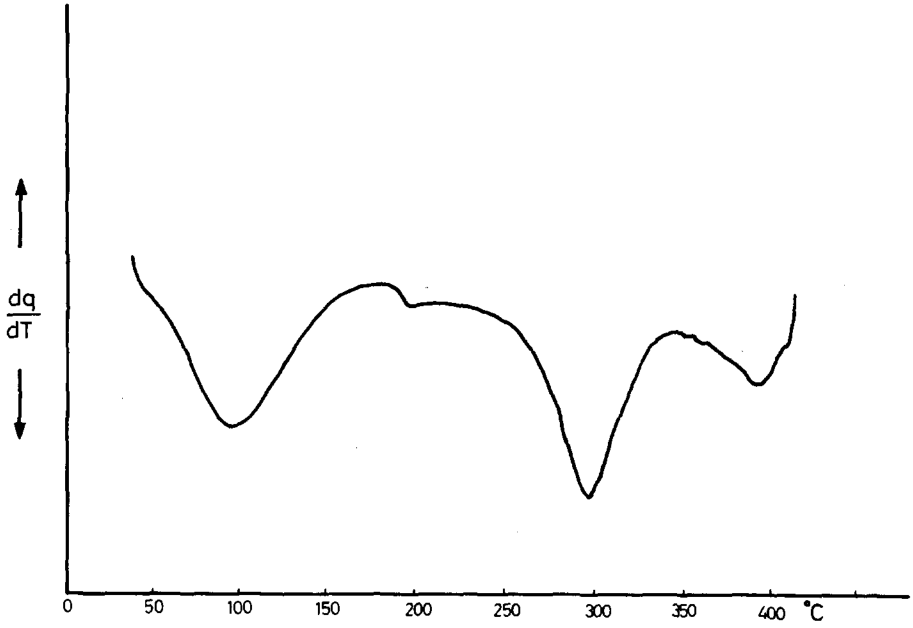

Fig. 2. DSC curves of polyacrylamide.

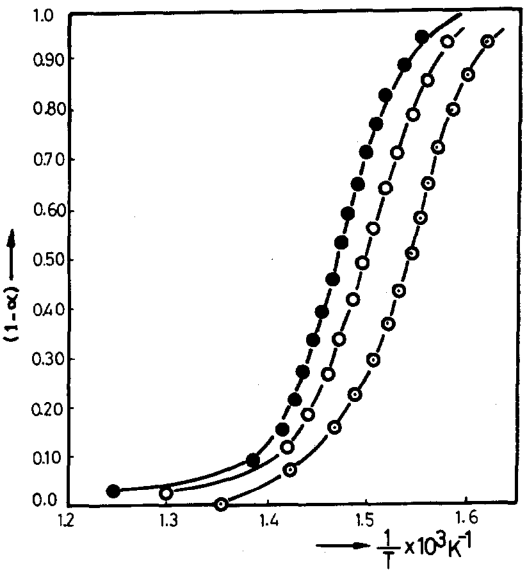

Fig. 3. Plot of $(1-\alpha)$ against $1/T$ for polyacrylamide. (⊙) 5°C min, (○) 10°C min^{-1}, (●) 20°C min^{-1}.

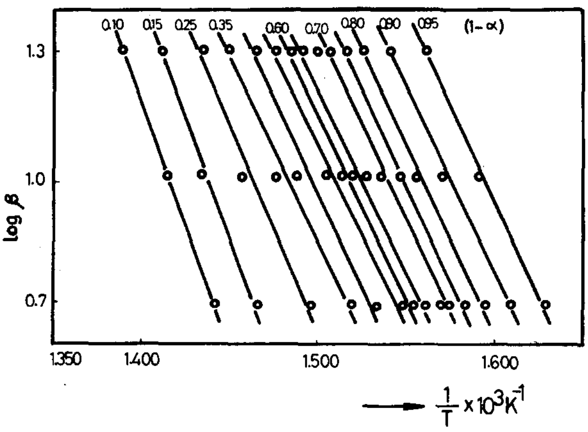

Fig. 4. Plot of log β against $1/T$ for polyacrylamide.

TABLE 1

The activation energies of decomposition of polyacrylamide for each $(1-\alpha)$ value

$1-\alpha$	E (kJ mol^{-1})	$1-\alpha$	E (kJ mol^{-1})	$1-\alpha$	E (kJ mol^{-1})
0.25	172.88	0.50	153.85	0.75	162.51
0.30	159.24	0.55	149.70	0.80	160.66
0.35	154.47	0.60	155.44	0.85	162.88
0.40	147.57	0.65	153.84	0.90	160.66
0.45	154.05	0.70	152.05	0.95	162.51

TABLE 2

Pre-experimental factors in the decomposition of polyacrylamide

$1-\alpha$	$(1/T)\times 10^3$	$\log A$ (s^{-1})
0.25	1.497	11.55
0.30	1.510	11.72
0.35	1.520	11.87
0.40	1.530	11.94
0.45	1.535	11.92
0.50	1.543	11.93
0.55	1.550	11.92
0.60	1.555	11.89
0.65	1.563	11.90
0.70	1.572	11.89
0.75	1.575	11.83
0.80	1.585	11.81
0.85	1.595	11.75
0.90	1.610	11.69
0.95	1.630	11.55

By using the activation energy, thus determined, the weight changes were plotted against $\log(E/\beta R)P(E/RT)$ and this experimental plot was superimposed to fit one of the theoretical thermogravimetric curves [3,5]. From this comparison, the mechanism of decomposition of polyacrylamide may be determined to conform to the first-order equation. The best fit determined as $g(\alpha)$ and the length of the lateral shift was found to be equal to $\log A$ and is given in Table 2. The average value of $\log A$ was found as 11.81 ∓ 0.03 from Table 2.

DISCUSSION

The decomposition of polyacrylamide up to 600 °C has been studied using simultaneous TG, DTG and DSC. TG and DTG data were determined at 5 °C $\min^{-1}$, 10 °C $\min^{-1}$ and 20 °C $\min^{-1}$ heating rates.

The DTG curve reveals a weight-loss peak and the TG curve gives three steps at 110 °C, 330 °C and 400 °C. The DSC curve also gives three peaks at about the same temperatures and one inflection point at about 200 °C. Polyacrylamide gives an almost 10% weight loss at 110 °C which is hydrogen bonded water in the polymer. Ammonia and water may be evolved partly from a polyacrylonitrile structure and partly from the remaining polyacrylamide at about 400 °C. The weight loss is 17% in this region.

There is evidence that there may be a slight exothermic decomposition of polyacrylonitrile, presumably caused by cross-linking. Endothermic decomposition of polyacrylamide and some of its products and exothermic decomposition of polyacrylonitrile take place in the same region. It, of course, does not give any exothermic peak. The weight-loss is about 56% in this region. The products of decomposition of polyacrylamide in this region are very complex. However, the chromatogram of the pyrolysis products of polyacrylamide partly resembles that of polyacrylonitrile [6–8]. It shows a 17% of residue at 600°C.

The energy of activation found in this study was 157.48 $\mp$ 1.66 kJ mol^{-1} between 350 and 500°C.

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