Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Studies on Thermal Polymerization of Acrylamide

K. Kishore[a]; K. N. Santhanalakshmi[a]
[a] Department of Inorganic and Physical, Chemistry Indian Institute of Science, Bangalore, India

To cite this Article Kishore, K. and Santhanalakshmi, K. N.(1981) 'Studies on Thermal Polymerization of Acrylamide', Journal of Macromolecular Science, Part A, 16: 5, 941 — 951

To link to this Article: DOI: 10.1080/00222338108056451

URL: http://dx.doi.org/10.1080/00222338108056451

J. MACROMOL. SCI.–CHEM., A16(5), pp. 941-951, 1981

Studies on Thermal Polymerization of Acrylamide

K. KISHORE and K. N. SANTHANALAKSHMI

Department of Inorganic and Physical Chemistry
Indian Institute of Science
Bangalore 560012, India

ABSTRACT

Thermal polymerization of acrylamide has been followed by the DSC technique, and the activation energy (E) values at different stages of the fraction polymerized (α) have been determined from the exotherm of the thermograms obtained. The trend of variation of E with α shows that E remains constant up to $\alpha = 0.5$ and decreases with a further increase in α. A close look at the composite nature of the exotherms, α-t, and α-T curves shows that the polymerization of acrylamide involves two processes. The first process is the formation of linear polyacrylamide and the second is the simultaneous cross-linking of the linear chains together with the formation of linear polyacrylamide. Experiments such as NH_3 detection by differential thermal analysis techniques and annealing studies have been made to shed further light on the polymerization process.

INTRODUCTION

Solid-state thermal polymerization of acrylamide has been carried out by differential scanning calorimetry (DSC). The activation energy (E) of the polymerization at different stages of the fraction polymerized (α) have been determined. The examination of the shape of the exotherm of the thermograms obtained as well as the variation of E with an increase in α value reveals that the polymerization is composite in nature. The exact explanation for the decrease in E value from $\alpha = 0.6$ was not clearly understood. The reason for the change in E values could be due to cross-linking of the linear polymer chains. However, this remained only a speculation.

In the present work, experiments such as the effect of annealing by DSC and the detection of NH_3 by the thermal analysis technique have been carried out to investigate the complexity of the polymerization process.

EXPERIMENTAL

Material

Acrylamide obtained from West Germany (EGA-Chemie Ca 96%) and from Poole, England (BDH, Ca 99%) were used for annealing and NH_3 detection experiments, respectively.

DSC Studies

DSC thermograms were obtained on a Perkin-Elmer instrument (model DSC 2B). The essential operations of the instrument are described elsewhere [1, 2]. Indium was used as the reference for calibrating the temperature axis and the enthalpy output. From the ratio of the segmental area to the total area of the exotherm which gives the α value at that instant, α-t and α-T plots have been generated and are presented in Figs. 1 and 2, respectively.

Annealing Studies

The effect of annealing below and above the melting point of acrylamide on melting and the polymerization process has been studied. Annealing was done at 320, 330, 340, 350 K for 60 min and at 360, 370, 380, and 390 K for 30 min. Soon after the annealing, the sample was brought down to 310 K by cooling at the rate of 10°C/min. After solidification, the sample was scanned at a heating rate of 10°C/min to obtain the endotherm of melting, followed by the exotherm of polymerization. In a separate experiment the weight loss during annealing was determined by weighing the sample before and after annealing. One milligram of the sample was taken for all annealing experiments. The plots of annealing temperature versus beginning and end polymerization temperatures and enthalpy of polymerization (ΔH_p) are shown in Fig. 3.

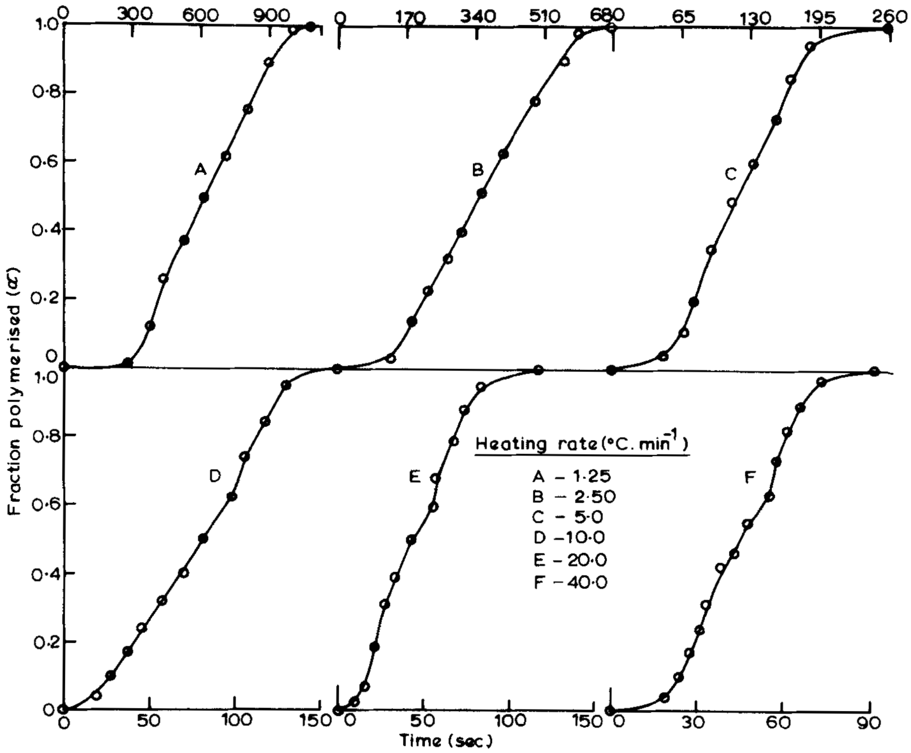


FIG. 1. α vs time plot for the polymerization of acrylamide.

NH$_3$ Detection Experiment

A special glass assembly (shown in Fig. 4, which is self-explanatory) was used to detect the evolution of NH$_3$. The thermocouple output was fed to a strip chart recorder to measure the temperature and the differential temperature (ΔT) for analyzing the events occurring during the reaction. This assembly was similar to DTA. About 3 g of the powdered sample was placed in the reaction tube and the furnace was heated at the programmed rate of 2°C/min. The temperature at which NH$_3$ evolution begins was noted on the recorder. The ΔT plot from this experiment showed the presence of an endotherm followed by a composite exotherm for polymerization as shown in Fig. 5.

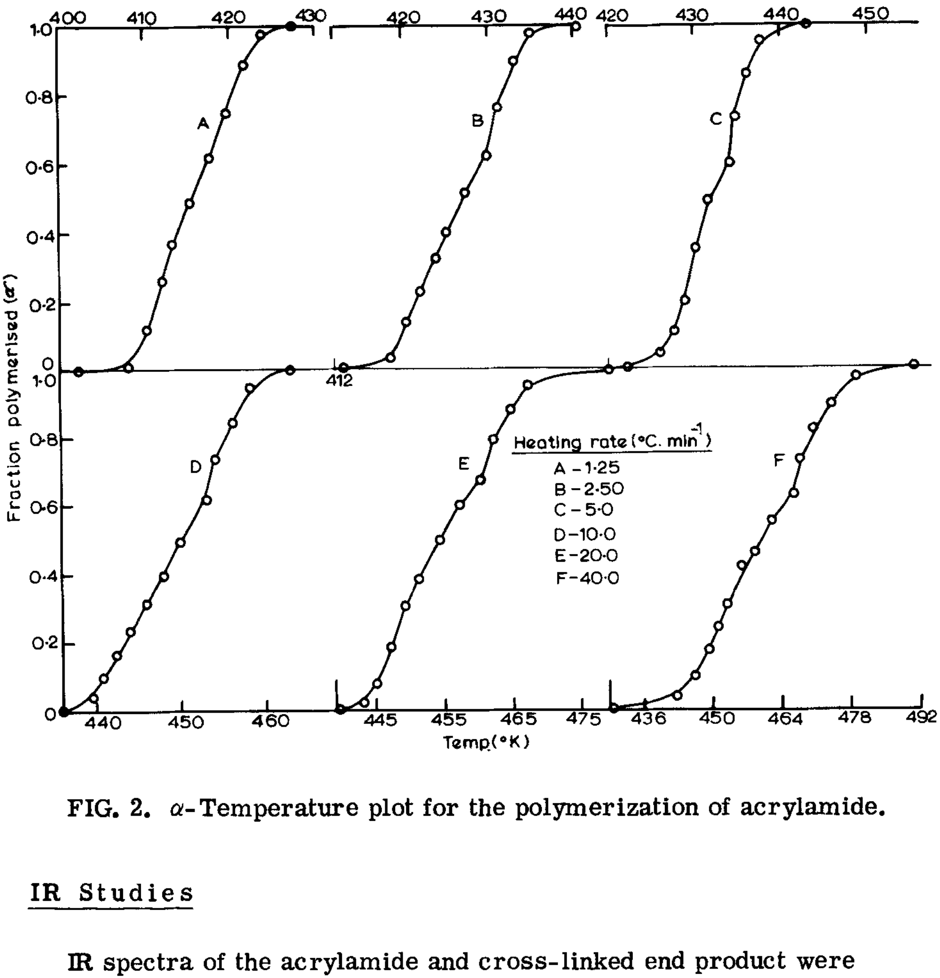


FIG. 2. α-Temperature plot for the polymerization of acrylamide.

IR Studies

IR spectra of the acrylamide and cross-linked end product were taken on an UR-10 infrared spectrometer. The respective spectra are shown in Fig. 6.

RESULTS AND DISCUSSION

A typical DSC thermogram (shown in Fig. 7) contains an endotherm of melting followed by an exotherm of polymerization. A close look at the exotherms of the thermogram obtained at different heating rates shows that the polymerization process is composite in nature. A similar observation was made in plots of α-T and α-t where a break around α = 0.6 occurs, thus supporting the complexity of the polymerization process. In order to understand the nature of the reactions

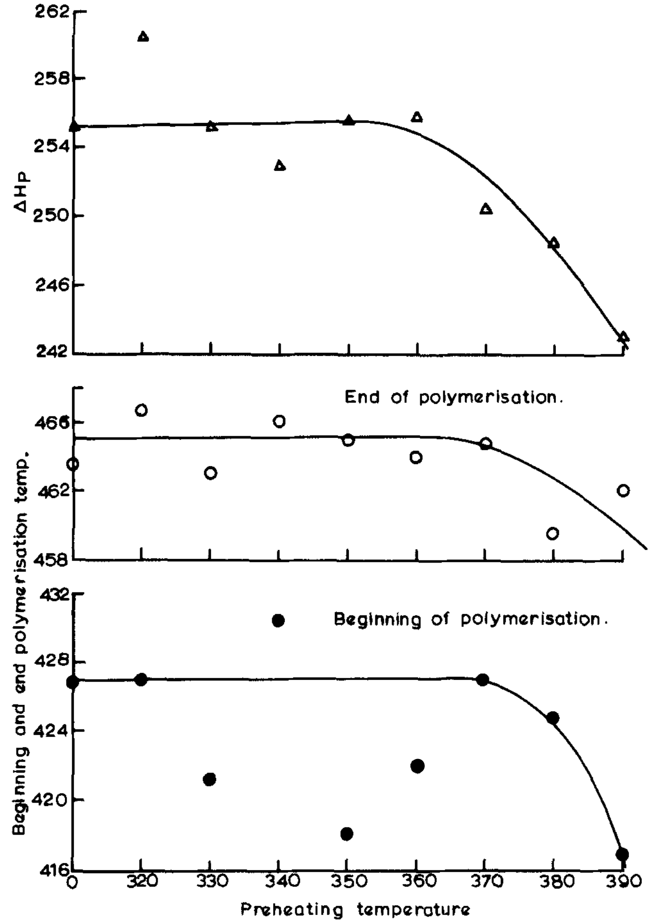


FIG. 3. Dependence of ΔH_p and beginning and end polymerization temperatures on annealing temperature.

taking place, a simple experiment similar to DTA but that also gives the instant of NH_3 evolution was devised (discussed in the Experimental Section). From this experiment it has been clearly shown that no NH_3 gas evolution takes place in the first portion of the polymerization which is shown in Fig. 5. From a comparison of the observations made from the NH_3 detection experiment, and from an examination of the thermograms and also the α-t and α-T curves, it can be

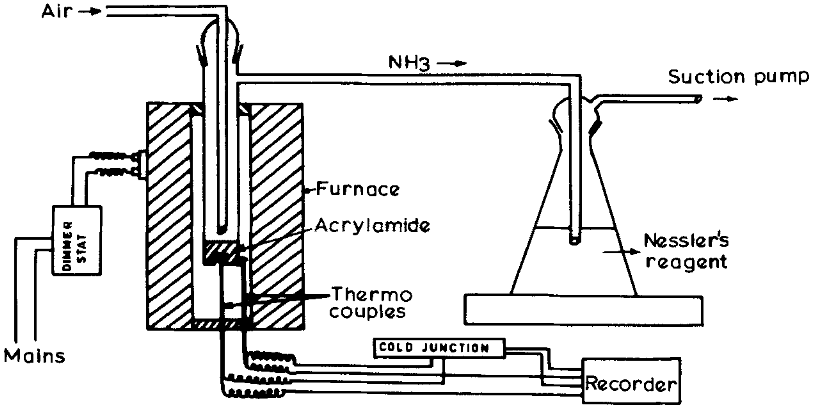


FIG. 4. Assembly for detecting NH_3 evolution.

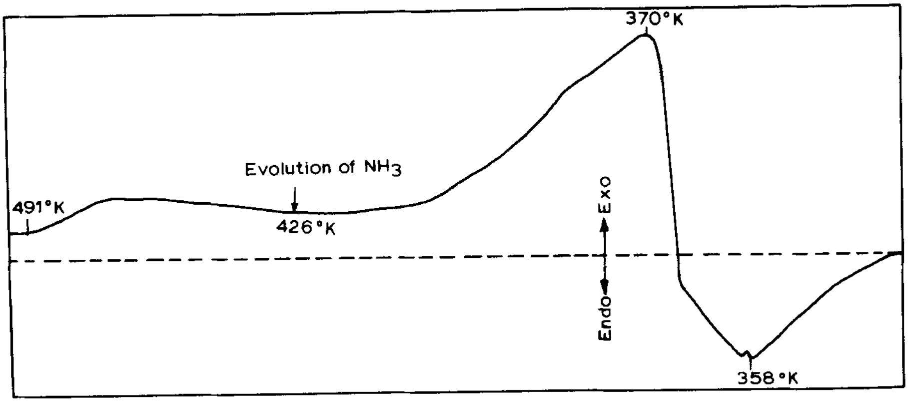


FIG. 5. Reaction history of the polymerization of acrylamide.

of linear polyacrylamide which upon further heating cross-links, evolving NH_3 gas according to Eq. (1).

In support of the formation of the cross-linked product, IR spectra of the end polymerized product were taken as shown in Fig. 6. It may be seen that in the IR spectra of the end polymerized product, a band around 1500 cm^{-1} is found which is characteristic of the imidization process taking place during cross-linking. Also, the presence of secondary amide band along with the primary amide bands shows that the first part of the polymerization involves only linear polymer formation while the second part corresponds to the formation of both linear and cross-linked polymers.

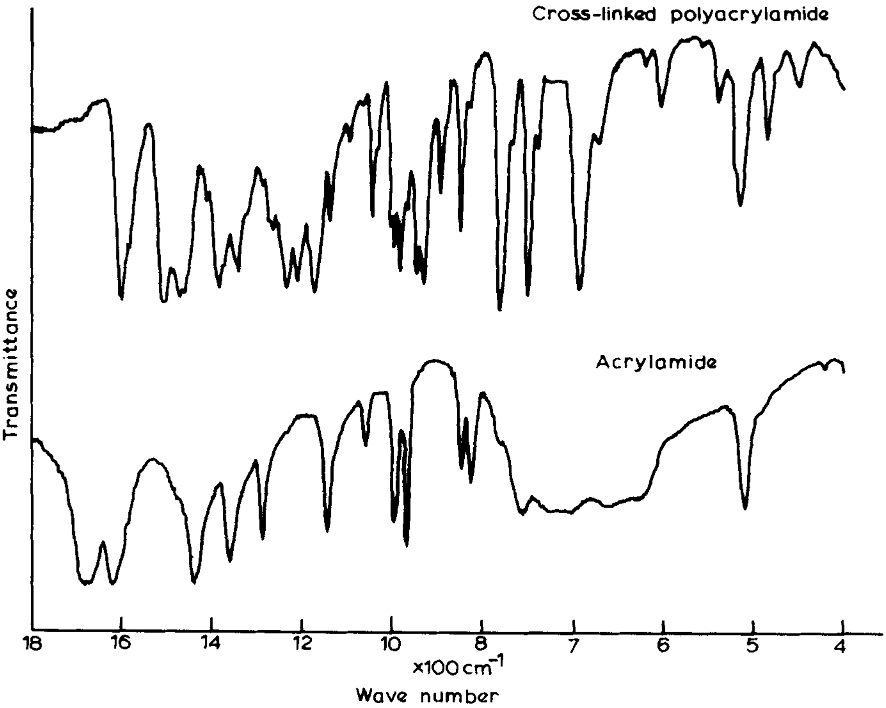
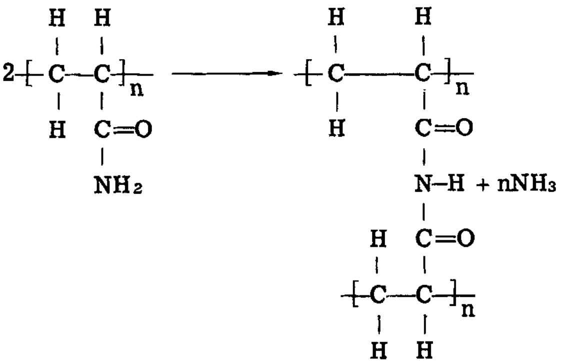


FIG. 6. IR spectra of the acrylamide and cross-linked polymer.



$$2\left[\begin{array}{cc} \mathrm{H} & \mathrm{H} \\ | & | \\ \mathrm{C}- & \mathrm{C} \\ | & | \\ \mathrm{H} & \mathrm{C{=}O} \\ & | \\ & \mathrm{NH_2} \end{array}\right]_n \longrightarrow \begin{array}{c} \left[\begin{array}{cc} \mathrm{H} & \mathrm{H} \\ | & | \\ \mathrm{C}- & \mathrm{C} \\ | & | \\ \mathrm{H} & \mathrm{C{=}O} \\ & | \\ & \mathrm{N{-}H} \\ & | \\ & \mathrm{C{=}O} \end{array}\right]_n \\ \left[\begin{array}{cc} \mathrm{H} & \\ | & | \\ \mathrm{C}- & \mathrm{C} \\ | & | \\ \mathrm{H} & \mathrm{H} \end{array}\right]_n \end{array} + n\mathrm{NH_3} \qquad (1)$$

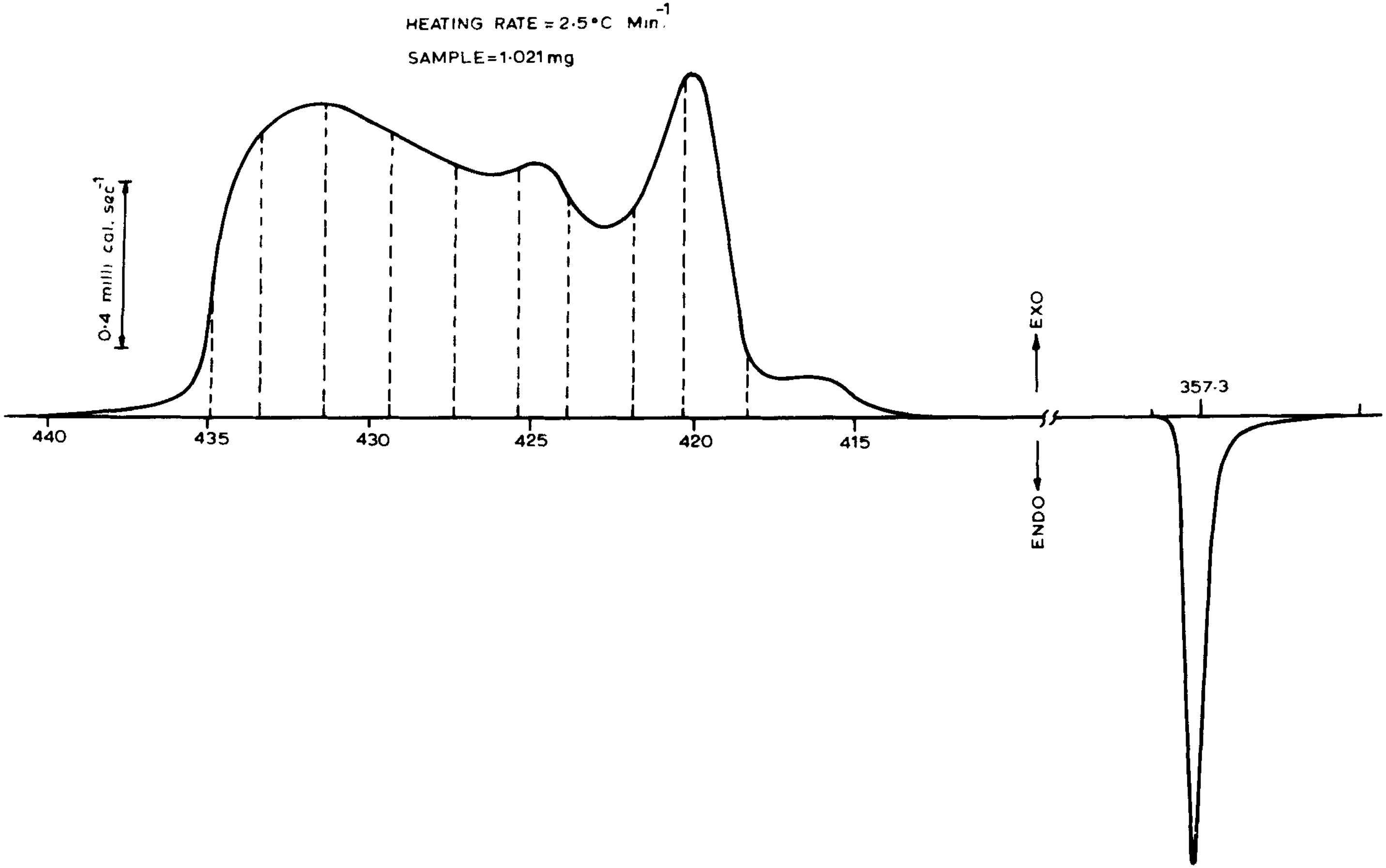
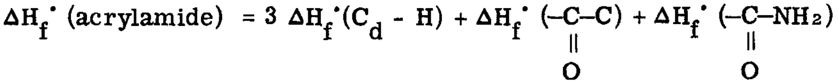


FIG. 7. A typical DSC thermogram of acrylamide.

The overall exotherm corresponding to the formation of linear and cross-linked polymers gives $\Delta H_p = 19$ kcal/mol. If we consider the formation of linear polymer in any vinyl polymerization, the ΔH_p value should correspond to the difference between the bond energies of two single C–C bonds and one C=C bond which is about 20 kcal/mol. Thus the observed enthalpy of polymerization agrees with the theoretically expected value for the formation of a linear polymer. Based purely on enthalpy considerations, it can be suggested that either only linear polyacrylamide is formed, which then accounts for the observed ΔH_p value, or cross-linking occurs following the linear polymerization but with negligible heat evolution during cross-linking. To confirm one of these two possibilities, thermochemical calculations were made for the crosslinking process by adopting the method of additivity of bond contributions proposed by Benson [3]. Derived values of ΔH_f° of different types of bonds are used for such calculations. The assumed values of ΔH_f° are usually within ±2 kcal/mol and may be poorer for heavily branched compounds. The calculations involved are made in the following manner for the reaction represented by Eq. (1):



$$\Delta H_f^{\circ}\,(\text{acrylamide}) = 3\,\Delta H_f^{\circ}(C_d - H) + \Delta H_f^{\circ}\,(-\underset{\underset{O}{\|}}{C}-C) + \Delta H_f^{\circ}\,(-\underset{\underset{O}{\|}}{C}-NH_2)$$

$$= -19.0\ \text{kcal/mol}$$

where C_d = a double bonded carbon atom.

Similarly, $2(\Delta H_f^{\circ}\,(\text{polyacrylamide})) = -75$ kcal/mol and ΔH_f° (cross-linked polymer) + ΔH_f° (ammonia) = -76 kcal/mol. Therefore, the heat evolved during cross-linking is -76 - (-75) or approximately -1 kcal/mol of monomer.

Even though the above ΔH_f° values are only approximate, the heat evolved during cross-linking could be determined from the difference in the ΔH_f° value of the cross-linked products and that of the linear polymer which is about 1 kcal/mol. This suggests that although cross-linking is occurring, the total enthalpy is not greatly altered, and this explains why the observed value is equal to the formation of linear polymer in spite of the cross-linking process taking place.

Table 1 gives E values at different α values. The trend of variation of E with α shows that E remains constant up to $\alpha = 0.5$ and decreases gradually with a further increase in α. Correlating this observation with the composite nature of the exotherms and the α-t, α-T plots, it can be said that the E value up to $\alpha = 0.5$ corresponds to a process with E equal to 19.0 kcal/mol. Beyond $\alpha = 0.5$ a different process (cross-linking) occurs which requires less E. This behavior can be explained as follows.

TABLE 1. Kinetic Parameters for the Polymerization of Acrylamide

α	E (kcal/mol)
0.1	19.5
0.2	19.6
0.3	20.5
0.4	18.2
0.5	18.1
0.6	17.5
0.7	15.6
0.8	14.8
0.9	11.9

It has been stated earlier that the second half of the DSC exotherm represents a cross-linking process. Based on the observed total enthalpy and the calculated enthalpy for the cross-linking process, it was proposed that the cross-linking and linear polymer formation occur simultaneously during the second half of the polymerization. The E for the linear polymer formation is 19 kcal/mol and the minimum E for cross-linking can be taken as the dissociation energy of the C–N bond (~ 73 kcal/mol). Since one cross-link is formed between two monomer molecules, it may be assumed that 36 kcal/mol is the E associated with cross-linking. The potential energy (P.E.) diagram is shown in Fig. 8, wherein it can be seen that a net energy corresponding to 17 kcal/mol is needed for the simultaneous occurrence of linear and cross-linked polymer. Therefore, E in the second half should be around 17 kcal/mol which is the observed value in the present study. This again supports the inference based on thermochemical calculations that the second portion of the polymerization exotherm corresponds to both a linear and a cross-linking process.

Effect of Annealing

The effect of annealing on the polymerization of acrylamide was studied from plots of annealing temperature versus ΔH_p, T_b, and T_e (i.e., the temperatures at which polymerization begins and ends) as shown in Fig. 3. Observation on the shape of the plot of ΔH_p versus annealing temperature shows that ΔH_p values remain constant for annealing up to the melt temperature of acrylamide. This could be due to the fact that, when acrylamide is heated, it first melts and

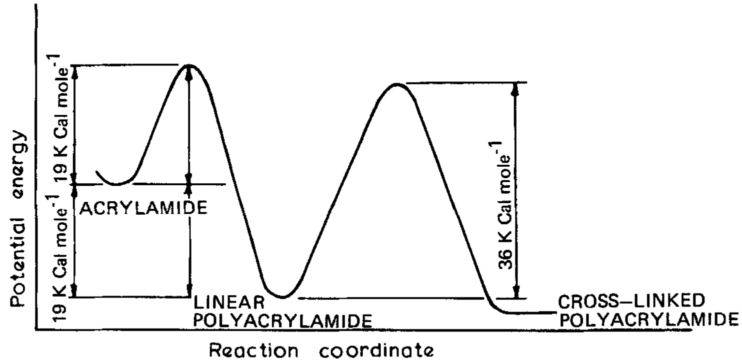


FIG. 8. Potential energy diagram for the polymerization of acrylamide.

then polymerizes in the melt. Hence preheating of the sample below its melting point does not cause any change in the course of polymerization. Then the decrease of ΔH_p values with the annealing temperature equal to and above the melt temperature could be explained in the following manner. It has been shown that free radicals are generated during the melting of acrylamide. When annealing is carried out at or above the melt temperature, the free radicals that are already present can initiate the polymerization process to a certain extent. After the annealing, the temperature of the sample was brought down to 310 K and the sample was again scanned up to the end of polymerization. The ΔH for melting was estimated again and found to decrease as compared to the unannealed acrylamide.

In a similar fashion the decrease in the T_b and T_e values can be explained for annealing at or above the melting point of acrylamide. Due to annealing, the free radicals that are already present may sensitize the polymerization process. The extent of sensitization would be governed by the extent of the free radicals present during annealing.

REFERENCES

[1] K. Kishore, V. R. Pai Verneker, and V. K. Mohan, Thermochim. Acta, 13, 277 (1975).
[2] K. Kishore, Anal. Chem., 50, 1079 (1978).
[3] S. W. Benson, Thermochemical Kinetics, 2nd ed., Wiley-Interscience, New York, 1976, pp. 24-28, 272-280.

Accepted by editor June 20, 1980
Received for publication September 4, 1980