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Polymerization of Acrylamide in Solid State and Melt: A Review

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

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Polymerization of Acrylamide in Solid State and Melt: A Review

K. KISHORE and K. N. SANTHANALAKSHMI

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

INTRODUCTION

Studies on the polymerization of vinyl monomers in the solid and molten phase have received widespread attention in recent years, especially in vinyl polymerization reactions conducted in the molten state of solid monomers which seems to offer encouraging and intriguing possibilities for the production of polymers with respect to their syntheses, properties, and applications. The genesis of solid-state polymerization and its development was based on the following reasons. First, polymerization of crystalline monomers was visualized to produce crystalline and stereoregular polymers and, second, the desire for polymers devoid of any sort of impurities such as occlusion of solvents, catalysts, and initiators. Also, polymerization studies on molten monomer have been undertaken for the same reasons in an analogous manner.

Among the available solid vinyl monomers, acrylamide ($CH_2{=}CH{-}\underset{\underset{O}{\|}}{C}{-}NH_2$) readily undergoes vinyl polymerization in solid, melt, and solution phases. Its homopolymers and copolymers have immense industrial significance due to their solubility in aqueous solutions. Since they belong to the class of water-soluble polymers, few of their special uses are in mineral processing, water treatment, oil well stimulation, friction reduction, paper and textile chemicals,

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and synthetic gels to be used as substrates for analytical separations involving column chromatography and gel electrophoresis. In the present review, special attention is given to the free radical polymerization reaction of acrylamide and acrylamide-based monomers in their solid and molten states. Recently, Kurenkov et al. [1] reviewed the kinetics and mechanism of the free radical polymerization and copolymerization of acrylamide conducted in various solvents and its dependence on such factors as pH, temperature, complexing agents, and surfactants. In the past few decades the subject of solid-state polymerization has been reviewed many times [2-14] and a great deal of literature is available on the topic [15-24]. Unlike solid-state polymerization, studies on the polymerization in the molten state of the monomer have been started very recently and hence, apart from published papers, no collective information such as reviews has appeared until now. Therefore, in this presentation special emphasis is placed on melt-phase polymerization in regard to technical and experimental details and as well as to discussions of the results obtained. Prior to this, several salient features of the solid-state polymerization of acrylamide will be discussed.

SOLID-STATE POLYMERIZATION

A detailed understanding of solid-state polymerization mechanisms has been put forward by various authors, in particular on solid-state systems, including the effect of crystal lattice, lattice imperfections, phase transitions, molecular mobility, and stability. In spite of the wide scope of information available, restrictions are imposed on the initiation techniques which crucially determine the nature of the polymer product.

Initiation Techniques

Generally, high energy radiation (x-, γ-, UV-rays and high energy electrons) has been used as the energy source for initiation in crystalline solid monomers. This is carried out by irradiating monomers at the polymerization temperature or by introducing reactive centers at low temperatures and subsequently warming the sample to obtain a postirradiation reaction. The former method is called "in-source polymerization" and the latter method is called a "postpolymerization" reaction. Mesrobian et al. [24] first described the radiation-induced polymerization of crystalline acrylamide monomer. Since then, investigations covering several aspects of solid-state polymerization of acrylamide have been reported by others.

Apart from the irradiation techniques, photolysis of solid monomers [25], action of light on sensitizers introduced into the solid crystalline acrylamide matrix [26], and directly passing UV-radiation of suitable wavelengths [27, 28] have been studied. Along similar lines, solid-state polymerization of acrylamide initiated using shock wave techniques [29, 30] and by the application of high pressures [31, 32] have gained significant notice. In certain cases some of the pure monomers have been found to undergo spontaneous thermal initiation in the solid state [33], while others require an additive. For example, solid vinylcarbazole polymerizes spontaneously in the presence of carbon tetrachloride upon applying heat [34]. Recently the use of an irradiation procedure for the copolymerization of some of vinyl monomers with acrylamide in the solid state have been carried out by Kucukyavuz et al. [35] by adopting a procedure similar to that of solid-state polymerization reactions.

Polymerization by γ Irradiation

The first definite proof that polymerization of acrylamide occurs within the solid state well below the melting point was established by Mesrobian et al. [24] and Restaino et al. [36]. Since then, both in-source and postirradiation reactions have been studied extensively. The in-source polymerization of acrylamide [37] was carried out by irradiating the monomer crystals in vacuum at temperatures between 5 and 55°C and the residual crystallinity of the monomer crystals was deduced from x-ray diffraction intensity studies. After a 5-h exposure to γ-rays at 35°C, only 50% conversion (polymer yield) and 10% crystallinity was found. In spite of the possibility of in-source solid-state polymerization, studies on the postirradiation reactions were found to be more fruitful since radiation damage to the polymer product does not have to be accounted for. In the postpolymerization technique the acrylamide crystals were γ-irradiated using a ^{60}Co source at low temperatures (-80°C) so as to prevent any significant polymerization. Subsequent polymerization was achieved by raising the temperature of the irradiated solids to 60°C (below the melting point). This experimental technique, followed by various studies on the postirradiation reactions of acrylamide, has been used by many others [38-44].

Even though several alternative techniques have been developed and their results are comparable, the irradiation technique was widely used in solid-state polymerization because with a small amount of ionizing radiation, the distribution of the initiating centers can be considered to be uniform in the crystal, and thus the concentration of initiation centers can be easily varied by varying the irradiation dosage. However, in several cases the polymer yield was found to depend on the radiation dosage, temperature, pressure, etc. [43]. The techniques adopted to follow the postirradiation reactions include x-ray diffraction [24], optical methods [37], electron microscopy [45, 46], and electron spin resonance [47].

In earlier work, Mesrobian et al. [24], Schultz et al. [38, 39], Fadner et al. [41], and Adler et al. [48, 49] adopted the method of x-ray diffraction in order to investigate the crystalline nature of both monomer and polymer products. The results confirmed the amorphous and unoriented nature of the polymer formed. Sella et al. [45, 46] and Bensasson et al. [50] used electron microscopy to follow the different stages of the postpolymerization reaction and proved that polymerization occurred rapidly at the defect sites of the crystal. The nuclei at which the polymerization took place were not randomly distributed but were concentrated at the polymer-monomer interface. This technique appears to be a remarkably vivid and conclusive method for studying the growth of heterogeneous polymerization.

By combining x-ray and optical method results, it was concluded that polymerization proceeds at the polymer-monomer interface created at defect sites of the crystal. Defect sites are created by radiation impinging on different planes of the crystal. Eventually, nucleation for polymerization takes place at slide planes and other internal dislocations of the crystal. It was also established that post-irradiation reactions occur nonuniformly and often result in a polymerization front ahead of which nucleation centers appear, grow, and subsequently submerge into the polymerized region.

A physical reason for the initiation of polymerization reactions only at defect sites of the irradiated crystal was put forth by Adler et al. [37]. Since the polymer formed (viz., polyacrylamide) is insoluble in the molten monomer acrylamide, and since the polymer is denser than the monomer, a strain develops within the crystal domain along the interface wherein propagation of polymerization occurs. Additionally, imperfect sites and dislocations in the crystal create strains. In order to release the strain, polymer propagation occurs disorientedly, resulting in an amorphous polymer.

Baysal et al. [51, 52] studied the heterogeneous feature of postpolymerization of acrylamide by carrying out fractionation studies on the polymer product. The fractionation studies were carried out for both in-source and postpolymerization reactions. The broad molecular weight distribution in in-source polymerization was attributed to continuously increasing polymerizing units of different chain lengths due to continued exposure to radiation. On the contrary, a significantly larger percentage of constant molecular weight formation occurred in postpolymerization reactions. This is because all the polymer growing ends are initiated simultaneously and the rate of propagation depends on the crystal environment. These facts were further confirmed by others [53, 54]. Thus solid-state polymerization may be pictured as proceeding by a nucleation mechanism in which free radicals initiate the reaction at defects and propagate at the monomer-polymer interface. This results in a decrease of the crystallinity of the monomer crystals. However, a contradictory result was observed by Pekala et al. [55] who undertook studies on the changes of crystallinity during γ-irradiation polymerization of vinyl monomers including acrylamide and substituted acrylamides. A rapid increase in the crystallinity for small conversions along with a slow rate of polymerization at the beginning of polymerization was observed. These observations were attributed to the release of the heat of polymerization. The evolution of thermal energy (due to exothermic polymerization) into the monomer crystal lattice increases the thermal vibrations of both the monomer and polymer molecules which break the polymer-monomer interface where polymer chain growth originates. The production of a polymer-monomer interface decreases crystallinity while the reverse effect increases crystallinity.

Polymerization by UV Irradiation

Solid-state polymerization may be induced in some monomers directly by UV radiation of suitable wavelengths [27, 28]. Owing to the high molar extinction coefficient of many monomers, the applied UV radiation may be completely absorbed by a thin layer of the crystal. One advantage of the photolytic process is that the input energy into the crystal may be controlled by using different wavelengths. Baysal et al. [56] first studied the UV-irradiated solid-state polymerization of crystals of acrylamide and acrylic acid. The high polymer yields of Fig. 1 indicate that polymerization takes place

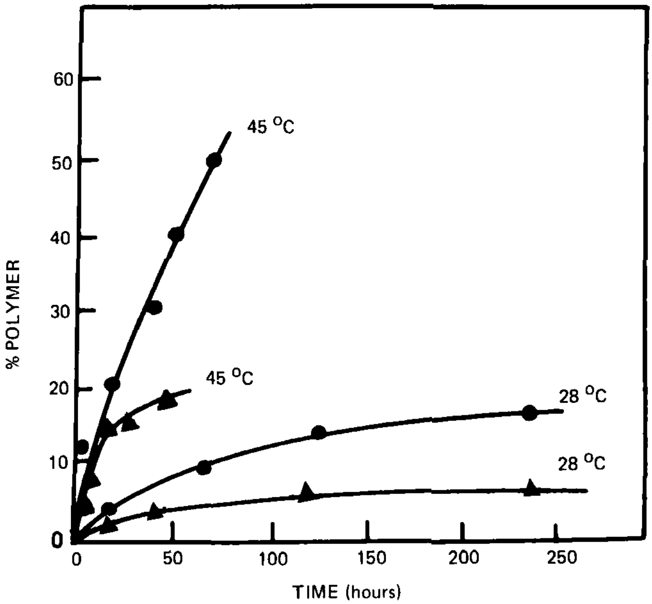


FIG. 1. Postpolymerization by UV irradiation in air. For runs at 45°C under a strong UV source, sample weight 0.8 g (▲); for runs at 28°C under low source, sample weight 0.3 g (●); sample weight 0.8 g (○); sample weight 2.0 g (●) [79].

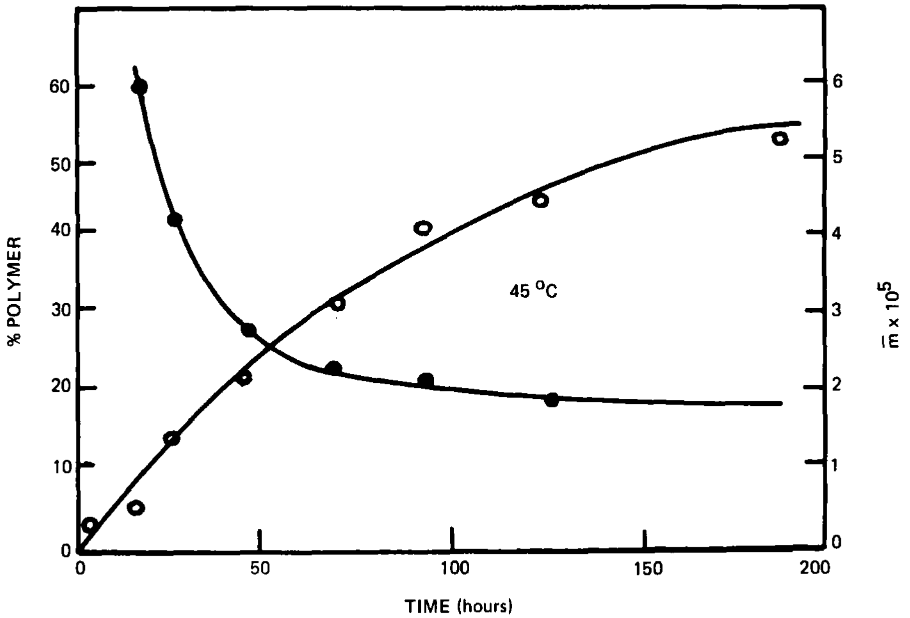


FIG. 2. Plots of conversion (o) and molecular weight (●) for the polymerization of acrylamide by UV radiation in vacuo under a strong source at 45°C [79].

essentially on the surface of the crystal. Baysal et al. [56] observed a decrease in the rate and degree of polymerization due to the presence of O_2 by comparing the data obtained in Figs. 1-3. Ramelow et al. [57] extensively studied several aspects of the UV-irradiated solid-state polymerization of acrylamide by using the electron spin resonance (ESR) technique. The ESR spectra of the irradiated crystals show that the free radicals are stable at room temperatures and decay slowly at higher temperatures [57]. Studies on γ-irradiated acrylamide [58-60] have shown that O_2 has no effect on the postpolymerization of acrylamide. Despite this observation, the addition of O_2 gas seems to cause a change in the ESR spectra. This is due to the interaction of O_2 molecules with the free radicals generated at the surface of the crystal. The reason for this surface phenomenon may be because UV irradiation involves less energy than γ-irradiation. Therefore, on warming acrylamide crystals, polymerization proceeds from the surface toward the interior of the crystal.

ESR spectra taken before and during postpolymerization show that the initiating and propagating radicals are the same as those of the γ-irradiated postpolymerization process. The same studies were also carried out on amorphous polyacrylamide and propionamide-acryl-

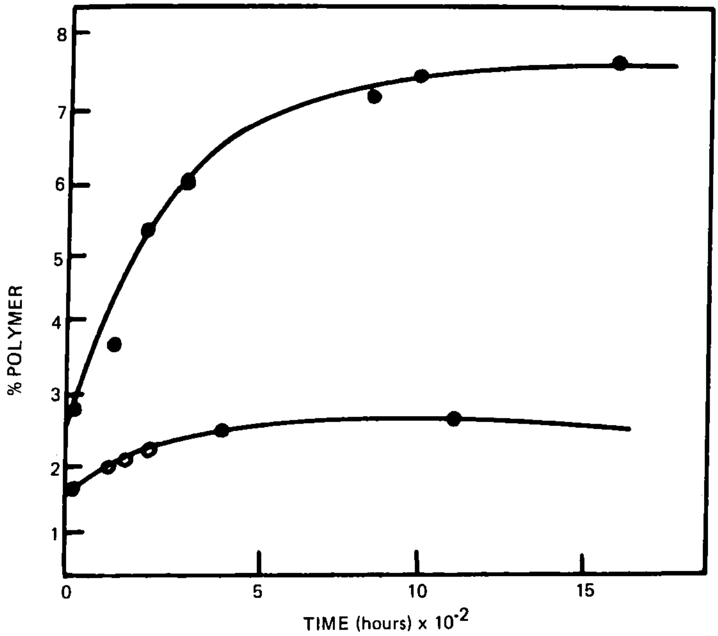


FIG. 3. Postpolymerization of acrylamide by UV radiation at 36°C: 2.1 g samples irradiated 4.5 h at 45°C under a strong source (●); 1.3 g samples irradiated 19 h at 28°C under a low source (○) [79].

amide solid solutions [57]. Upon UV irradiation the free radicals produced in acrylamide as well as in polyacrylamide were not affected by the addition of H_2 or SO_2 gases. The kinetics as determined by ESR signals were found to be consistent with the reaction kinetics established for the γ-irradiated solic-state polymerization of acrylamide. Apart from the surface phenomena, the observations and the inferences made were the same as in the case of γ-irradiated postpolymerization reaction of acrylamide.

Kinetic Studies

Detailed kinetic studies are available for both in-source and postpolymerization solid-state reactions of acrylamide. Baysal et al. [61] obtained time-conversion curves for the in-source polymerization reaction and from them found the activation energy value for the in-source polymerization to be ≃ 3 kcal/mol. The conversion-time curves obtained for in-source polymerization are similar to the sigmoid curves obtained from normal solid-state reactions.

The kinetics of postpolymerization of solid acrylamide have been investigated by several authors [40, 42, 58]. It was observed that the polymer yield Y is related to the reaction time t by

$$Y = A \log (1 + Bt) \tag{1}$$

where A and B are constants. Equation (1) is an empirical equation obtained from the conversion-time plots. The polymer yield was determined by dissolving the unreacted monomer at any instant of time. Equation (1) was found to be consistent with bimolecular termination of the propagating radicals. The postpolymerization rate was found to decrease gradually with time. An expression similar to Eq. (1) was obtained by Fadner et al. [62] by using light-scattering experiments. In most of the cases where the polymer yield is determined by dissolving or melting the unreacted monomer, no accurate resolution of the kinetics was possible. Therefore, spectroscopic studies were used.

ESR and wide line nuclear magnetic resonance (NMR) studies are well-suited for the study of the kinetics of solid-state polymerization. NMR has been successfully applied to a few cyclic monomers [63, 64] and to acrylamide [47, 58]. NMR allows the determination of 1) the actual temperature region in which a reaction occurs; 2) the conversion rates in a continuous manner on the same sample, thus reducing the lack of reproducibility inherent in the preparation of samples; and 3) the structure of the solid monomer and to a certain extent that of the polymer, thus complementing x-ray diffraction results. The ESR technique, on the other hand, gives information regarding the nature of the initiation and propagation steps as well as the radicals involved (which vary with time and temperature). Therefore, a combination of NMR and ESR results gives a clear picture of the solid-state polymerization of acrylamide.

Chachaty et al. [47, 65-67] extensively studied the kinetics of solid-state postpolymerization reactions using wideline NMR and ESR techniques. The conversion yields have been determined from the amplitude of the narrow line which grows during polymerization, Figs. 4 and 5 [65, 66]. Thus, at each temperature interval the rate of conversion with respect to time was determined by means of the ratio between the amplitude of the narrow line and that recorded before the final conversion. The kinetic results from the NMR technique also agree with Eq. (1). From the NMR conversion-time results, a kinetic expression for a bimolecular termination step was put forth as

$$\ln \left(\frac{1}{1 - x} \right) = \frac{k_p}{k_t} \ln \left(1 + k_t(R_0')t\right) \tag{2}$$

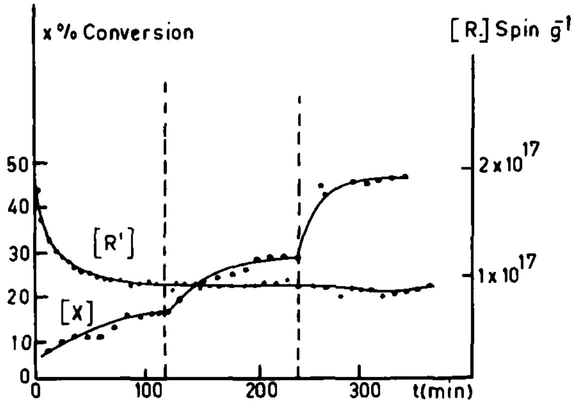


FIG. 4. "Reanimation" of postpolymerization of acrylamide by a stepwise increase of temperature. Corresponding variation of free-radical concentration [61].

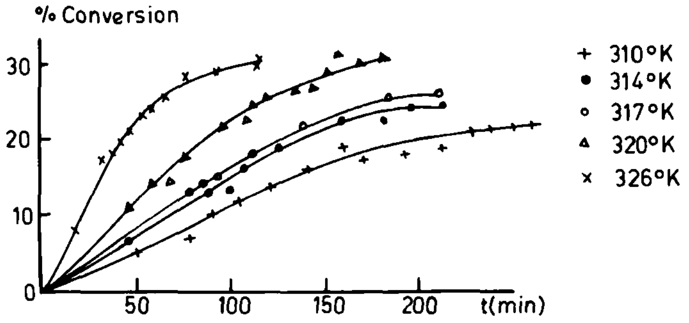


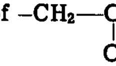
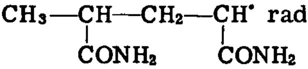
FIG. 5. Plots of postpolymerization curves of acrylamide at various temperatures (irradiation dose 1.8×10^{20} eV/g) [61].

where k_p and k_t are the rate constants for the propagation and termination steps, respectively, and (R_0') is the initial concentration of the initiating radicals. By comparing Eqs. (1) and (2), it is seen that constants $A = k_p/k_t$, $B = k_t(R_0')$, and $Y = \ln(1/1 - x)$. For sufficiently longer periods of time, Eq. (2) becomes

$$\ln\left(\frac{1}{1 - x}\right) = \frac{k_p}{k_t} \ln(k_t(R_0')t) \qquad (3)$$

By using Eq. (3), Chachaty et al. [65, 66] determined the value of the activation energy of the propagation (E_p) and termination (E_t) steps to be 36 ± 5 and 38 ± 5 kcal/mol, respectively. It was also observed that, once the limiting conversion yield is attained, the reaction may be "reanimated" (Fig. 4) by increasing the temperature until a new limiting conversion yield is obtained. A virtually complete polymerization of the monomer can be approached by a stepwise increase of the temperature. The chain reanimation effect has also been observed in many other monomers [68, 69] and appears to be characteristic of solid-state polymerization. A similar observation was also reported by Zurakowska-Orszagh et al. [70] based on studies on the effect of temperature on the kinetics of the radiation-induced solid-state polymerization of substituted acrylamides. An increase in temperature from 300 to 360 K increased the rate of γ-induced polymerization. It was also observed that isomers of the highest reactivity in solid-state polymerization have the lowest activation energy and those with the lowest reactivity have the highest activation energy.

Nature of the Reacting Species

All polymerization reactions must be initiated by some active species, usually a free radical or an ionic group. However, in the case of the solid-state polymerization of irradiated acrylamide, there has been much evidence based on ESR and kinetic measurements suggesting that a free radical is the initiating species. The nature of the initiation process may be elucidated by an examination of the changes in the ESR spectra of the species present before and during past polymerization [71, 72]. A similar study was undertaken by Rogers et al. [60] on other types of amide solids irradiated with γ-rays. It was shown by Adler [73] that irradiated acrylamide shows an ESR spectrum at room temperature which is relatively stable with respect to time in a manner consistent with the reaction kinetics. Adler and Petropoulos [71] identified the initiating radical as $CH_3{-}CH{-}CONH_2$, corresponding to five broad peaks obtained in the ESR spectra of the irradiated acrylamide crystal at -196°C (77 K). This radical was thought to be produced by the ready abstraction of a mobile hydrogen atom which is produced by γ-radiolysis of the monomer crystals. Hence random polymerization does not occur at this stage. On warming the crystals to -145°C and then cooling to -196°C, a new ESR signal with a triplet was observed [71-74]. The new signal was attributed to the presence of  $-CH_2{-}\underset{\displaystyle CONH_2}{\underset{|}{CH^{\bullet}}}$ radical. However five fine structured broad ESR peaks were detected by Adler et al. (16) (Fig. 6), which are reasoned to be due to the formation of  $CH_3{-}\underset{\displaystyle CONH_2}{\underset{|}{CH}}{-}CH_2{-}\underset{\displaystyle CONH_2}{\underset{|}{CH^{\bullet}}}$ radicals. If the free

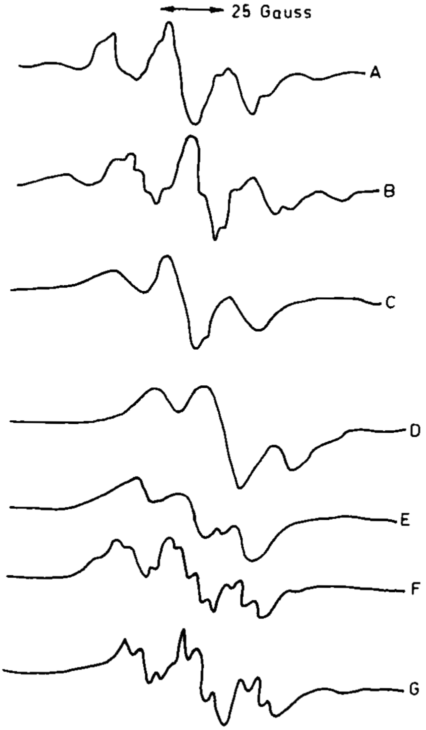
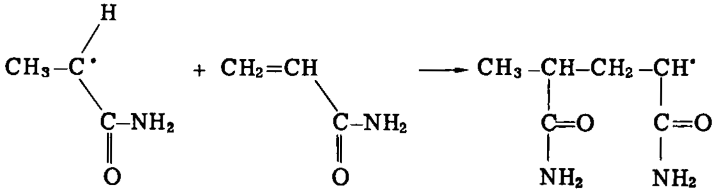
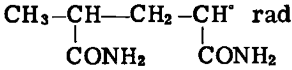


FIG. 6. ESR spectra of irradiated acrylamide at -196°C (A), propionamide (B), acrylamide stored at -80°C for 16 h (C), acrylamide stored at -20°C for 16 h (D), acrylamide single crystal at -100°C (E), acrylamide single crystal at -85°C (F), and acrylamide single crystal at -70°C (G) [16].

radical in acrylamide is produced by hydrogen scavenging, it should have the same structure as that resulting from a loss of hydrogen in propionamide, suggesting the initiating radical to be $CH_3{-}CH{-}CONH_2$ and the propagation in the crystal to be



$$CH_3{-}\overset{H}{C^{\bullet}}{-}\underset{\substack{\Vert\\ O}}{C}{-}NH_2 + CH_2{=}CH{-}\underset{\substack{\Vert\\ O}}{C}{-}NH_2 \longrightarrow CH_3{-}\underset{\substack{|\\ C=O\\ |\\ NH_2}}{CH}{-}CH_2{-}\underset{\substack{|\\ C=O\\ |\\ NH_2}}{CH^{\bullet}} \qquad (4)$$

Studies on the crystal structure [16] show that the distance between successive monomer units in the crystal does not permit the addition of another monomer unit to the  $CH_3-\underset{CONH_2}{CH}-CH_2-\underset{CONH_2}{CH^{\cdot}}$ radical in the same direction but instead permits propagation at random sites in the crystal. Thus the dimer or trimer propagating radical formation results in a contraction in the volume of the crystal lattice, thus additionally building up a strain. These types of strain are concentrated at defected sites of the crystal and hence only an amorphous polymer results. Irradiation of acrylamide at higher temperature (at 20°C) also leads to the formation of free radicals which exhibit a normal triplet ESR signal. Ueda and Kuri [59] reported that after low radiation doses ($\simeq 10^5$ rad), storage at 25°C causes a slight change in the spectrum but with constant radical concentration. Subsequent heating to 50-60°C results in the melting of crystal (rupture of the crystal lattice) with simultaneous polymerization.

In fact, the postpolymerization reaction is the outcome of the effect of temperature on the γ-irradiated acrylamide crystals. It was noted [24, 66] that upon warming up the crystals from -196°C (the temperature at which the crystals are γ-irradiated), a significant postpolymerization reaction begins only at a particular temperature which is higher than the in-source polymerization temperature. Since the postpolymerization of acrylamide is exothermic in nature, there is a temperature rise of the crystal during the postpolymerization reaction. Hence a sudden increase in the crystal temperature is observed when the external temperature (heating temperature) equals the temperature at which significant propagation occurs. Also, the crystal temperature can only rise up to the melting point of the crystal (T_m) since no crystal exists above T_m. The temperature at which significant postpolymerization starts, which equals the critical external temperature (T_e), is given by

$$\frac{T_e}{T_m} = \frac{1 - RT_m}{E} \tag{5}$$

where R is the universal gas constant and E is the overall activation energy for polymerization. The value of T_e can be determined by adopting a method similar to the differential thermal analysis method wherein the crystal temperature is recorded with respect to a reference by simultaneous warming both the crystal and the reference at a definite heating rate. By this method, Chachaty et al. [66] determined E to be 19.0 ± 1 kcal/mol using Eq. (5)

ESR studies have also been used [65, 66] to measure the concentration of the radicals present at any instant of the postpolymerization reaction of the acrylamide. In the absence of any other propagating radical, the concentration of the initiating radicals ($R_0{}^{\cdot}$) is given by

$$(R_0') = k_i(I)t \tag{6}$$

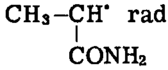
where I is the intensity of the radiation in rad/s and t is the time in seconds. The polymerization rate or the loss of monomer is expressed as

$$\frac{-d(M)}{dt} = k_p(R_0')(M) \tag{7}$$

Therefore

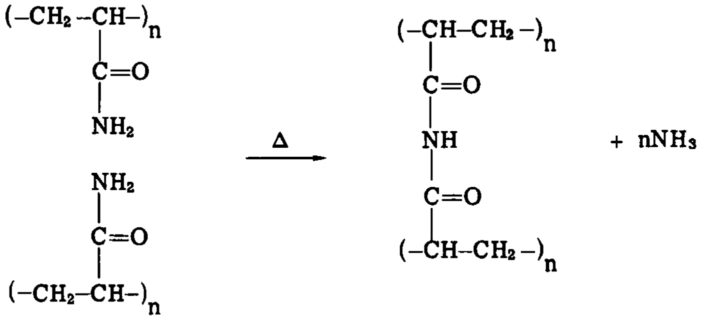
$$\log\left(\frac{M}{M_0}\right) = -\frac{k_i k_p (I)t^2}{2} \tag{8}$$

where M and M_0 are the monomer concentrations at time t = t and 0, respectively, and k_p is the propagation rate constant. However, this relationship was obeyed only at initial conversions and failed at later stages. ESR experiments [74] proved that termination occurs very slowly and that radicals remain for long periods (of the order of several days) due to the trapping of propagating radicals within the polymer region.

The effect of O_2, which behaves as a free radical scavenger, on solid-state polymerization was studied [58, 72, 73]. The pressure of O_2 did not have any significant effect on either polymerization rate or yield. This is due to the fact that O_2 gas cannot penetrate deeply into the crystal lattice, and once the polymer chain is initiated, propagation is unaffected by surface effects. Another method of confirming the initiating and propagating radicals consists of introducing small amounts of nonpolymerizable units within the crystal and following their effect on polymerization yield and rate [66-68]. For this purpose solid solutions of acrylamide-propionamide were studied and the polymerization rate was observed to be unaffected while a drastic decrease in the molecular weight was seen. This was attributed to rapid chain termination steps by  $CH_3{-}\underset{\displaystyle CONH_2}{\underset{|}{CH^\bullet}}$ radicals. Similar studies were undertaken by Yakovleva et al. [75] with such additives as benzanilide and benzamide in acrylamide crystals. These solid additives tend to form binary crystalline eutectic systems with acrylamide, and the polymerization rate increases with an increase in the concentration of acrylamide due to the rapid release of the additional strain created by the presence of these solid additives. Attempts have also been made to analyze the reaction kinetics on theoretical grounds (applying statistical mechanics) for the solid-state polymerization of cyclic monomers and N-substituted acrylamides [76-78]. Assumptions such as the nonstationary, the nonisochoric, and the nonexistence of chain termination reactions were made in the theoretical approach describe the dependence of conversion on irradiation time.

Effect of Pressure

If the initiation or propagation steps are dependent on the presence of crystal defects, it is possible that the application of external stresses may affect the rate of polymerization within the crystal. The influence of pressure on the course of solid-state polymerization falls into two categories: the effect of small pressures (of the order of tens to hundreds of atmospheres) and the effect of large pressures (of the order of thousands of atmospheres). Of these, the latter effect has greater importance due to its effect on the polymerization reaction. Tabata et al. [79] and Fydelor et al. [80] studied the in-source polymerization of acrylamide crystals under 5000 to 6000 atm. Prince and Hornyak [81, 82] investigated the influence of high pressure on the postpolymerization of acrylamide when the monomer crystals were initiated by high energy electrons and by γ-rays. In all these cases the application of pressure increased the rate and the yield of conversion to polymer by a factor of 2 for low radiation dosages as well as for low percent conversions. However a reverse effect was that a new polymer with an imide group was formed with the evolution of ammonia. The imide group formation was found to be due to the following type of cross-linking process:



$$\begin{array}{l}(-CH_2-CH-)_n\\ \qquad |\\ \qquad C{=}O\\ \qquad |\\ \qquad NH_2\\ \\ \qquad NH_2\\ \qquad |\\ \qquad C{=}O\\ \qquad |\\ (-CH_2-CH-)_n\end{array} \xrightarrow{\Delta} \begin{array}{l}(-CH-CH_2-)_n\\ \quad |\\ \quad C{=}O\\ \quad |\\ \quad NH\\ \quad |\\ \quad C{=}O\\ \quad |\\ (-CH-CH_2-)_n\end{array} + nNH_3$$

(9)

The effect of shock waves on solid-state irradiation polymerization was also studied [29]. An increase in the molecular weight of the polymer was observed up to the pressures of 40-80 kbar. However, at 1.20 kbar the molecular weight of the soluble polyacrylamide decreases with an increasing yield of cross-linked polyacrylamide polymer. Massinev et al. [83] studied the effect of shock waves at low temperatures on the solid-state polymerization of acrylamide. It was observed that the yield of polymer increases when shock waves are applied to the previously γ-irradiated acrylamide crystals at -196°C.

POLYMERIZATION REACTIONS IN THE MELT

Similar to the importance of irradiation techniques in solid-state polymerization, initiation by thermal techniques gains importance in polymerization reactions conducted in the molten state of the monomer. Staudinger and Urech in 1929 [84] first pointed out that an insoluble polymer is obtained when thermal polymerization of acrylamide is carried out using benzoyl peroxide as the free radical initiator [85]. The experimental method adopted was of the bulk polymerization type in which an acrylamide and benzoyl peroxide mixture is heated for 3 h at 110°C. The polymer thus produced is insoluble in the molten monomer. Subsequently Schulz et al. [86] and Schurz et al. [87], using infrared spectroscopy studies, showed the formation of polyacrylamide polymer. It was also shown that upon further heating the bulk polymerized material, a yellow horny insoluble solid was obtained, accompanied by the evolution of ammonia gas.

Jones et al. [88] have shown the yellow horny material to be the cross-linked product of polyacrylamide. The occurrence of intermolecular links resulting in the cross-linked product was deducted by the method of Hoffman's reaction during the preparation of polyacrylamines using polyacrylamides [88]. Also no polymerization of acrylamide in the solid or near solid state (below the melting point) was initiated purely by thermal means when the authors carried out thermal polymerization in the absence of initiators. However, polymerization in the near solid state was possible provided the acrylamide crystals were initially irradiated. A complete theoretical approach to thermally and photochemically initiated polymerization of vinyl monomers in the solid state has recently been accomplished by Burdett [89].

The advantage of thermal polymerization over irradiation techniques is that no tedious set-up for the irradiation of the sample is needed. Despite its versatility, further studies on the thermal polymerization of pure acrylamide without the addition of initiators or catalysts relating to the kinetic, thermodynamic, mechanistic, physical, chemical structure of the polymers obtained have not been carried out. An extensive literature survey is available for the homopolymerization of vinyl monomers initiated purely by thermal means [90]. Very recently a detailed investigation on the thermally initiated heterogeneous bulk polymerization of acrylamide has been undertaken by Kishore et al. [91]. The differential scanning calorimetry (DSC) technique was adopted to follow the polymerization reaction. The acrylamide solid first melts upon heating and then polymerizes in the molten state of the monomer. Figure 7, which is a typical DSC thermogram of acrylamide, depicts these processes. The detailed experimental procedure of the study has been dealt with elsewhere [91]. The latent heat of fusion of acrylamide was determined from the melting endotherms to be 36.0 ± 0.7 kcal/mol. After melting, the sample was further heated and exotherms corresponding to the polymerization process were obtained at different heating rates. The respective thermograms are de-

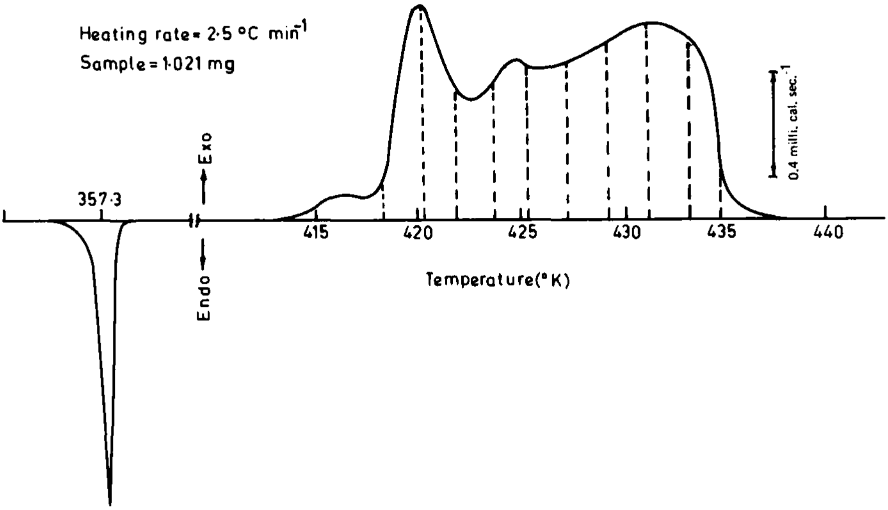


FIG. 7. A typical DSC thermogram of acrylamide.

picted in Figs. 8 and 9. The total enthalpy of polymerization was determined from the area measurements of the exotherms. The value was determined to be -17.6 ± 0.4 kcal/mol.

Methods of Study

Based on thermal studies, attempts to derive the kinetics as well as the energetics of the polymerization process have been made [91, 92].

The fraction polymerized (α) versus time and α versus temperature (T) curves were generated from thermograms by segmental area measurements. The ratio of the segmental area to the total area gives the fraction polymerized (α) at that instant of time and temperature. Figures 10 and 11 show α-t and α-T plots. For the determination of the overall activation energy of the process, a method independent of the assumption of the reaction order was used. From the α-T plots the Arrhenius plot was generated based on [93]

$$S/\Delta H_p = (1 - \alpha)^n A e^{-E/RT} \tag{10}$$

where S is the DSC signal in mcal/s for a full-scale deflection, ΔH_p is the total heat of polymerization, A is the frequency factor, and R is the gas constant. Using Eq. (10), the value of E was obtained from the

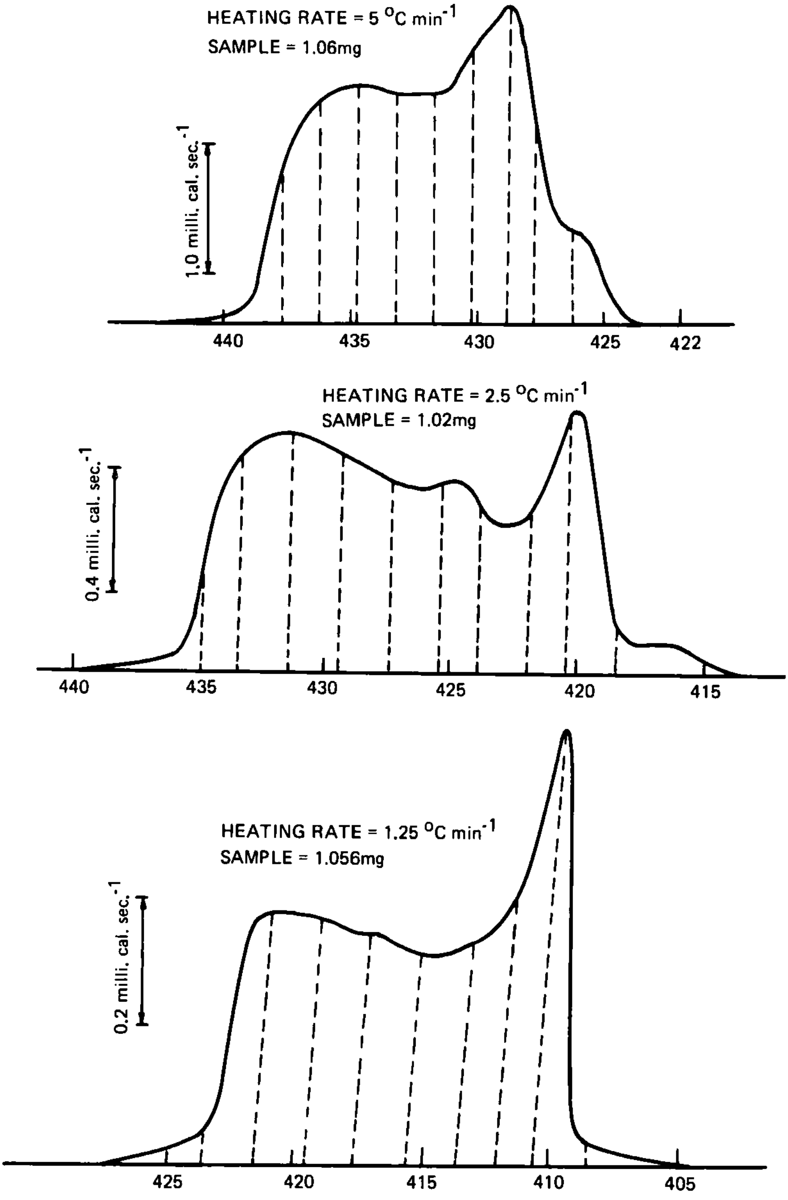


FIG. 8. DSC thermograms of the polymerization of acrylamide.

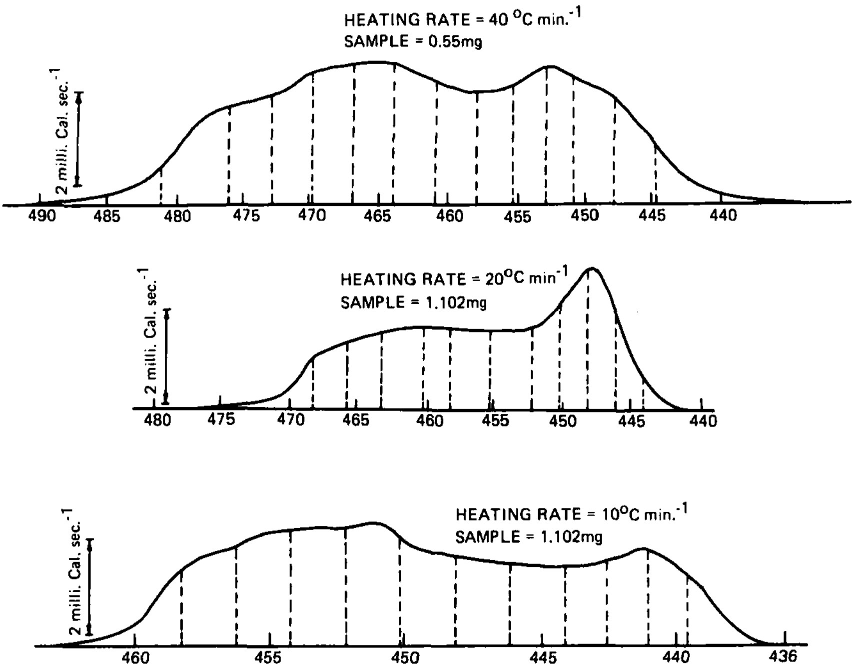


FIG. 9. DSC thermograms of the polymerization of acrylamide.

slope of a plot of ln $(S/\Delta H_p)$ vs 1/T. In so doing, α and n are kept constant. For a fixed value, the constancy of n was checked by the so-called reduced-time plot [94]. The α vs reduced time plot is shown in Fig. 12. The reduced time plot shows that the general kinetic pattern of the reaction is independent of the heating rate employed, suggesting thereby that n could be considered constant for all practical purposes. The values of E and A at different values of α are given in Table 1.

An examination of the shape of the exotherm of the thermograms (see Figs. 8 and 9) and the variation in the values of E from $\alpha = 0.5$ reveals that the polymerization is composite in nature. The change in E values could be due to cross-linking processes. In order to understand the nature of the reactions taking place, experiments such as DTA with EGA (evolved gas analysis) and infrared spectral studies of the samples intercepted at different fractions polymerized, have been adopted by Kishore et al. [92]. The IR spectra of the acrylamide monomer, the polyacrylamide polymer, and the cross-linked polymer are shown in Fig. 13. The presence of secondary amide bands along with primary amide bands strongly supports the cross-linking process via the ionization of primary amide groups.

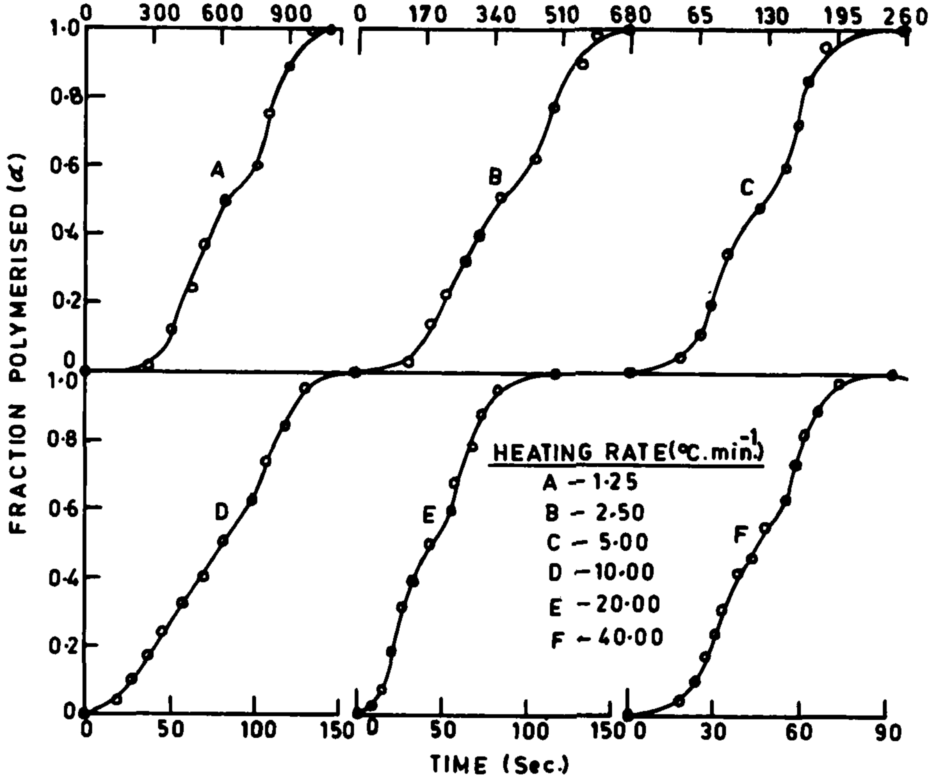


FIG. 10. α vs time plot for the polymerization of acrylamide.

DSC thermograms in the presence and absence of benzoquinone, which is a free radical scavenger (Fig. 14), clearly show that the polymerization is desensitized drastically because of the inhibition of the free radicals produced [91]. Since no conclusive evidence of free radicals could be obtained from ESR techniques, annealing studies were undertaken by Kishore et al. [92]. The effect of annealing below and above the melting point of acrylamide on the melting and polymerization process has been studied by the DSC technique [92]. Plots of annealing temperature versus beginning (T_b) and end polymerization (T_e) temperatures and enthalpy of polymerization (ΔH_p) are shown in Fig. 15. The shapes of the plots in Fig. 15 show that T_b, T_e, and ΔH_p values remain constant for annealing temperatures up to the melting temperature. Hence, preheating the sample below its melting point does not cause any change in the course of

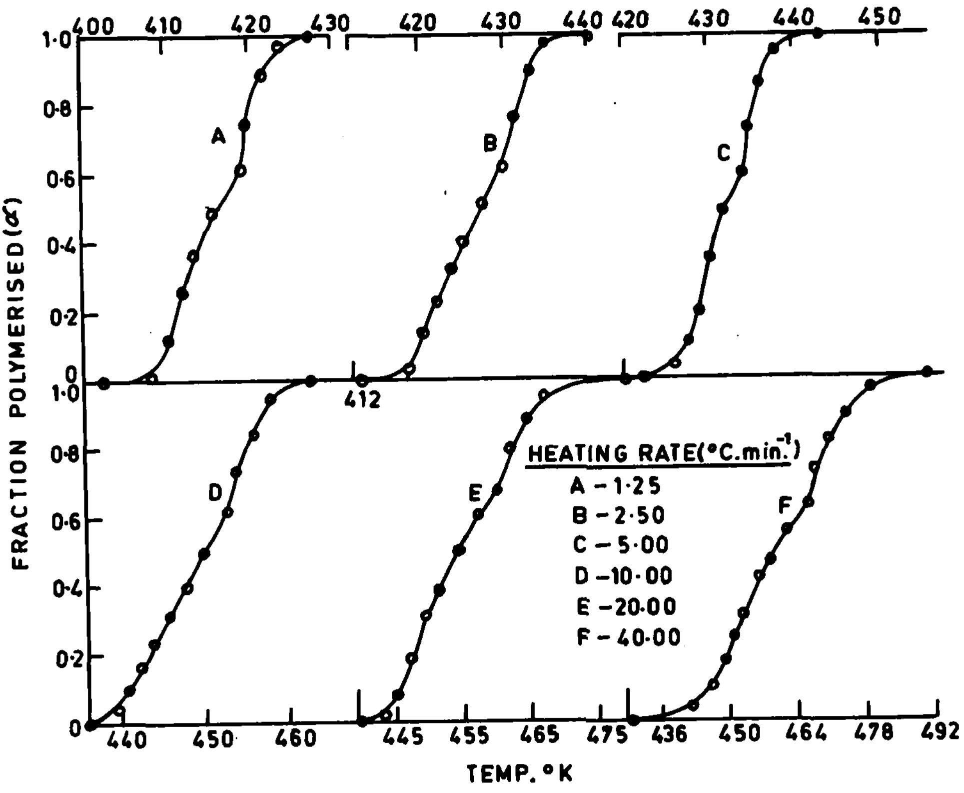


FIG. 11. α vs temperature plot for the polymerization of acrylamide.

polymerization. The decrease in ΔH_p values and the lowering of T_b and T_e values with annealing temperatures equal to and above the melt temperature could be due to the free radicals generated during the polymerization process. Therefore, when annealing is carried out at or above the melt temperature, the free radicals present can initiate the polymerization process to some extent. Similarly, the decrease in the T_b and T_e values can be explained for annealing at and above the melting point as due to sensitization caused by the presence of the initiated species. DSC studies conducted on the effect of O_2 and N_2 atmospheres on the thermal polymerization of acrylamide show that the presence of oxygen molecules drastically reduces the rate of polymerization. The DSC thermograms of acrylamide in air, N_2, and O_2, shown in Fig. 16, depict this effect. The

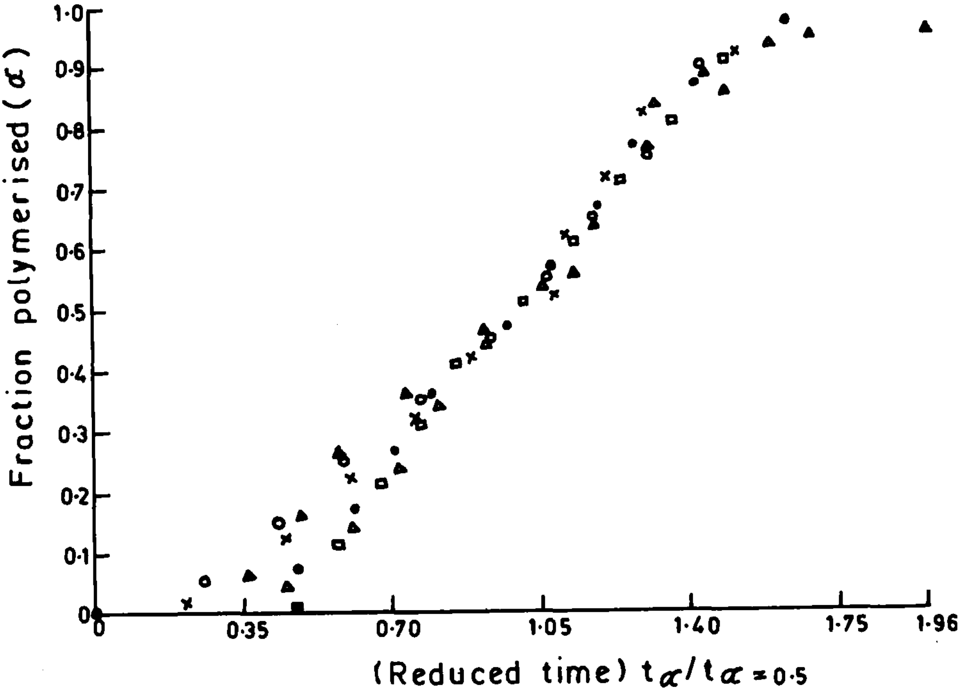


FIG. 12. Fraction polymerized vs reduced time at various stages of reaction. Heating rate (°C/min): 1.25 (□), 2.50 (×), 5.0 (△), 10.0 (○), 20.0 (▲), 40.0 (●).

results from air and O_2 do not show any difference, indicating that the presence of O_2 in the slightest amount reduces the polymerization front drastically. These observations conclusively prove the free radical polymerization of acrylamide.

Kinetic Studies

The polymer product obtained, i.e., polyacrylamide, is insoluble in molten monomer acrylamide, thus rendering the polymerization system heterogeneous. Therefore, this type of thermal polymerization of acrylamide represents a typical heterogeneous bulk polymerization (in the absence of initiators) initiated purely by thermal means. In general, the rate R_p of the thermally initiated homogeneous polymerization of vinyl monomers has been given as [90]

TABLE 1. Kinetic Parameters for the Polymerization of Acrylamide

	E (kcal/mol)	A (s^{-1})
0.1	19.5	6.8×10^4
0.2	19.6	6×10^4
0.3	20.5	1.7×10^4
0.4	18.2	1.4×10^4
0.5	18.5	1.1×10^4
0.6	17.5	0.7×10^4
0.7	15.6	0.01×10^4
0.8	14.8	-
0.9	11.9	-

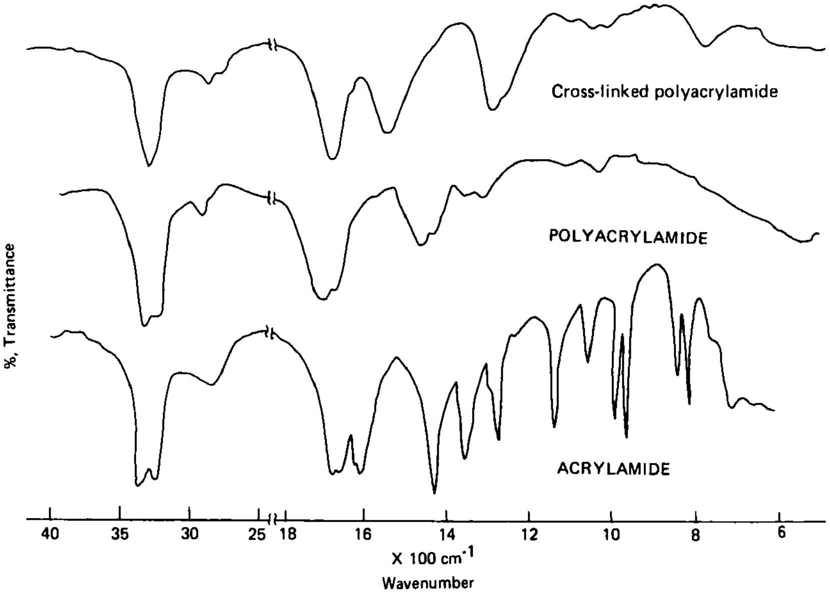


FIG. 13. IR spectra of acrylamide, polyacrylamide, and cross-linked polyacrylamide in KBr pellet.

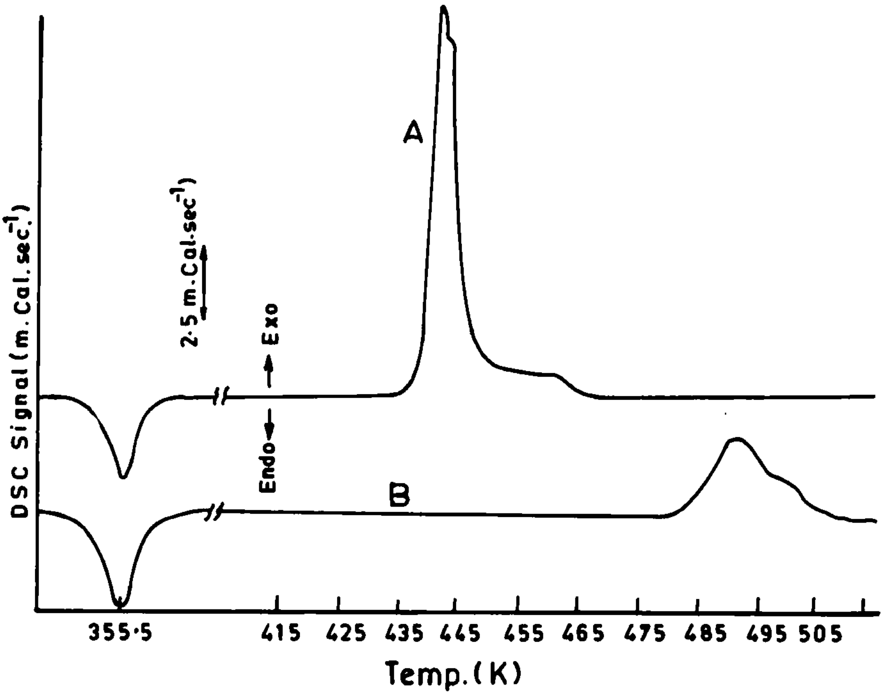


FIG. 14. DSC thermograms of acrylamide in the presence and the absence of benzoquinone. A: Acrylamide (3.015 mg) (ΔH_p = -17.9 kcal/mol). B: Acrylamide (4.950 mg) + benzoquinone (0.149 mg) (ΔH_p = -11.5 kcal/mol).

$$R_p = k_p \left(\frac{k_i}{k_t} \right)^{1/2} (M)^2 \tag{11}$$

where k_p, k_i, and k_t are the rate constants of the propagation, initiation, and termination steps, respectively, and (M) is the monomer concentration. For the heterogeneous polymerization of vinyl monomers (in the presence of an added initiator), the following rate equation has been given (where polymerization in a homogeneous liquid and in precipitated polymer phases is considered to be simultaneous [95, 96]):

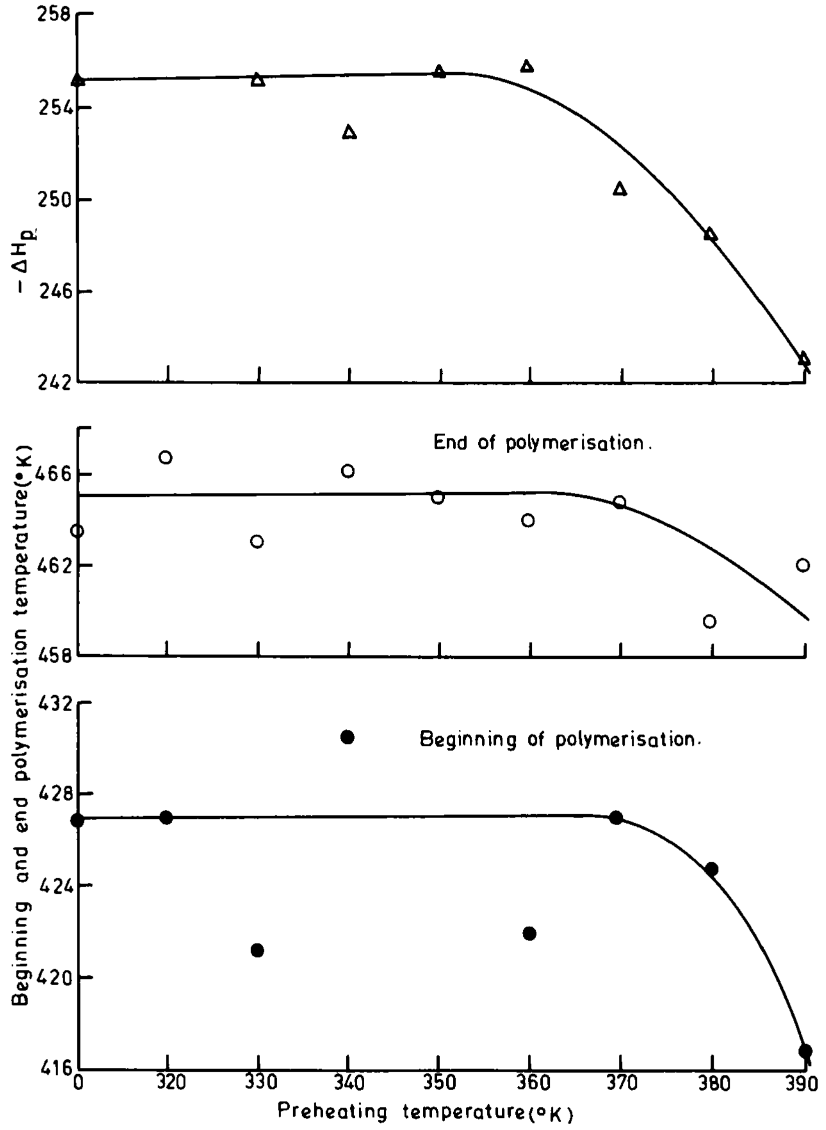


FIG. 15. Dependence of ΔH_p and beginning and end polymerization temperatures on annealing temperature.

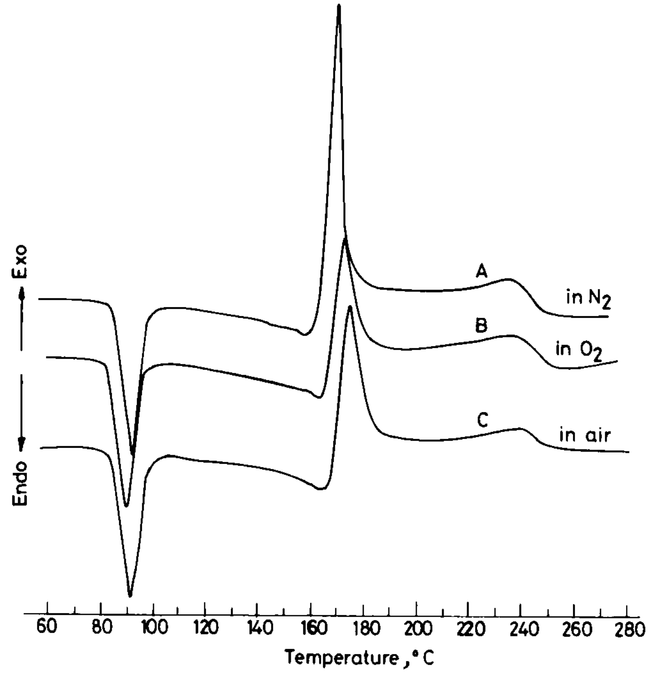


FIG. 16. DSC thermograms of acrylamide in air, N_2, and O_2:

	A	B	C
Weight:	5.865	5.900	5.900
Y-axis sensitivity:	50 mV/cm		
Heating rate:	20°C/min		

$$R_p = k_p\left(\frac{fk_d(I)}{k_t}\right)^{1/2}[(M) + f(p)] \qquad (12)$$

where f is the initiator efficiency, k_d is the rate constant for initiator dissociation, and (I) is the initiator concentration. The function f(p) is proportional to the polymer concentration $(P)^x$, where x is an empirical factor similar to the order of the reaction. By making use of Eqs. (11) and (12), the rate equation for the thermally initiated (without initiators) heterogeneous bulk polymerization of acrylamide can be written as

$$R_p = k_p\left(\frac{k_i}{k_t}\right)^{1/2} [(M)^2 + f(p)] \tag{13}$$

At any instant (P) is equal to the extent of the reaction (α) which in terms of (M), is

$$1 - (M) = \alpha = (P)$$

Substituting f(P) in terms of (M), Eq. (13) becomes

$$R_p = k_p\left(\frac{k_i}{k_t}\right)^{1/2} [(M)^2 + k\,(1 - (M))^n] \tag{14}$$

where k is a proportionality constant which can be determined experimentally.

At lower polymer conversions, (M)) is much larger than (p), so that the term $k(1 - (M))^n$ will become negligible, resulting in Eq. (11). At higher conversions, the term $(M)^2$ becomes negligible in comparison with the term $k(1 - (M)^n$, resulting in a rate equation of the form

$$R_p = k_p\left(\frac{k_i}{k_t}\right)^{1/2} k(1 - (M))^n \tag{15}$$

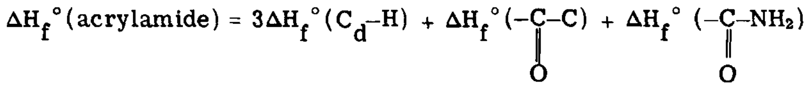
It is obvious that Eqs. (14) and (15) give the same overall E for the polymerization process:

$$E = E_p + \frac{E_i}{2} - \frac{E_t}{2} \tag{16}$$

where E_p, E_i, and E_t are the activation energies for the initiation, propagation, and termination steps, respectively.

Significance of E and ΔH_p of Thermal Polymerization

All vinyl polymerizations are exothermic in nature. The heats of polymerization values of a number of vinyl monomers are available in the literature [97]. Generally, the ΔH_p values of almost all vinyl polymerization reactions are around 20.0 kcal/mol. In vinyl polymerization the process is accompanied by the opening of a C=C double bond to form two C–C single bonds. Therefore, the difference in the normal average bond energy of a C=C bond (146.0 kcal/mol) and the sum of two single C–C bonds (2 × 83 = 1.66.0 kcal/mol) is equal to ~-20.0 kcal/mol. This is the observed ΔH_p in any normal vinyl polymerization involving 1 mol of vinyl group per mole of the monomer. Any deviation, either higher or lower than this value, is due to the presence of substituent groups exhibiting steric hindrance or electromeric or inductive effects. The experimentally determined ΔH_p value of thermal polymerization of acrylamide in the molten state (which is -17.6 ± 0.4 kcal/mol) falls around -20.0 kcal/mol. The implication of this value is that during thermal polymerization acrylamide undergoes a vinyl group opening resulting in the formation of a linear polyacrylamide product. However, in practice, cross-linking of linear polymers is also seen at later stages of the polymerization reaction. Since cross-linking involves exothermic processes, one should expect a significant deviation in the value of the overall polymerization of acrylamide. However, the observed values do not show such a change which further indicates that cross-linking occurs with negligible heat change following linear polymerization. This inference can be confirmed by calculating the enthalpy change involved in the cross-linking of polyacrylamide by adopting Benson's method of thermochemical calculations [98] in the following manner for all the products and reactants involved in the whole thermal polymerization reaction:



$$\Delta H_f^\circ(\text{acrylamide}) = 3\Delta H_f^\circ(C_d\text{–H}) + \Delta H_f^\circ(\text{–}\underset{\underset{O}{\|}}{C}\text{–C}) + \Delta H_f^\circ\ (\text{–}\underset{\underset{O}{\|}}{C}\text{–NH}_2)$$

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

where C_d = a double bonded carbon atom.

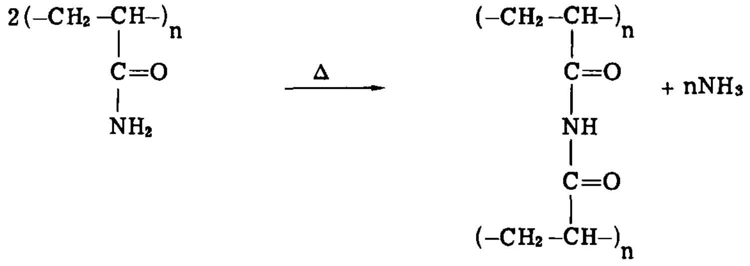
Similarly,

$\Delta H_f^\circ(\text{polyacrylamide}) = -37.5\ \text{kcal/mol}$

$\Delta H_f^\circ(\text{cross-linked polyacrylamide}) = -65.0\ \text{kcal/mol}$

$\Delta H_f^\circ(\text{ammonia}) = -11.0\ \text{kcal/mol}$

So that in the reaction



$$2\begin{array}{l}(-CH_2-CH-)_n \\ \qquad\quad | \\ \qquad\ C{=}O \\ \qquad\quad | \\ \qquad\ NH_2 \end{array} \xrightarrow{\Delta} \begin{array}{l}(-CH_2-CH-)_n \\ \qquad\quad | \\ \qquad\ C{=}O \\ \qquad\quad | \\ \qquad\ NH \\ \qquad\quad | \\ \qquad\ C{=}O \\ \qquad\quad | \\ (-CH_2-CH-)_n \end{array} + nNH_3 \qquad (17)$$

the ΔH_r° value would be around -1.0 kcal/mol, which is a negligible amount. This suggests that although cross-linking is occurring, the total enthalpy is not greatly altered. 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 variation of E with α shows that E remains constant up to $\alpha = 0.5$ and decreases gradually with a further increase in α. Since the first half of the reaction involves the formation of a linear polymer, E = 19.0 kcal/mol indicates a linear polymerization process. The overall activation energy for the polymerization process can be calculated by using Eq. (16). The E values for thermal polymerization (in the absence of initiators) using Eq. (16) have been determined by Flory [99] as 60 and 30 kcal/mol for monomeric diradical and dimeric diradicals, respectively. However, E values calculated using these E_i values do not concur with the observed values. If one considers only the propagation and termination steps as in the case of the postpolymerization of γ-irradiated acrylamide (as carried out by Chachaty et al. [65, 66]), and substitutes the values of E_p and E_t from

$$E = E_p - \frac{E_t}{2}$$

the value of E is around 19.0 kcal/mol.

This suggests that the polymerization exotherm involves only propagation and termination steps and that initiation has occurred before the inception of polymerization. Beyond $\alpha = 0.5$ the value of E decreases, which can be explained as follows. The minimum E for cross-linking can be taken as the dissociation energy of the C–N bond ($\simeq$ 73 kcal/mol). Since one cross-link is formed between two monomer molecules, it may be assumed that 36 kcal/mol will be the E associated with cross-linking. The potential energy diagram (Fig. 17) depicts these processes for the polymerization of acrylamide. For the simultaneous cross-linking and occurrence of a linear polymer, the net energy E will be around 17.0 kcal/mol, which is the observed value. Additionally, these discussions clearly support the inference based on thermochemical calculations to be adequate and equivalent to those derived by other methods.

Effect of UV Irradiation on Thermal Polymerization

Studies on the kinetics and several other aspects of the solid-state polymerization initiated by UV radiation have been discussed in the previous sections. The role of UV irradiation on the thermal polymerization of acrylamide in the molten state of the monomer was studied by Kishore et al. in 1981 [100]. Free radicals were generated by UV-irradiation and further polymerization in the presence of UV irradia-

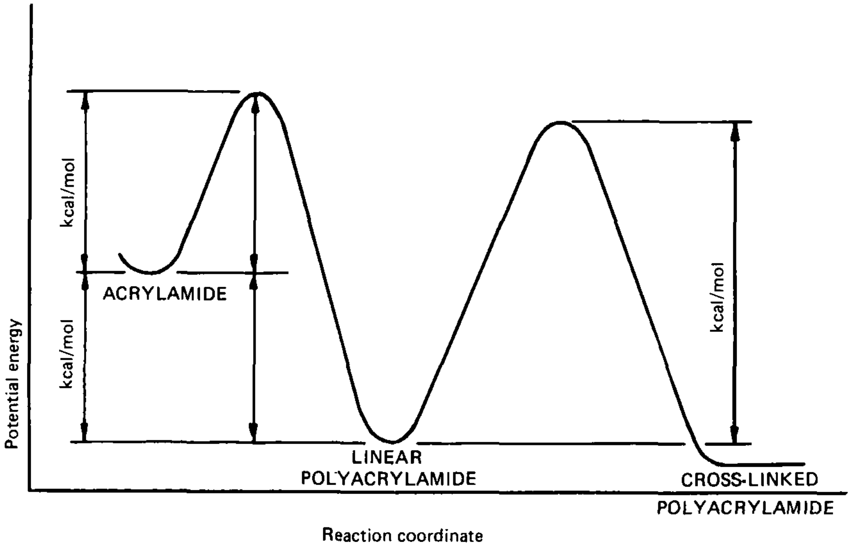


FIG. 17. Potential energy diagram for the polymerization of acrylamide.

tion was avoided. Subsequent polymerization was carried out in the molten state in the absence of UV radiation by using the DSC technique. DSC thermograms of pure unirradiated and irradiated acrylamide in the presence and absence of air are shown in Fig. 18. A summary and details of the results of the thermograms are given in Table 2.

The temperature at which the polymerization starts is always lower for irradiated samples than for unirradiated ones. This suggests that UV irradiation sensitizes the polymerization process. However, the extent of sensitization in air is less than in vacuum. This is because UV irradiation causes radiation damage which results in the production of free radicals [57] and therefore the molten monomer requires less energy for initiation, resulting in an earlier start of the polymerization process. The observed desensitization in air compared to that in vacuum is due to the oxygen molecules present interacting with the free radicals produced. Apart from temperature measurements, enthalpy considerations help in the analysis of sensitization and desensitization processes. According to Table 2 there is a relative desensitization of the 17-h exposed sample compared to the 10 and 5 h exposed samples. This relative desensitization can be explained on the basis of enthalpy considerations. It may be seen that for unirradiated as well as for the 5 and 10 h irradiated samples the values of the heats of polymerization ($-\Delta H_p$) do not change, suggesting that no significant

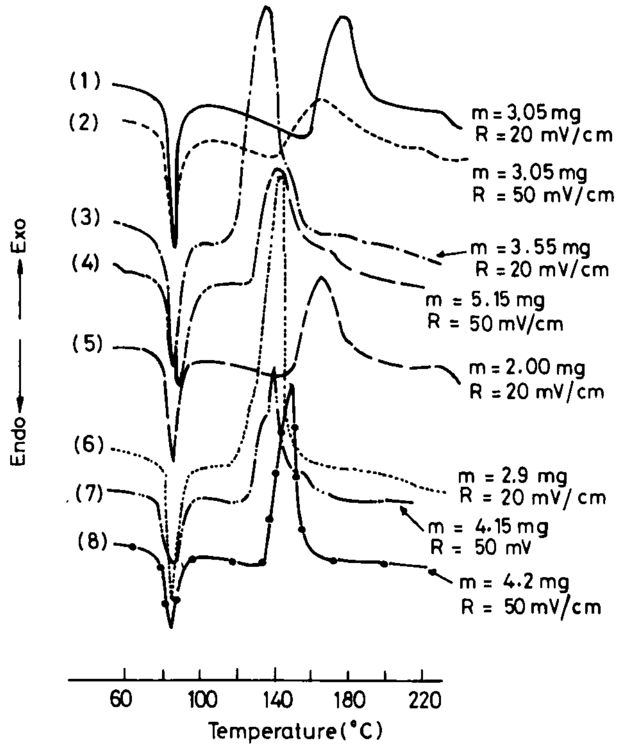


FIG. 18. DSC thermograms of unirradiated and UV-irradiated acrylamide. Heating rate: 50°C/min for Samples 2 and 4; 20°C/min for Samples 1, 3, 5, 6, 7, and 8. R = Y-axis sensitivity for full-scale deflection; m = weight of sample.

polymerization takes place during irradiation. Prolonged exposure to radiation (i.e., 1-17 h) would kindle polymerization to a certain extent. That is, each monomer particle unit is coated with a film of polymer during such a prolonged irradiation process. Since polymers are generally bad conductors of heat, the heat evolved during the subsequent polymerization of entrapped monomer material would be sensed instantaneously by the DSC probe. This results in a decrease in enthalpy and an increase in the starting temperature of the polymerization process. It was also found [100] that the effect of annealing on the UV irradiated thermal polymerization of acrylamide in its molten state produces an opposite effect, i.e., a desensitization. This behavior may be attributed to the fast quenching by thermal energy of the free radicals produced during irradiation.

The effect of pressure on the thermal polymerization of acrylamide as followed by the DSC technique seems to show desensitization. Figure 19 represents the DSC thermograms of acrylamide taken at differ-

TABLE 2. Details and Data of the DSC Thermograms

DSC thermogram no.	Sample	mp (°C)	Exotherm starting temperature (°C)	$-\Delta H_p$ values (kcal/mol)
1	Unirradiated	84	154	18.1 ± 0.4
2	Irradiated in vacuum for 5 h	84	140	17.0 ± 0.4
3	Irradiated in vacuum for 10 h	84	111	17.4 ± 0.4
4	Irradiated in vacuum for 17 h	87.5	125	9.9 ± 0.2
5	Irradiated in air for 10 h	84	147	18.1 ± 0.5
6	Irradiated in vacuum for 10 h, kept 15 min at 50°C	84	113	16.9 ± 0.4
7	Irradiated in vacuum for 10 h, kept 30 min at 50°C	84	120	17.3 ± 0.4
8	Irradiated in vacuum for 10 h, kept 45 min at 50°C	84	132	17.3 ± 0.4

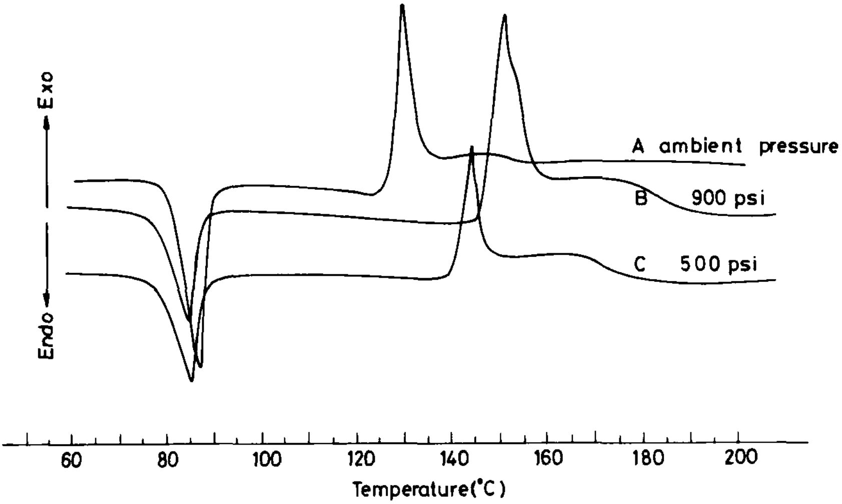


FIG. 19. DSC thermograms of acrylamide at N_2 atmospheric pressures. Heating rate: 10°C/min. Y-axis sensitivity: 20 mV/cm. Time base setting: 0.5 min/cm. Weight (mg): 3.780 (A and B), 3.765 (C).

erent pressures in an N_2 atmosphere. The possible reason for this may be that, unlike in the solid state, an increase in pressure increases tension (i.e., surface force = force per unit area) of the liquid drop of the monomer. This creates a decrease in the free volume available for the propagation of the polymerization process. That is, there is a decrease in the Δ V and hence a late start in polymerization. However, more detailed investigations regarding this aspect are required.

PROSPECTIVES

In the previous sections an attempt was made to present the major features of the solid-state polymerization of acrylamide. The polymerization kinetics involves initiation, propagation, and termination steps. In solid-state polymerization, inhibition or enhancement may be affected by any of these steps. In the solid-state polymerization of acrylamide it is the initiation step which appears to be the limiting factor. It was found that radiation initiation is more facile than thermal initiation in the solid state of the monomer. Hence, even for polymerization carried out in the molten state, the mode of initiation and the type of initiating species have the same significance. Since the molten state of the monomer has to be maintained during polymerization, there is obviously a need for thermal energy, and hence thermal methods of analysis are the best modes of investigation. However, information on the initiation steps of thermal polymerization conducted in the molten state of the monomer exhibits ambiguity. The overall activation energy of acrylamide obtained for polymerization in the molten state agrees with that obtained for the postpolymerization reaction of γ-irradiated acrylamide in the solid state. Upon examining the conversion plots (i.e., α-t and α-T) of the molten state polymerization of acrylamide, it is seen that they resemble the sigmoid curves of solid-state reactions. Studies on the effect of UV irradiation on the thermal molten-state polymerization of acrylamide agree extremely well with observations obtained on the similar solid-state reaction. The end product (polyacrylamide) is the product obtained from both solid-state and molten-state polymerization, thereby suggesting that once polymerization is initiated, propagation and termination proceed along the same lines. These facts clearly confirm that in the thermally initiated (without any initiator) molten state, polymerization take place exactly in the same manner as in the solid-state postpolymerization reaction. The differences are the change in the physical state of the monomer and the energy source.

Even though it was established long ago (1929) that thermal polymerization of acrylamide was possible in the molten state in the presence of an initiator, studies probing into these reactions were not available in the literature until 1980. Recent studies on molten-state polymerization have given a clear understanding of the subject of polymerization in regard to the different physical states of solid monomers. The polyacrylamide product obtained on polymerizing acrylamide is insoluble in the monomer matrix, thus rendering a heterogeneous polymerization system in general. Apart from formulating empirical kinetic expressions in the case of the solid-state irradiation polymerization of acrylamide, no kinetic schemes derived from first principles depicting the physical significance of the heterogenity of the reaction are available. Hence the kinetic schemes reported in the literature need to be altered to suit a heterogeneous kinetic scheme. The expressions derived by Kishore et al. [92] successfully explains the thermal behavior of acrylamide. In earlier studies based on the kinetics of the solid-state polymerization of acrylamide, no understanding of the mechanism (via free radicals) via thermochemical considerations was attempted. Reports on the different activation energies for the propagation and termination steps for the in-source and postpolymerization of acrylamide crystals are difficult to reconcile (Table 3), since irradiation is effective in the initiation step but not in the propagation step. It can be clearly seen from Table 3 that even though experiments were carried out to determine the activation energy of the various steps of solid-state polymerization, no clear-cut studies accounting for the significance of the energetics (either theoretical or practical) are available in the literature. The end product (polyacrylamide) was found to be an amorphous solid both in the solid-state and molten-state polymerization of acrylamide.

TABLE 3. Energetics of Polymerization of Acrylamide

Type	Activation energies (kcal/mol) Propagation (E_p)	Termination (E_t)	Overall (E)	Heat of polymerization $-\Delta H_p$ (kcal/mol)	Refs.
Solid-state postpolymerization	35.0	38.0	19.0	-	60
			18.5	-	60
	25.0	-	-	-	56
	-	-	10.0	-	55
	-	-	4.07	-	40
In-source	-	-	3.0	-	55
In-source (from pressure effect)	-	-	14.0	-	75
			8.0	-	
			8.8	-	
	16.0	-	-	-	48
					49
Solution polymerization	7 to 10.0	-	-	-	56
	-	-	-	19.5 (in H_2O	87
	-	-	-	13.8 (in hexane)	88
	-	-	-	14.4 (in C_6H_6)	

These facts tell us that the difference in the monomer reactivities in the solid and the liquid state can only be attributed to the different activation energies involved and not to changes in the mechanism.

In principle, the influence of the solid state (in fact, of any physical state) of the monomer on the polymerization reaction can be deduced from a comparison of the activation energies and the reaction rate constants of the different steps involved. Moreover, studies of the effect of irradiation on the thermal polymerization of acrylamide would serve as a link between the observations made from irradiation and from thermal initiation. Apart from studies carried out on the polymerization of acrylamide, no similar studies have yet been conducted on other vinyl monomers. Such investigations would provide an understanding of the unresolved areas mentioned above.

REFERENCES

[1] V. F. Kurenkov and V. A. Myagchenkov, Eur. Polym. J., 16, 1229 (1980).

[2] M. Magat, Makromol. Chem., 35, 159 (1959).

[3] A. Charlesby, Atomic Radiation and Polymers, Pergamon, London, 1960.

[4] P. G. Garrat, Polymer, 3, 323 (1962).

[5] M. Magat, Ibid., 3, 449 (1962).

[6] A. Chapiro, Radiation Chemistry of Polymeric Systems, Wiley-Interscience, New York, 1962.

[7] H. Morawetz, in Physics and Chemistry of Organic Solid State (D. Fox, M. M. Labes, and A. Weissberger, eds.), Wiley-Interscience, New York, Vol. I, 1963; Vol. II, 1965.

[8] A. Chapiro, J. Polym. Sci. Part C, 4, 1551 (1964).

[9] H. Morawetz, Ibid., 12, 79 (1966).

[10] H. Morawetz, Pure Appl. Chem., 12, 20 (1966).

[11] N. S. Marans, Polym. Eng. Sci., 6, 14 (1966).

[12] C. H. Bamford and G. C. Eastmond, Rep. Prog. Appl. Chem., 50, 472 (1965).

[13] N. M. Bikales, in High Polymer Series, Vol. 24, Part 1, Chap. 2 (E. C. Leonard, ed.).

[14] C. H. Bamford, A. Bibby, and G. C. Eastmond, Polymer, 9, 629 (1968).

[15] Chemistry of Acrylamide, Process Chemicals Department, American Cyanamid Co., Wayne, New Jersey, 1969.

[16] G. Adler and B. Baysal, Mol. Cryst. Liq. Cryst., 9, 361 (1969).

[17] C. E. Schildnecht, Vinyl and Related Polymers, Wiley, New York, 1952.

[18] W. M. Thomas, in Encyclopedia of Polymer Science and Technology, Vol. 1, 1964, p. 177.

[19] J. E. Wilson, Radiation Chemistry of Monomers, Polymers and Plastics, Chap. 6.

[20] A. Chapiro, High Polymer Series, Vol. 25, Wiley-Interscience, New York, 1962, p. 236.

[21] S. S. Labana, J. Macromol. Sci.–Rev. Macromol. Chem., C12, 314 (1975).

[22] Y. Tabata, Adv. Macromol. Chem., 1, 283 (1968).

[23] H. Morawetz, J. Polym. Sci. Part C1, 65 (1963).

[24] R. B. Mesrobian, P. Ander, D. S. Ballantine, and G. J. Dienes, J. Chem. Phys., 22, 565 (1954).

[25] C. H. Bamford, A. D. Jenkins, and J. C. Ward, J. Polym. Sci., 48, 37 (1960).

[26] C. S. H. Chen, J. Polym. Sci., Part B2, 891 (1964).

[27] C. H. Bamford, G. C. Eastmond, and J. C. Ward, Proc. R. Soc., 271, 357 (1963).

[28] G. C. Eastmond, J. Appl. Chem., 13, 221 (1963).

[29] T. N. Ignatovich, I. M. Warkalov, I. N. Dusin, V. N. Zubarve, and P. A. Yampolskii, Chem. High Energies, 4(5), 443 (1970).

[30] I. M. Barkalov, G. A. Adadurov, A. N. Dremin, V. I. Gol'danskii, T. N. Ignatovich, A. N. Mikhailov, V. L. Talroze, and P. A. Yampolskii, Paper Presented at IUPAC Symposium, Prague, 1965.

[31] Y. Tabata and T. Suzuki, Polym. Prepr., 5, 997 (1964).

[32] P. J. Fydelor and A. Charlesby, Paper Presented at IUPAC Symposium, Prague, 1965.

[33] S. Z. Jakabhazy, H. Morawetz, and N. Morosoff, J. Polym. Sci., Part C4, 805 (1964).

[34] A. Chapiro and G. Hardy, J. Chem. Phys., 59, 993 (1962).

[35] S. Kucukyavuz and B. M. Baysal, J. Polym. Sci., Polym. Chem. Ed., 16, 2901 (1978).

[36] A. J. Restaino, R. B. Mesrobian, D. Ballantine, and C. J. Dienes, Ric. Sci., 25, (1955).

[37] G. Adler, D. Ballantine, and B. Baysal, J. Polym. Sci., 48, 195 (1960).

[38] R. Schultz, A. Henglein, H. E. Vonsteinwehr, and H. Bambauer, Angew. Chem., 67, 232 (1955).

[39] R. Schultz, A. Henglein, and W. Kern, Makromol. Chem., 12, 20 (1959).

[40] A. Restaino, R. B. Mesrobian, H. Morawetz, D. Ballantine, G. J. Dienes, and D. J. Metz, J. Am. Chem. Soc., 78, 2939 (1956).

[41] T. A. Fadner, I. Rubin, and H. Morawetz, J. Polym. Sci., 37, 549 (1959).

[42] G. Adler, J. Chem. Phys., 31, 848 (1959).

[43] H. Morawetz and T. A. Fadner, Makromol. Chem., 34, 162 (1959).

[44] W. Burlant and A. Adicoff, J. Polym. Sci., 27, 269 (1958).

[45] C. Sella and R. Bensasson, Ibid., 56, S1, (1962).

[46] C. Sella and J. J. Trillat, C. R. Acad. Sci. Paris, 252, 1511 (1961).

[47] A. Forchioni and C. Chachaty, J. Polym. Sci., Polym. Chem. Ed., 10, 1923 (1972).

[48] G. Adler and W. Reams, J. Polym. Sci., Part A2, 2617 (1964).

[49] G. Adler and W. Reams, J. Chem. Phys., 32, 1698 (1960).

[50] R. Bensasson, A. Dworkin, and R. Marx, J. Polym. Sci., Part C, 4, 881 (1964).

[51] B. Baysal, Ibid., 4, 935 (1963).

[52] B. Baysal, G. Adler, D. Ballantine, and A. Glines, J. Polym. Sci., Part B, 1, 257 (1963).

[53] I. M. Barkalov, V. I. Gol'danskii, N. S. Enycolopyan, S. F. Terekhova, and G. M. Trofimova, J. Polym. Sci., Part C, 4, 897 (1964).

[54] I. M. Barkalov, V. I. Gol'danskii, N. S. Enycolopyan, S. F. Terekhova, and G. M. Trofimova, Ibid., 4, 909 (1964).

[55] W. Pekala, I. Zchowich, and Z. Gladecki, Radiochem. Radioanal. Lett., 37(4-5), 289-297 (1979).

[56] B. M. Baysal, H. N. Erten, and U. S. Ramelow, J. Polym. Sci., Part A-1, 9, 581 (1971).

[57] U. S. Ramelow and B. M. Baysal, Appl. Polym. Symp., 35, 329 (1979).

[58] T. A. Fadner and H. Morawetz, J. Polym. Sci., 45, 475 (1960).

[59] H. Ueda and Z. Kuri, J. Polym. Sci., 61, 333 (1962).

[60] M. T. Rogers, S. J. Bolte, and P. S. Rao, J. Am. Chem. Soc., 87, 1875 (1965).

[61] B. Baysal, G. Alder, D. Ballantine, and P. Colombo, J. Polym. Sci., 44, 117 (1960).

[62] T. A. Fadner, I. Rubin, and H. Morawetz, Ibid., 33, 95 (1959).

[63] Ya. G. Urman, G. M. Trofimova, A. A. Berlin, and I. Ya. Slonim, Vysokomol. Soedin., A10, 1524 (1968).

[64] I. Ya. Slonim, Ya. G. Urman, A. V. Kesseniker, and E. V. Prut, Ibid., A10, 119 (1968).

[65] C. Chachaty and A. Forchioni, J. Polym. Sci., Part B, 9, 483 (1971).

[66] C. Chachaty and A. Forchioni, J. Polym. Sci., Polym. Chem. Ed., 10, 1905 (1972).

[67] C. Chachaty, M. Latimer, and A. Forchioni, Ibid., 13, 189 (1975).

[68] A. M. Kaplan, D. P. Kiryouchine, I. M. Barkala, and V. I. Goldansky, Dokl. Akad. Nauk SSSR, 190, 1387 (1970).

[69] A. I. Mikhailov, A. I. Bolshokov, I. M. Barkalov, and V. I. Goldansky, Paper Presented at the Third Symposium on Radiation Chemistry, Tihany, 1971.

[70] J. Zurakowska-Orszagh and A. Gurmulka, Proc. Tihany Symp. Radiat. Chem., 4, 401-409 (1976).

[71] G. Adler and J. H. Petropoulos, J. Phys. Chem., 69, 3712 (1965).

[72] G. Adler, J. Polym. Sci., Part C, 16, 1211 (1967).

[73] G. Adler, D. Ballantine, and B. Baysal, J. Polym. Sci., 48, 195 (1960).

[74] H. Morawetz and T. A. Fadner, Makromol. Chem., 34, 162 (1959).

[75] M. K. Yakovleva, V. G. Nekhoroshev, A. P. Sheinker, and A. D. Abkin, Vysokomol. Soedin., Ser. B, 17(3), 212 (1975).

[76] K. Hayashi and S. Okamura, Makromol. Chem., 47, 230 (1961).

[77] S. Okamura, K. Hayashi, and Y. Kitanishi, J. Polym. Sci., 58, 925 (1962).

[78] J. Zurakowska-Orszagh, Polymer, 19(6), 717 (1978).

[79] Y. Tabata and T. Suzuki, Polym. Prepr., 5, 997 (1964).

[80] P. J. Fydelor and A. Charlesby, Paper Presented at IUPAC Symposium Prague, 1965.

[81] M. Prince and J. Hornyak, J. Polym. Sci., Part B, 4, 493 (1966).

[82] M. Prince and J. Hornyak, J. Polym. Sci., Part A-1, 5, 531 (1967).

[83] M. Yu. Messinev, G. A. Adadurov, V. V. Gustov, and A. G. Kazakevich, Khim. Vys. Energ., 11(5), 376 (1977).

[84] Staudinger and Urech, Helv. Chim. Acta, 12, 1107 (1929).

[85] P. J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York, 1953.

[86] R. Schulz, G. Renner, A. Henglein, and W. Kern, Makromol. Chem., 12, 20 (1954).

[87] V. J. Schurz, H. Bayzer, and H. Stubenchen, Ibid., 23, 152 (1957).

[88] G. D. Jones, J. Zomlefer, and K. Hawkins, J. Org. Chem., 9, 500 (1944).

[89] J. K. Burdett, J. Am. Chem. Soc., 102, 5458 (1980).

[90] P. J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York, 1953.

[91] K. Kishore and K. N. Santhanalakshmi, J. Polym. Sci., Polym. Chem. Ed., 19, 2367 (1981).

[92] K. Kishore and K. N. Santhanalakshmi, J. Macromol. Sci.-Chem., A16(5), 941 (1981).

[93] K. Kishore, Anal. Chem., 50, 1079 (1978).

[94] K. Kishore, Indian J. Chem., 16A, 553 (1978).

[95] F. W. Billmeyer, Jr., Textbook of Polymer Science, 2nd ed., Wiley, New York, 1971, pp. 357-358.

[96] H. S. Mickley, A. S. Michael, and A. L. Moore, J. Polym. Sci., 60, 121 (1962).

[97] R. M. Joshi and B. J. Zwolinski, in Vinyl Polymerization, Vol. 1, Part 1 (G. E. Ham, ed.), Dekker, New York, 1967, Chap. 8.

[98] S. W. Benson, Thermochemical Kinetics, 2nd ed., Wiley, New York, 1976. S. W. Benson and J. H. Buss, J. Chem. Phys., 29, 546 (1958). S. W. Benson, F. R. Cruickshank, O. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Waish, Chem. Rev., 69, 279 (1969).

[99] P. J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York, 1953.

[100] K. Kishore and K. N. Santhanalakshmi, J. Polym. Sci., Polym. Lett. Ed., 19, 637 (1981).

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