Thermal Polymerization of Acrylamide in the Solid State

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The role of imperfections in thermal polymerization of acrylamide in the solid state was studied. The polymer yield and the degree of polymerization are highly dependent on the particle size and on the pressure to which the monomer is subjected prior to polymerization reaction. There is an enhancement in the rate of polymerization in air unlike in the case of radiation-induced polymerization. Thermal polymerization of acrylamide in pelletized form results in the formation of water-soluble linear polymer and water-insoluble cross-linked product with the evolution of ammonia. The activation energy (E) values obtained in the present investigation reveal that basically there are two processes taking place, one with $E = 34$–36 kcal/mole, corresponding to the initiation process, and the other with $E = 19 \pm 3$ kcal/mole for the propagation process.

Introduction

The polymerization of numerous monomers in the crystalline state has led to a large number of investigations in the past decade with the objective of obtaining polymers with structures different from those obtained by liquid phase polymerizations (i.e., polymerization in the melt or solution). In most studies on solid-state polymerization the reaction was initiated using uv or high-energy radiation such as X rays, γ rays, or fast electrons either by irradiating monomers at the polymerization temperature or by introducing reactive centers at low temperatures and subsequently warming the sample to give a postirradiation reaction. In recent years the solid-state polymerization of acrylamide, acrylates and methacrylates initiated by γ radiation has been studied extensively (1–11) and it has been shown that the resulting polymer is amorphous (12, 13); uv-initiated solid-state

polymerization of acrylamide and acrylic and methacrylic acids, including the radical mechanism of initiation and termination, the effects of applied pressure as a function of temperature, and the effect of additives on the polymerization have also been reported (14–17).

There are very few solid monomers which undergo purely thermal polymerization reaction. For example, p-acetamido styrene, p-benzamido styrene, and a few conjugated diacetylenes undergo spontaneous thermally initiated polymerization below their melting points (18–22). In the present investigation acrylamide was chosen because it is typical of a class of vinyl monomers which has been shown to exhibit solid-state polymerization by γ rays, uv, X rays, high pressure, and in the presence of initiators (16, 23–28). Acrylamide has a melting point of 84–85°C; it has been reported that below its melting point it shows very little or no tendency to polymerize

thermally (29). Many of the solid-state polymerization reactions proceed at lattice imperfections where the local mobility is larger. The present work describes in a systematic manner our attempts on the study of thermally initiated solid-state polymerization of acrylamide crystals which have been pretreated to produce varying concentrations of imperfections.

Experimental

Acrylamide was recrystallized from acetone and dried under vacuum. The melting point was found to be 85°C. Acrylamide of different particle sizes, ranging from an average of 82.5 to 500 μm was prepared by grinding in mortar and sieving by the use of standard sieves (30–600 μm).

Acrylamide of particle size 185 μm was used for the application of pressure; the pressurization was accomplished with a hydraulic press.

Thermal polymerization was carried out at 70 ± 1°C in an air oven. About 1–2 g of acrylamide of different particle sizes was used in order to study the effect of particle size on the polymerization in air, nitrogen, and vacuum. The effect of pressure was studied in two ways. In one experiment acrylamide pellets obtained at different pressures were used as such, and in another the pressed pellets were dismantled, sieved to the average particle size of 185 μm, and used for polymerization. Since the polymerization rate was slow, the samples were removed from the oven after 14 days, treated with methanol to dissolve the unreacted monomer, and the polymer was then dried under vacuum and weighed. Thus the percentage polymer yields were determined under different experimental conditions. The conversion was almost linear with time in the region of interest (10–20 days) for all the particle sizes. The polymer was analyzed for gel content by treating it with water and filtering through a

sintered crucible. Percentage yields of water-insoluble gel and water-soluble polymer (sol) were thus determined. Polymer samples were characterized by molecular weight determination with an Ubbelohde viscometer at 30°C, using the relationship (30)

$$(n) = 4.07 \times 10^{-6} Mn^{-1.07}.$$

ESR spectra was recorded with a Varian E-109 Xb and ESR spectrometer at 70°C for an acrylamide sample (~ 82.5 μm) heated to 10°C for 4 days.

In order to study the effect of pressure on line defects, acrylamide of particle size 185 μm was pelletized at different pressures, then dismantled, and sieved to the same particle size of 185 μm. X-Ray diffraction patterns were recorded on a Phillips X-ray diffractometer with $CuK\alpha$ radiation at 25 kV, 12 mA with a scanning speed of ½°/min and a chart speed of 4 cm/min for half-width measurement. A high chart speed was employed so that the half-widths of the peaks could be measured and compared accurately.

A Phillips MS 10 mass spectrometer was used to identify the gaseous products formed during the polymerization of acrylamide pellets.

The kinetics of solid-state polymerization were followed by conducting polymerization experiments with 82.5-μm acrylamide at different temperatures from 65 to 80°C in air.

Results and Discussion

Acrylamide maintained at 70°C for 14 days resulted in the formation of polyacrylamide. This was confirmed qualitatively by the insolubility of the product in methanol and by ir spectra, as well as quantitatively later on by molecular weight determination ($\overline{M}n$ is of the order of 5×10^4).

Acrylamide maintained for 4 days at 70°C shows an ESR signal (Fig. 1) at a micro-
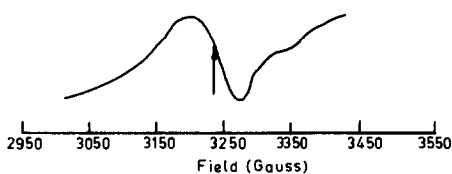
FIG. 1. ESR spectrum of acrylamide at 70°C after 4 days.

wave frequency of 9.045 GHz at 3230 G, corresponding to a g value of 2.003. Although the polymer yield was not very significant after 4 days at 70°C the ESR signal was quite prominent. Thus one can infer that thermal initiation of acrylamide also proceeds via a free radical mechanism, in conformity with the results of the earlier investigations on solid-state polymerization initiated by high-energy radiation (25). Further X-ray diffraction study of the polymer reveals that it is amorphous as in earlier studies (12, 13) where the polymerization was brought about by high-energy radiation.

Effect of Particle Size

An analysis of the study of the effect of particle size on the rate of polymerization reveals that for the polymerization in air and nitrogen atmosphere, the percentage polymer yield is inversely proportional to the particle size of the monomer (Fig. 2). The reactions are initiated at imperfections, and polymerization takes place initially in the more imperfect regions of the monomer lattice. Further formation of polymer from a vinyl monomer involves a change in hybridization of olefinic carbon atoms of the monomer, requiring a change in geometrical disposition of the substituent groups which becomes difficult in a perfect crystal. It is well known that surface itself constitutes a major imperfection in a solid. As the particle size of the monomer decreases, its surface area increases. One can therefore infer that the percentage polymer yield is dependent on the defect concentration.
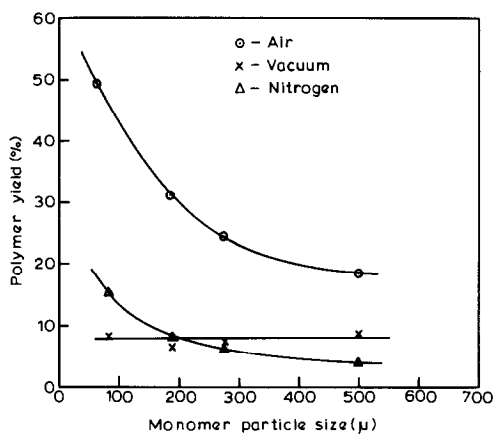

FIG. 2. Dependence of polymer yield on the monomer particle size.

It should be pointed out at this stage that when the polymerization was carried out in vacuum, the polymer yield was found to be independent of the particle size. It was also noted that vacuum polymerization was accompanied by a very high degree of sublimation and, probably, by recrystallization.

Irrespective of the atmosphere (air, nitrogen, and vacuum) in which the polymerization was carried out, the molecular weight of the polymer was found to be proportional to the particle size of the monomer (Fig. 3). At any given particle size the mo-
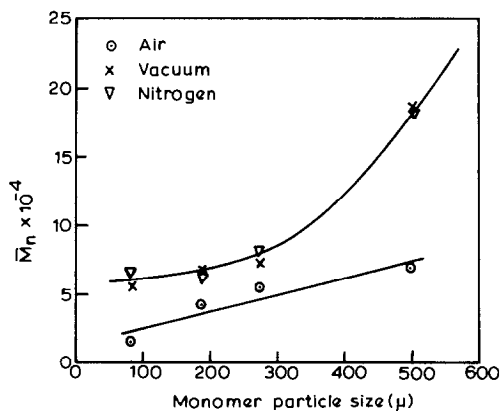

FIG. 3. Molecular weight of polymer, $\bar{M}n$, as a function of monomer particle size.
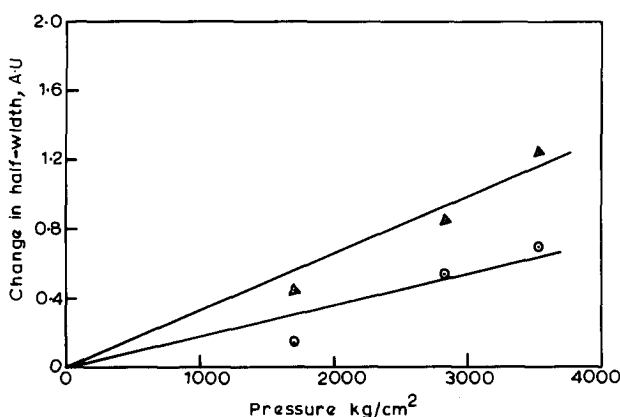
FIG. 4. Variation of change in half-width of X-ray peaks at $2\theta = 11.8°$ (O) and $2\theta = 23.9°$ (△) with applied pressure.

lecular weight of the polymer obtained in vacuum and in nitrogen atmosphere was found to be higher than that obtained in air (all other conditions being constant, such as temperature and time of polymerization). Baysal et al. (31) have observed that the degree of polymerization for polymerization of acrylamide initiated by uv radiation is decreased by the presence of oxygen, due to the fact that chain initiation is faster in air, perhaps following the formation of peroxides. This could therefore explain why polymerization in air produces lower molecular-weight material.

Effect of Pressure

An effective way of increasing the defect concentration in a solid is to subject the solid to a uniaxial pressure as is done during pelletization. If the pellet is now dismantled and a proper particle size is chosen for polymerization, one would then be studying the effect of the imperfections produced as a result of prepelletization on the subsequent polymerization. A measure of the concentration of imperfections produced in this fashion can be obtained by measuring the half-width of the X-ray diffraction peaks (32–35). Figure 4 shows the effect of pressure on the change in half-

width of the X-ray diffraction peaks obtained (for acrylamide monomer subjected to different pressures, dismantled, and then sieved to the particle size of 185 μm) at $2\theta = 11.8°$ and $2\theta = 23.9°$, the half-widths of other 2θ peaks remaining unchanged. There is a significant increase in half-width with pressure, indicating clearly that the imperfections increase with the pressure.

When the pretreated acrylamide (pelletized, dismantled, and sieved to 185 μm) is kept for polymerization in air under identical conditions of temperature and time, the polymer yield was found to increase with the pressure to which the acrylamide was subjected prior to polymerization (Fig. 5). Together with the results obtained from the correlation between change in width of the X-ray diffraction peaks and pressures (Fig. 4), this shows that the polymer yield is dependent on concentration of imperfections of monomer crystals. It is appropriate to recall that the experiments seeking correlation between particle size and yield (Fig. 2) also lead to the same inference. As was observed in the study on the particle size, the polymer yield from the pretreated monomer was independent of pressure when the polymerization was carried out in vacuum.

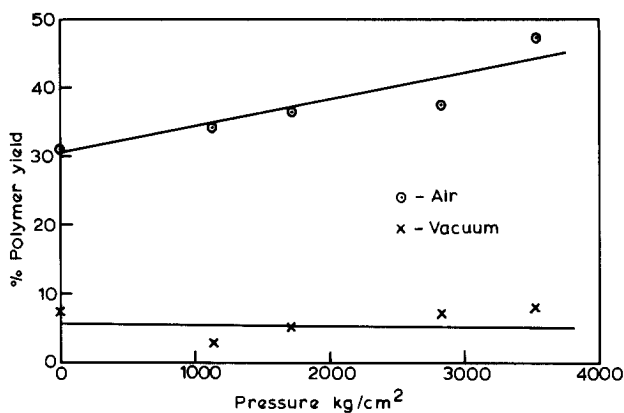In conformity with the studies on the par-

FIG. 5. Polymer yield as a function of applied pressure (pellet dismantled).

ticle size the studies of the effect of pressure on the polymerization reveal that (a) the molecular weight of the polymer is independent of the applied pressure when the polymerization was carried out in air and (b) when polymerized in vacuum the molecular weight increases with the increase in the pelletized pressure (Fig. 6). Nicholson and Norrish (36) studied the effect of pressure on the radical polymerization of styrene in vacuum and found that an increase in pressure and a decrease in catalyst concentration led to an increase in the average degree of polymerization. Similar results have been found on the radical poly-

merization of methyl methacrylate by Vereshchagin et al. (37).

Polymerization of acrylamide pelletized at different pressures and left in the form of pellets (not dismantled) reveals that the polymer yield increases with an increase in applied pressure. As already mentioned in the earlier experiments, larger pressure introduces more imperfections, which in turn leads to an increase in the polymer yield. It is appropriate to point out that Bamford et al. (14) report that for the case of acrylic and methacrylic acids the polymer yield decreases with an increase in the pressure. Apart from the fact that the monomer under
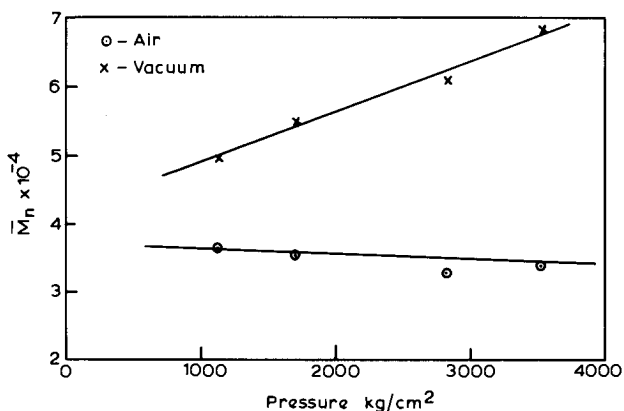

FIG. 6. Variation of molecular weight, $\overline{M}n$, as a function of pressure (pellet dismantled).

investigation was different (acrylic and methacrylic acids by Bamford and acrylamide in the present work) there are two other differences in the experimental procedures. Whereas (i) Bamford used low pressures, such as 5 atm, in the present investigation we used pressures on the order of 10^3 kg/cm^2; and (ii) in Bamford's case polymerization was done *in situ,* i.e., polymerization was carried out with pressure on, whereas in the present investigation the pressure was eliminated before polymerization. Bamford points out that during the application of pressure imperfections such as dislocations move away from the propagating chains, and that this is the reason for the decreased yield. A detailed analysis of the plot of yield versus pressure (Fig. 7) reveals that the polymer yield from an acrylamide pelletized at a pressure of 1100 kg/cm^2 is substantially lower than that using unpelletized acrylamide with particle size 185 μm. This result could have been understood in terms of Bamford's interpretation, except that the later part of the plot shows that the polymer yield increases with pressure, i.e., the concentration of imperfections increases with pressure (Fig. 4). The understanding of the change in polymer yield as one changes from pellets to a powder of 185-μm particle size can be facili-

tated by recalling the results on the effect of particle size on the polymer yield (Fig. 2). If the acrylamide pellet is assumed to be a large particle with a size of 5000 μm (the size of the pellet used in this investigation for polymerization), then there is a significant decrease in surface area as one proceeds from 185 μm at zero pressure to a pellet at 1000 kg/cm^2 pressure. The dependence of polymer yield on particle size is exponential (Fig. 2), and when this is extrapolated to the particle size of ~5000 μm it is evident that it corresponds roughly to the minimum observed in Fig. 7.

The results of the study on the polymer yield as a function of the applied pressure clearly show that the polymer yield is dependent on the pressure, viz., concentration of imperfections if the particle size is kept constant. This is independent of whether acrylamide pellet is polymerized as such or whether the polymerization is carried out by dismantling the pellet. A major difference, however, is observed, depending on the state of acrylamide during polymerization; i.e., whether the pellet is used as such or whether it is dismantled. Whereas polymerization of dismantled pellet of acrylamide yields a linear water-soluble polymer, the polymerization of acrylamide in pelletized form results in both
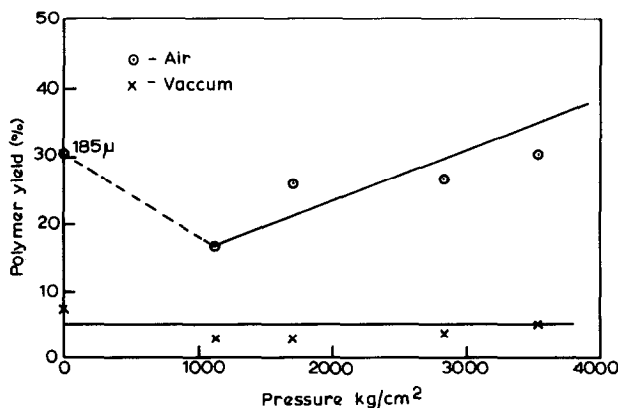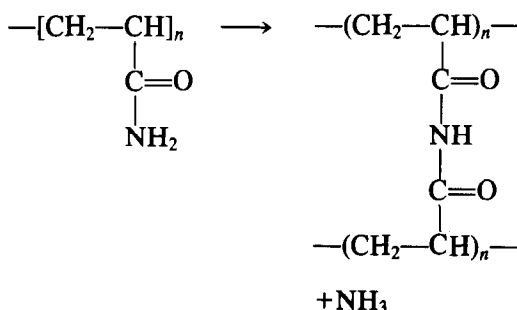

FIG. 7. Polymer yield as a function of pressure (acrylamide in pellet form).

water-soluble linear polymer (sol) and water-insoluble gel. A possible reason for the gel formation is the crosslinking of the linear polyacrylamide molecules through the pendant–$CONH_2$ group, with the loss of ammonia, as per the equation

$$-[CH_2-CH]_n \longrightarrow -(CH_2-CH)_n-$$
$$ \underset{NH_2}{\overset{C=O}{|}} \underset{NH}{\overset{C=O}{|}}$$
$$\underset{|}{\overset{C=O}{|}}$$
$$-(CH_2-CH)_n-$$
$$+NH_3$$

Mass spectrometric analysis of the gaseous product of acrylamide pellet polymerized at 70°C for 14 days in fact reveals the presence of ammonia, confirming the crosslinking process that occurs in the pressed pellets during the polymerization.

The absence of gel formation in the case of acrylamide pellet dismantled shows that the proximity of the molecules in the pressed pellet is important in giving rise to the crosslinked products. This is clearly shown in Fig. 8, where the percentage gel and sol are plotted versus pressure. In air atmosphere percentage gel increases with the applied pressure, while that of soluble polymer increases first, and then decreases, suggesting that more soluble linear molecules are getting crosslinked to produce gel at high pressures. When the experiment is done in vacuum, gel formation is still observed. However, the polymer yield (whether gel or sol) is practically independent of the applied pressure, probably due to sublimation and recrystallization, as explained earlier.

Kinetics of Polymerization

The kinetics of solid-state polymerizations have been investigated both during irradiation and after irradiation (*3, 25*). In various sources polymerizations are often characterized by sigmoidal conversion–time curves with an induction period, an acceleratory region, and finally a deceleratory region. The thermal polymerization reaction of acrylamide also follows a sigmoidal type of curve with an induction period followed by an acceleratory region (Fig. 9). Due to the slowness of the reaction, the final deceleratory region is not recognized in the plot.

Activation energy (*E*) studies can throw light on the mechanism of the polymerization reaction. Generally this is achieved by fitting the kinetic data to different equa-
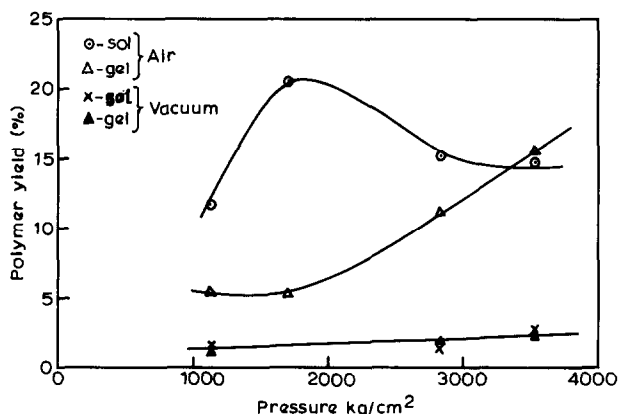

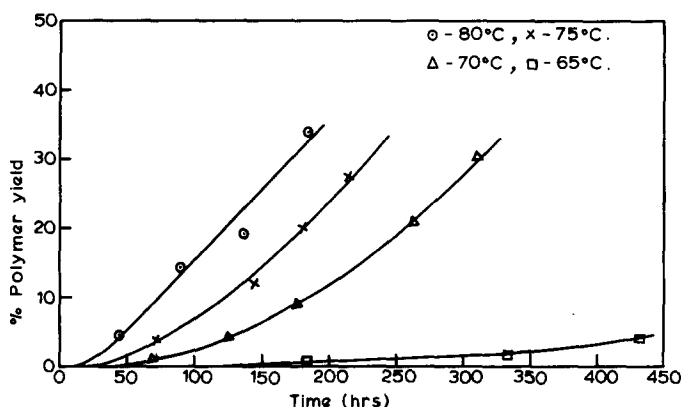FIG. 8. Influence of pressure on the yield of soluble and gel fractions.

FIG. 9. Thermal polymerization of acrylamide at different temperature.

tions. In the present investigation the thermal polymerization rate is extremely slow and, therefore, the kinetic plots have not been taken to completion. It has been shown in solid-state chemistry that the Jacobs–Kureishy technique (38) can be fruitfully utilized to determine E in cases where one is not certain about the topochemical equation to be used or where, due to experimental difficulties, the reaction cannot be taken to completion. Thus the activation energy E was calculated by plotting log $1/t$ versus inverse temperature, where t is the

time taken for the polymer conversion from some finite degree to another. (Details of the method of calculation are discussed by Jacobs and Kureishy (38).)

The activation energy for polymerization of acrylamide induced by γ rays has been attempted by several workers. Their values are listed in Table I. Before applying the Jacobs–Kureishy technique to the polymerization of acrylamide it is worthwhile to test the equation on the data listed in Table I, which also lists the values of E obtained by the Jacobs–Kureishy technique. The

TABLE I

Source	Method	Activation energy (kcal/mole)		Author
		Reported	Calculated	
1. γ ray in-source	Gravimetry	3.0	5 ± 1	Baysal et al. (39)
2. γ ray postirradiation	Gravimetry	10.0	18.4	Baysal et al. (39)
3. γ ray postpolymerization	NMR	19 ± 1	19 ± 1	Chachaty et al. (25)
4. γ ray chain propagation	Gravimetry	25	24.9	Fadner and Morawetz (40)
5. Thermal	Gravimetry		35 ± 1; 19 ± 3	Present work

TABLE II

Percentage conversion	Activation energy (kcal/mole)
0 (intercept on X axis)	35.8
1	36.2
2	36.8
4	35.1
5	34.1
6	23.5
7	23.4
8	22.9
10	21.6
15	19.7
20	17.7
25	15.8

values thus obtained are in good agreement with those calculated by Chachaty and Fadner, irrespective of the percentage conversion. Recalculation of E based on the data of Baysal et al. using the Jacobs–Kureishy technique shows that whereas they report a value of 10 kcal/mole for postirradiation reaction, our calculation yields a value of 18.4 kcal. It can thus be concluded that the E for the propagation reaction is approximately 19–25 kcal/mole.

The E values obtained in the present investigation (Table II) reveal that basically there are two processes taking place, one with E = 34–36 kcal, and the other with E = 19 ± 3 kcal, depending on the extent of conversion. The lower value, 19 ± 3 kcal, is in good agreement with values of the earlier workers (Table I); by analogy it seems to refer to the mechanism of propagation of the chain. This is also apparent by examining the shape of the curve, where the propagation refers to the acceleratory part of the sigmoidal portion. The higher value of 35 kcal/mole would then refer to the initiation process. In a sigmoid curve the induction period is generally related to the initiation process. The induction period could be arbitrarily calculated by equating it with the time required to reach a finite conversion,

say, 1%. Alternatively, one can extrapolate the straight-line portion of the sigmoid curve to the X axis; the intercept represents the induction period in this method. The E values using the above two techniques are in good agreement (Table II). The gradual decrease of the activation energy with an increase in percentage conversion suggests that the actual values obtained represent the resultant of the initiation and propagation.

It is worthwhile to discuss the activation energy obtained by Baysal et al. for polymerization of acrylamide by γ rays in source. Although the activation energy for initiation should be high, the energy provided by the γ rays is much higher; therefore, in principle, the initiation should be independent of temperature. The value of 3–5 kcal/mole which is obtained experimentally is an indication in that direction.

Conclusions

1. The thermal polymerization of acrylamide in solid state takes place via a free radical mechanism as shown by ESR experiments (Fig. 1).

2. The polymer yield and molecular weight are highly dependent on the particle size and pressure to which the monomer was subjected prior to polymerization reaction. The atmosphere also plays an important role in the thermal polymerization of acrylamide in the solid state.

3. Thermal polymerization of acrylamide in pelletized form results in the formation of water-soluble linear polymer and water-insoluble crosslinked product, with the evolution of ammonia.

4. It was shown (39) that γ radiation-initiated solid-state polymerization of acrylamide was not influenced by the presence of oxygen, and that oxygen cannot penetrate into the lattice of acrylamide (41). In the present work on thermally initiated solid-state polymerization of acrylamide an

air atmosphere is shown to enhance the rate of polymerization, presumably due to the formation of peroxides.

5. The activation energy obtained in the present investigation is found to change from an initial value of 34–36 kcal/mole to a value of 19 ± 3 kcal/mole at a later stage, as the percentage conversion is increased.

References

1. H. Morawetz and T. A. Fadner, *Makromol. Chem.* **34**, 162 (1959).
2. T. Fadner, I. Rubin, and H. Morawetz, *J. Polym. Sci.* **37**, 549 (1959).
3. B. Baysal, G. Adler, D. Ballantine, and P. Colombo, *J. Polym. Sci.* **44**, 117 (1960).
4. G. Adler, D. Ballantine, and B. Baysal, *J. Polym. Sci.* **48**, 195 (1960).
5. H. Morawetz and I. D. Rubin, *J. Polym. Sci.* **57**, 669 (1962).
6. J. B. Lando and H. Morawetz, in "Macromolecular Chemistry, Paris, 1963" (M. Magat, Ed.), p. 789, Interscience New York (1964). [*J. Polym. Sci. Part C*, 4]
7. H. C. Heller, S. Schick, H. C. Yao, and T. Colo, *Mol. Crystallogr.* **9**, 401 (1969).
8. B. M. Baysal, E. Erøgoz, and G. Adler, *J. Pure Appl. Sci. 1979* **12**(1), 1 (1979).
9. J. H. O'Donnell and R. D. Sothman, *J. Macromol. Sci. Chem. A* **14**(6), 879 (1980).
10. P. J. Grisard, *Diss. Abstr. Int. B* **38**(7), 3218 (1978).
11. J. H. O'Donnell and R. D. Sothman, *Radiat. Phys. Chem.* **13**(3–4), 77 (1979).
12. G. Adler, *J. Chem. Phys.* **31**, 348 (1959).
13. G. Adler and W. Reams, *J. Chem. Phys.* **32**, 1698 (1960).
14. C. H. Bamford, G. C. Eastmond, and C. Ward, *Proc. Roy. Soc. (London) Ser. A* **271**, 357 (1963).
15. G. C. Eastmond, *Mol. Crystallogr.* **9**, 383 (1969).
16. M. Prince and J. Hornyak, *J. Polym. Sci. Part A-1* **5**, 531 (1967).
17. K. Hayakawa, K. Kawase, and H. Yamakita, *J. Polym. Sci. Polym. Chem. Ed.* **16**(12), 3307 (1978).
18. S. Z. Jakabhazy, H. Morawetz, and N. Borosoft, *J. Polym. Sci. Part C* **4**, 805 (1964).
19. G. Wegner, *Makromol. Chem.* **135**, 219 (1970); **145**, 185 (1971).
20. A. R. McGhie, G. F. Lipscomb, A. F. Garito, K. N. Desai, and P. S. Kalyanaraman, *Makromol. Chem.* **182**(3), 965 (1981).
21. D. Bloor, R. L. Williams, and D. J. Ando, *Chem. Phys. Lett.* **78**(1), 67 (1981).
22. P. S. Kalyanaraman, A. F. Ganto, A. R. McGhie, and K. N. Desai, *Makromol. Chem.* **180**(5), 1393 (1979).
23. A. G. Kazakevich, A. A. Zharov, P. A. Yampolskii, and N. S. Enikolopyan, *Dokl. Akad. Nauk SSSR* **215**(6), 1404 (1974).
24. A. Chapiro, *Isr. J. Chem.* **10**(2), 129 (1972).
25. C. Chachaty and A. Forchioni, *J. Polym. Sci. Part A-1* **10**(7), 1905 (1972).
26. U. Ali and B. M. Baysal, *J. Pure Appl. Sci.* **8**(2), 201 (1975).
27. I. M. Bakalov, U. A. Benderskii, V. I. Goldansky, and S. S. Kuzinina, *Proc. Tihany Symp. Radiat. Chem. 2nd Tihany Hung.*, 607 (1966); 611 (1967).
28. T. Matsuda, T. Higashimura, and S. Okamura, *J. Macromol. Sci. Chem.* **4**(1), 1 (1970).
29. R. B. Mesrobian, Paul Ander, D. S. Ballantine, and G. J. Dienes, *J. Chem. Phys.* **22**, 565 (1954).
30. B. Baysal, G. Adler, D. Ballantine, and A. Glines, *J. Polym. Sci. B*, **1**, 257 (1963).
31. B. M. Baysal, H. M. Erten, and V. S. Ramelow, *J. Polym. Sci. Part A-1* **9**, 581 (1976).
32. D. J. Keating and S. Krasner, *J. Phys. Chem. Solids* **20**, 150 (1961).
33. E. H. Bogardus and R. Roy, *J. Amer. Chem. Soc.* **48**, 205 (1965).
34. V. R. Pai Verneker and K. Rajeshwar, *J. Phys. Chem. Solids* **37**, 63 (1976).
35. H. Lipson and H. Steeple, "Interpretation of X-Ray Powder Diffraction Patterns," Chap. 9, pp. 263, Macmillan, London (1970).
36. A. Nicholson and R. Norrish, *Discuss. Faraday Soc.* **22**, 104 (1956).
37. L. Vereshchagin, V. Derevitskaya, and Z. Rogovin, *J. Gen. Chem. USSR* **21**, 233 (1947).
38. P. W. M. Jacobs and A. R. T. Kureishy, *J. Chem. Soc.* **910**, 4718 (1964).
39. B. Baysal, G. Adler, D. Ballantine, and P. Colombo, *J. Polym. Sci.* **44**, 117 (1960).
40. T. A. Fadner and H. Morawetz, *J. Polym. Sci.* **45**, 475 (1960).
41. G. Adler, in "Macromolecular Chemistry, Prague 1965" (O. Wichterle and B. Sedlecek, Eds.), p. 1211, Interscience, New York (1967). [*J. Polym. Sci. Part C*, 16]