ion could attract a proton to become an $HO_2$ free radical which in turn could enter into subsequent reactions.

The observed radiation induced reaction between hydrogen and hydrogen peroxide (Fig. 4) can occur only at temperatures where the diffusion of atoms, molecules, or ions is possible. The high yields at temperatures above −50° suggest the possibility of a chain reaction such as has been postulated for liquid solution[9,11]

$$H_2O_2 + H \longrightarrow H_2O + OH$$
$$H_2 + OH \longrightarrow H_2O + H$$

This mechanism involves the diffusion of H and OH free radicals and could occur in ice only at temperatures where these free radicals could diffuse.

The yield for the radiation induced reaction between hydrogen and hydrogen peroxide in ice is nearly constant above −50°, indicating that no step in the process is inhibited by lack of the necessary activation energy. On lowering the temperature from −50 to −100° the yield is greatly reduced and it may be assumed that some step in the mechanism which predominates at high temperatures is much less probable at low temperatures. It is possible that a different mechanism is applicable below −100°.

The data plotted in Fig. 5 show that during irradiation of ice at −196° some of the absorbed energy is stored, possibly as trapped electrons or free radicals. When the irradiated sample is warmed, the release of this stored energy leads to disappearance of hydrogen peroxide.

The absorption spectrum measurements confirm the production, during irradiation at −196°, of an entity which disappears on warming.

It is of interest to compare the annealing temperatures observed in these experiments with the temperatures observed by Matheson and Smaller[16] for annealing of paramagnetic species in irradiated ice. The resonance peaks which they attribute to hydrogen atoms disappeared completely at −158 ± 10°. Within experimental error this corresponds with the upper limit of the temperature range in which hydrogen peroxide disappears following irradiations at −196°. The 2800 Å. absorption band anneals out in two temperature ranges which appear to correspond with the annealing temperatures for the paramagnetic resonance absorption which Matheson and Smaller attributed to OH. It seems reasonable that anything which would react with $H_2O_2$ (such as H atoms or trapped electrons) in the temperature range −180 to −160° could also react with OH. Therefore if the 2800 Å. absorption band is due to OH, part of the band should anneal out in the temperature range where $H_2O_2$ has been shown to undergo reaction. The remainder of the OH free radicals should disappear at a temperature where they can diffuse in some manner to react with each other.

OAK RIDGE, TENN.

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[CONTRIBUTION FROM THE POLYMER RESEARCH INSTITUTE, POLYTECHNIC INSTITUTE OF BROOKLYN AND THE BROOKHAVEN NATIONAL LABORATORY]

# γ-Ray Initiated Polymerization of Crystalline Monomers[1]

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Acrylamide, methacrylamide, methylene-bis-acrylamide, vinyl carbazole, vinyl stearate, acrylic acid, methacrylic acid and potassium, calcium and barium acrylates have been polymerized in the solid state by irradiation with γ-rays. The molecular weight of polyacrylamide obtained at low conversion was constant over a 270-fold variation of radiation intensity and in the temperature range 20 to 65°, but increased slightly with the energy of the radiation. The polymerization rate, however, was linear with field intensity, independent of the energy of radiation and had an over-all activation energy of 4.7 kcal./mole. Irradiation of acrylamide at −179° produced "frozen-in" radicals in concentrations of the order of $10^{-4}$ molal. In the polymerization of vinyl stearate the temperature dependences of rate and molecular weight exhibit a discontinuity on passing through the melting point of the monomer. With barium acrylate there is no significant variation in polymerization rate between 10 and 65°. Crystalline maleic anhydride, allylamine hydrochloride and picrate, and stilbene did not polymerize on exposure to γ-rays.

In an earlier communication[3] it was reported that acrylamide undergoes rapid polymerization in the solid state upon irradiation with γ-rays. In this paper detailed results are presented on the polymerization of acrylamide and other crystalline monomers in order to ascertain any unique features that may be characteristics of solid state polymerizations.

## Experimental

**Materials.**—Acrylamide monomer (American Cyanamid Co.) was purified by sublimation at 50–60° under reduced pressure to produce a white, crystalline substance of m.p. 84°. Methacrylamide, m.p. 110°, and N,N′-methylene-bis-acrylamide, m.p. 185° dec. (American Cyanamid Co.) were dried over phosphorus pentoxide prior to use.

Acrylic acid (Monomer-Polymer, Inc.) was separated from methylene blue inhibitor by vacuum distillation through a column packed with copper gauze to inhibit polymerization, b.p. 30° (3 mm.) and m.p. 11°. To prepare potassium acrylate, a portion of distilled acrylic acid was added slowly to a solution of potassium hydroxide in methanol maintained at 12–15° to the end-point of phenolphthalein indicator. The methanol solution was then added in small portions to a large volume of diethyl ether and the crystals that precipitated were filtered, dried *in vacuo* at room temperature and stored at Dry Ice temperature. Barium acrylate was prepared in a similar manner

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[1] Work done under contract with the United States Atomic Energy Commission. A portion of this paper was presented at the American Chemical Society Meeting in New York City, September, 1954.

[2] (a) Portion of thesis submitted to the Chemistry Department of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the Ph.D. degree. (b) Members of the Brookhaven National Laboratory.

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

using methanolic barium oxide. The melting points of potassium and barium acrylate were measured in sealed capillary tubes heated in an aluminum block. Barium acrylate decomposed at 370°, while potassium acrylate was observed to melt with decomposition at 360°. Bromine titration of the salts in water according to the method of Rossman[4] gave unsaturation values of 99.7 and 99.6% of theoretical for potassium acrylate and barium acrylate, respectively.

Vinyl stearate (General Aniline and Film Corp.) was recrystallized from acetone according to the procedure of Craig, *et al.*[5]

Vinyl carbazole, stilbene, allylamine, methacrylic acid and maleic anhydride were obtained from commercial sources and purified by recrystallization or distillation. Calcium acrylate (Rohm and Haas Co.) was used as received.

Allylamine hydrochloride was prepared by dissolving distilled allylamine, b.p. 24° (200 mm.) in anhydrous diethyl ether followed by introduction of gaseous hydrogen chloride until no further precipitation of the salt occurs. The ether solvent was distilled away under vacuum which also removed any residual quantities of allylamine.

Allylamine picrate was prepared by dissolving picric acid in hot chloroform, followed by the addition of an equivalent amount of allylamine. The solution was cooled to ice temperature and crystals of the picrate collected on a fritted glass filter, washed with chloroform and dried *in vacuo*, m.p. 144° (lit. 141.5°).[7]

**Monomer Irradiations.**—Weighed quantities of the monomers were sealed in Pyrex ampules at pressures below $10^{-4}$ mm. The ampules were then inserted into an aluminum canister and lowered into a cobalt-60 γ-irradiation unit. The details of this unit have been described elsewhere.[6] Irradiations were carried out at temperatures from that of liquid nitrogen to 65° and over field intensities of approximately 3000 to 890,000 r.e.p. per hour.[8] In studies involving polymerization of acrylamide with X-rays, the monomer was maintained 13 cm. from the target of a General Electric Maxitron 250 machine.

The field intensities were measured using ceric or ferrous sulfate chemical dosimeters[9a] and ionization chambers.[9b] The results of the two methods were in good agreement. Thermocouples attached to samples during irradiation in preliminary experiments showed that temperature was maintained constant to ±1°.

**Polymer Isolation.**—In studies with acrylamide, methacrylamide and methylene-bis-acrylamide, the samples after irradiation were added with stirring to a large volume of methanol. The polymer was separated from dissolved monomer by filtration on tared fritted glass filters. It was established that this technique is stoichiometrically equivalent to isolation of polymer by precipitation from aqueous solution into methanol. Barium and calcium acrylate polymers were isolated from monomer by virtue of the insolubility of the polymer in water. Polyvinyl stearate was isolated from monomer by precipitation into excess acetone. The estimation of polymerization with the other monomers was based upon bromine titration for residual unsaturation and by viscosity determinations.

**Viscosity Measurements.**—These were performed with the aid of an Ubbelohde dilution viscosimeter having a flow time of 105 seconds for water at 28°. Intrinsic viscosities were obtained from viscosity values at four concentrations below 1.8 g. per 100 ml. of solution.

## Experimental Results

Table I summarizes in a qualitative fashion the response of various crystalline monomers to γ-irradiation.

TABLE I

EFFECT OF γ-IRRADIATION ON MONOMERS

| Monomer | Field intensity (r.e.p./hr.) × $10^{-5}$ | Polymerization temp. (°C.) | Initial rate, % conversion/hr. |
|---|---|---|---|
| Acrylamide | 1.9 | 30 | 12.8 |
| N,N′-Methylene-bis-acrylamide | 1.9 | 30 | 1.6 |
| Methacrylamide | 1.9 | 30 | 0.7 |
| Acrylic acid | 3.1 | −18 | >400 |
| Methacrylic acid | 3.1 | −18 | >400 |
| Calcium acrylate | 1.9 | 35 | 18.1 |
| Potassium acrylate | 1.9 | 35 | 56.8 |
| Barium acrylate | 1.9 | 35 | 75.1 |
| Vinyl stearate | 1.9 | 26 | 20.0 |
| Vinyl carbazole | 2.2 | 30 | 1.1[a] |
| Maleic anhydride | 2.2 | 30 | 0[b] |
| Allylamine hydrochloride | 2.2 | 30 | 0[c] |
| Allylamine picrate | 2.2 | 30 | 0[c] |
| Stilbene | 2.2 | 30 | 0[b] |

[a] Polymerization preceded by an induction period of 20 hours. [b] No polymerization up to 100 hours. [c] No polymerization up to 25 hours.

It is evident from Table II that the presence of oxygen and surfaces have little effect on the solid state polymerization of acrylamide. The presence of water, on the other hand, leads to variable effects. At small concentration, 0.1 weight %, there is no significant effect while at 3.5% concentration the rate of polymerization is markedly accelerated. This is believed to be due to the strong sensitizing action of water with γ-rays to produce hydroxyl and hydrogen radicals. The decrease of the polymerization rate with 6% water content is not clearly understood but could be due to changes in crystal form.

TABLE II

EFFECT OF PREPARATION PROCEDURE ON ACRYLAMIDE POLYMERIZATION[a] AT 35°

| Preparation | % Conversion after 1 hr. |
|---|---|
| Unpurified monomer | 10.8 |
| Sublimed and sealed under oxygen | 12.6 |
| Sublimed and sealed *in vacuo* | 12.9 |
| 63 parts powdered glass added | 16.7 |
| 0.1% water added | 11.6 |
| 3.5% water added | 43.6 |
| 6.0% water added | 27.2 |

[a] Polymerization initiated by cobalt-60 source of 220,000 r.e.p. per hour.

Table III summarizes the effect of temperature, field intensity and radiation energy on the polymerization of acrylamide. The values listed in the second column refer either to γ-rays of 1,300 kiloelectron volts (kev.) maximum energy derived from cobalt-60 or X-rays of 80 kev. maximum energy.

Part A of Table III lists the intrinsic viscosities of polymer and polymerization rates at four temperatures of polymerization. The samples remained at the stated temperatures and no sintering was ever observed. It is evident from the intrinsic viscosity values in the last column that the polymer molecular weight remains constant with tem-

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(4) E. Rossman, *Ber.*, **65B**, 1847 (1932).

(5) L. E. Craig, R. W. Davis and W. S. Port, *Ind. Eng. Chem.*, **47**, 1702 (1955).

(6) B. Manowitz, *Nucleonics*, **9**, No. 2, p. 10 (1952).

(7) W. Gensler, THIS JOURNAL, **69**, 1968 (1947).

(8) A r.e.p. (roentgen equivalent physical) is that quantity of radiation which upon absorption in water produces 6.08 × $10^{13}$ electron volts per gram. The energy absorbed per gram in the various monomers studied can be obtained by multiplying the field intensity in r.e.p. by 6.08 × $10^{13}$ and by the electron density factor $n/M \cdot M'/n'$ where $n$ is the number of electrons per molecule, $M$ is the molecular weight and $M',n'$ are corresponding values for water.

(9) (a) J. Weiss, *Nucleonics*, **10**, No. 7, 28 (1952); (b) W. Rosenzweig, BNL Report 1254 (1952) unpublished.

TABLE III

EFFECT OF TEMPERATURE, FIELD INTENSITY AND RADIATION ENERGY ON ACRYLAMIDE POLYMERIZATION

| Field intensity (r.e.p./hr.) × $10^{-3}$ | Radiation energy (kev.) | Temp. (°C.) | Initial rate (% conv./hr.) | $\frac{\text{Rate}}{\text{Intensity}}$ (% conv./r.e.p.) × $10^4$ | $[\eta]$ (dl./g.) |
|---|---|---|---|---|---|
| | | A. Effect of temperature | | | |
| 32.6 | 1300 | 0 | 1.1 | .. | .. |
| 32.6 | 1300 | 20 | 1.9 | .. | 1.73 |
| 32.6 | 1300 | 35 | 2.4 | .. | 1.73 |
| 32.6 | 1300 | 50 | 3.6 | .. | 1.71 |
| 32.6 | 1300 | 65 | 5.3 | .. | 1.75 |
| | | B. Effect of field intensity | | | |
| 3.3 | 1300 | 35 | 0.3 | 0.92 | 1.56 |
| 32.6 | 1300 | 35 | 3.5 | 1.07 | 1.73 |
| 220 | 1300 | 35 | 15.1 | 0.69 | 1.68 |
| 310 | 1300 | 35 | 22.0 | .71 | 1.74 |
| 316 | 1300 | 35 | 25.5 | .81 | 1.77 |
| 892 | 1300 | 35 | 42.1 | .47 | 1.68 |
| | | C. Effect of radiation energy | | | |
| 310 | 80 | 35 | 21.1 | .. | 1.38 |
| 310 | 1300 | 35 | 22.0 | .. | 1.71 |

perature. The over-all activation energy for polymerization is calculated to be 4.7 ± 0.46 kcal./mole (95% confidence limit)[10] based upon initial rates of polymerization at each temperature. All viscosity measurements were performed with polymer obtained between 10 and 20% conversion since at higher conversions there is a progressive increase in intrinsic viscosity up to 50% conversion whereupon gelation occurs.[3] The conversion *versus* time plots at each of the four temperatures were linear up to at least 40% conversion and then exhibited a downward curvature corresponding to a zero to one-half order dependence of the polymerization rate upon the monomer concentration. Using the equation $[\eta] = 3.73 \times 10^{-4}[M]^{0.66}$ reported by the American Cyanamid Co.,[11] the viscosity average molecular weight of polymer listed in Table III is 358,000 when $[\eta] = 1.73$. This equation was established for solution in 0.025 $N$ HCl and was applied to our intrinsic viscosities determined in water since the addition of HCl reduces the intrinsic viscosity by less than 5%.

The effect of field intensity on polymerization rate and molecular weight was determined over a 270-fold range. The results are summarized in Part B of Table III for studies at 35°. The constancy of the first five values in column 5 demonstrates the first-order dependence of rate upon field intensity. The reaction order may decrease below unity beyond 316,000 r.e.p./hour since the ratio of rate/intensity at 892,000 r.e.p./hour is significantly smaller than the other values. The viscosity values listed in the last column, determined from polymers obtained between 15 and 20% conversion, are essentially constant indicating no change in molecular weight with field intensity.

In order to determine the effect of radiation energy on rate and molecular weight, the monomer was polymerized with γ-rays and with X-rays of identical field intensities but differing 16-fold in energy. The data are summarized in Part C of Table III. The rates were based upon a series of experimental values below 40% conversion and the viscosity data on polymer below 15% conversion.

The paramagnetic resonance response at liquid nitrogen temperature of acrylamide irradiated at liquid nitrogen temperature showed the presence of free radicals. A series of irradiated samples (15, 25 and 50 megarep.) gave approximately 0.3 × $10^{-4}$ to $10^{-4}$ molal radicals by comparison with α,α-diphenyl-β-picryl hydrazyl.[12]

**Vinyl Stearate Polymerization.**—Polymerization studies of vinyl stearate initiated by γ-rays were performed at temperatures above and below the melting point of the monomer (34°). Rates of polymerization at four temperatures are presented in Fig. 1. Within the times of these experiments the monomer exhibited no thermal polymerization. The intrinsic viscosities (average of duplicate measurements) of initial polymer obtained below 20% conversion and prepared at 12, 26, 40 and 60° using a radiation intensity of 191,000 r.e.p./hr. were determined in benzene at 20°. It was established that the intrinsic viscosity of polymer prepared at 40° increases slightly with conversion, being 0.226 (dl./g.) at 14.7% conversion and 0.242 at 43.4% conversion. A semi-logarithmic plot of polymer intrinsic viscosity (upper region) and polymerization rate (lower region) against the reciprocal of absolute temperature is presented in Fig. 2. The vertical dotted line indicates the melting temperature of vinyl stearate monomer. The height of the vertical lines representing each experimental value in the lower region indicates the 95% confidence limit. The limits of error in the intrinsic

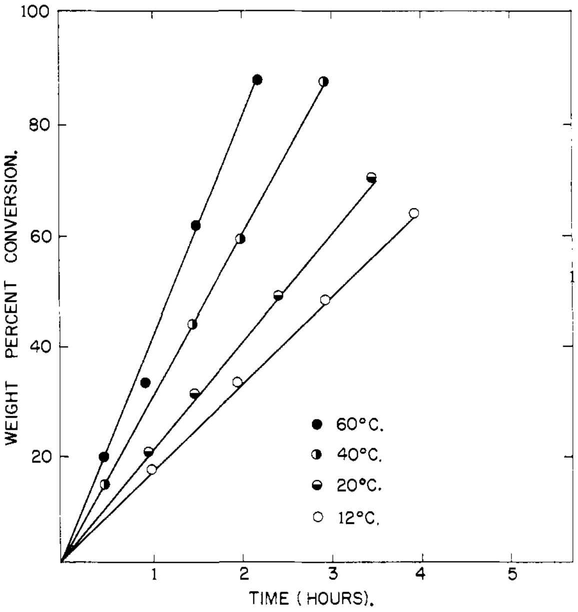

Fig. 1.—Polymerization of vinyl stearate at several temperatures initiated by cobalt-60 γ-rays of 191,000 r.e.p./hr. intensity.

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[10] W. J. Youder, "Statistical Methods for Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 19.

[11] New Product Bulletin No. 34, American Cyanamid Co., New York 20, N. Y., June 1955.

[12] We are grateful to M. M. Weiss and V. W. Cohen of Brookhaven National Laboratory for these measurements.

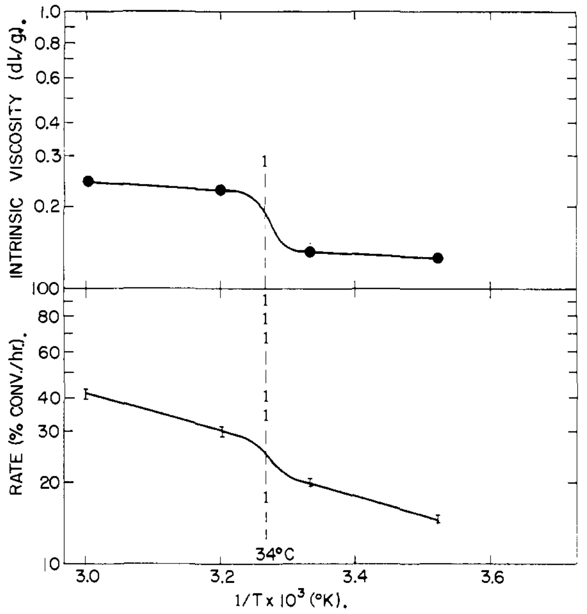

Fig. 2.—Effect of temperature on vinyl stearate polymerization initiated by cobalt-60 γ-rays of 191,000 r.e.p./hr. intensity.

viscosity measurements are too narrow to be seen on the scale of the graph. Whereas the statistical significance of the discontinuity in the viscosity plot cannot be questioned, the corresponding discontinuity in the polymerization rate is much less marked.

**Polymerization of Acrylic Acid Salts.**—Figure 3 presents a comparison of the relative rates of polymerization of barium, calcium and potassium acrylates at 35° as well as barium acrylate at 10, 50 and 65°. The temperature coefficient for polymerization of barium acrylate is extremely small or zero being 0.4 ± 1.9 kcal./mole (95% confidence limit). The intrinsic viscosity of polyacrylic acid obtained from potassium acrylate polymerization at 18% conversion (Fig. 3) was found to be 0.33 (dl./g.) in 0.4 *N* HCl at 30° denoting that a true polymer is obtained.

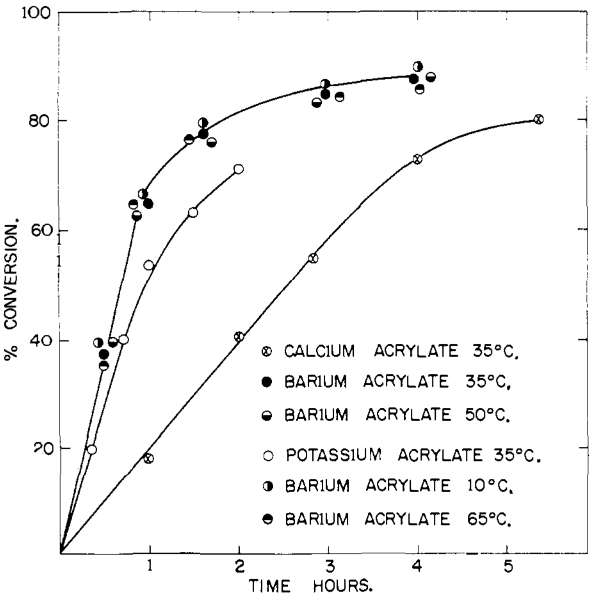

Fig. 3.—Polymerization of acrylic acid salts initiated by cobalt-60 γ-rays of 190,000 r.e.p./hr.

## Discussion

It has been previously established that β-[13a] and γ-ray[13b] initiated polymerizations are free radical processes. The paramagnetic response of irradiated acrylamide crystals leaves little doubt that this is also the case in the solid state.[14] The apparent first-order relation between polymerization rate of acrylamide and irradiation intensity (Table III, part B) at least up to 316000 r.e.p./hr. demonstrates that polymerization proceeds in discrete tracks.[15] The constancy of the molecular weight of polyacrylamide over a 270-fold intensity range also conforms with polymerization in discrete tracks. The constancy of molecular weight with variation in polymerization temperature, however, is difficult to reconcile with the temperature dependence of the polymerization rate unless the majority of growing chains are terminated by transfer to monomer and the activation energy for the propagation step is fortuitously the same as that for transfer. Alternatively, if it may be assumed that polymerization occurs in a preferred crystallographic direction, the molecular chain length could be limited by flaws in the crystal lattice. It might also be suggested that the spacing of spurs[16] (clusters of radicals) along a given track defines molecular weight, and in this respect it is noteworthy that the intrinsic viscosity of polymer obtained with γ-ray initiation was approximately 25% higher than that of polymer obtained with X-ray initiation (Table III, part C). Neither of these latter two interpretations, however, is consistent with the observed temperature dependence of the polymerization rate.

The fundamental question arises whether the regular arrangement of monomer molecules in the crystal lattice influences the specific rate constants of the individual steps in the polymerization reaction and the structure of the resultant polymer, or whether the energy release on addition of a monomer to a growing chain is sufficient to reduce the orientation of some of its neighbors to a degree not unlike that characterizing the liquid state. The over-all activation energy of 4.7 kcal. for the polymerization of crystalline acrylamide is similar to values of 6.7 and 4.3 kcal. reported[13b] for liquid state polymerization of styrene and methyl methacrylate, respectively, initiated by γ-rays. Also it may be noted from Table I that those monomers (acrylic acid salts, excluded) which readily polymerize in the liquid state are polymerizable in the solid state while the last four monomers are not

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(13) (a) W. H. Seitzer, R. H. Gockermann and A. V. Tobolsky, This Journal, **75**, 755 (1953); (b) D. S. Ballantine, P. Colombo, A. Glines and B. Manowitz, *Chem. Eng. Progress Symposium Series*, **50**, No. 11, 267 (1954).

(14) The relatively high concentration of "frozen in" radicals ($10^{-4}$ molal) can account for the earlier observation[3] that monomer irradiated at −18° and stored indefinitely at that temperature will violently polymerize on warming near room temperature.

(15) F. S. Dainton and E. Collinson, *Ann. Rev. Phys. Chem.*, **2**, 99 (1951).

(16) A. H. Samuel and J. L. Magee, *J. Chem. Phys.*, **21**, 1080 (1953).

polymerizable as liquids or solids. On the other hand, while the exposure of acrylamide to γ-rays results in a loss of crystallinity[3] as determined by X-ray diffraction, examination of the irradiated crystal with a polarizing microscope revealed[17] that the negative birefringence and orientation present in the unirradiated crystal are unchanged after polymerization. Heat sintering of the polymer or dissolution and precipitation from the solution totally destroys orientation originally present in the γ-ray polymerized monomer. These observations led Schulz, *et al.*,[17] to conclude that the growth reaction in the crystal takes place in a preferred crystallographic direction. It may be added that infrared studies[18] of polyacrylamide indicated that the sequence of monomer units in the polymer prepared by solid state polymerization was identical to that of polymer prepared in aqueous solution by peroxide initiation which normally produces the head-to-tail sequence.

The extension of studies with acrylamide to the solid state polymerization of vinyl stearate and acrylic acid salts was primarily performed in the former case to contrast the polymerization reaction above and below the melting point of the monomer, and in the latter case, to determine whether a monomer whose crystal lattice is stable up to a high temperature is subject to polymerization with γ-rays at room temperature. The heats of polymerization of liquid vinyl monomers range from 17.5 to 21.3 kcal. per mole for styrene and vinyl acetate, respectively.[19] The heat of polymerization of crystalline monomers will be less than that of the corresponding liquid monomer by the heat of fusion. Although in the case of acrylamide polymerization at room temperature, the heat of polymerization per mole is not sufficient to melt more than 3 to 5 molecules per reacted monomer, with crystalline monomers having high molar specific heats or monomers having high melting points the heat of polymerization will be insufficient to cause any melting.[20]

The data presented in Fig. 2 clearly indicate a marked discontinuity in vinyl stearate polymerization in passing through the monomer melting point. Since both polymer intrinsic viscosity and polymerization rate exhibit a lowering below the melting point of monomer, it is evident that this polymerization reaction is not facilitated when performed in the solid state. A comparison of the slopes of lines drawn through each pair of experimental points above and below 34° suggests that the frequency factor rather than the activation energy is changed on passing from the liquid to the solid state. It is possible that vinyl stearate was a poor choice for this study since it is an untypical monomer from two points of view; (a) its long aliphatic side chain may favor an ordered structure[21a] of the liquid above the melting point and (b) the molecular weight of polymer obtained by polymerization in the liquid state may be limited, like that of poly (vinyl acetate)[21b] by chain transfer to monomer. Both of these factors would tend to minimize the difference in the characteristics of liquid and solid state polymerizations.

The rapid polymerization of barium, potassium and calcium acrylate (Fig. 3) demonstrates that monomers which melt at very high temperatures are nevertheless polymerizable at considerably lower temperatures. As with acrylamide, the polymerized crystals show no evidence of sintering and the birefringence of poly(potassium acrylate) observed in a polarizing microscope is nearly identical to that of the unirradiated monomer. In addition, since it has been reported[22] that fully ionized acrylic acid will not polymerize in aqueous media due to electrostatic repulsion between the charged monomer and radical, one may conjecture that the order of acrylate ions in a crystalline lattice markedly enhances propagation along crystallographic directions. The most interesting feature of the polymerization of acrylic acid salts is the absence of any temperature coefficient for barium acrylate polymerizations between 10 and 65°. If such behavior should be found to be typical of the solid state polymerization of monomers with very high melting points, it would strongly indicate that lattice defects or spur spacings determine the kinetic chain length whenever the heat of polymerization is insufficient to disrupt the lattice order.

**Acknowledgment.**—The authors express appreciation to Mr. B. Manowitz for his interest and support of this work.

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[17] R. Schulz, A. Henglein, H. E. von Steinwehr and H. Bambauer, *Angew. Chem.*, **67**, 232 (1955).

[18] P. Ander, M.S. Thesis submitted to the Chemistry Faculty of the Polytechnic Institute of Brooklyn, June, 1954.

[19] M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, THIS JOURNAL, **73**, 5395 (1951).

[20] Assuming for potassium acrylate a specific heat of 0.3 cal./g./°C., a heat of fusion $\Delta H_m = 3$ kcal./mole, a heat of polymerization of the crystalline monomer (based on an assumed heat of polymerization of liquid monomer $\sim 20$ kcal./mole) of $20 - \Delta H_m = 17$ kcal./mole and neglecting heat conduction in the crystal, 80% of the heat of polymerization is required to raise one neighboring monomer molecule from room temperature to the melting point of 360°. It is evident that one is dealing here with some thermal excitation but nothing akin to melting.

[21] (a) G. W. Stewart, *Phys. Rev.*, **31**, 174 (1928); (b) O. L. Wheeler, S. L. Ernst and R. M. Crozier, *J. Polymer Sci.*, **8**, 409 (1952).

[22] A. Katchalsky and G. Blauer, *Trans. Faraday Soc.*, **47**, 1360 (1951).