Solid State Polymerization Reactions*

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In clarifying the properties of individual molecules chemistry has mainly been concerned with the gaseous and the liquid phase, but now it is proceeding to the solid phase for analysing the interactions between molecules. In some cases, molecules of a monomer fixed in a crystal lattice react easily forming a polymer, the crystal form of which is completely different from that of the monomer. These reactions which are now called *solid state polymerization* have seldom been cited in the literature, but they are attracting ever increasing attention. A special type of solid state polymerization initiated by high energy radiation is reviewed here.

1. Introduction

Many experimental results have been reported in the past on the polymerization reaction of monomers in the solid state. Yet there was a great deal of doubt left about the actual reaction mechanism. Consequently the reports hitherto have generally been disregarded. But now an increasing number of experimental results is being reported on the process of polymerization reactions in solid state, including reactions of monomers with high melting point and of monomers polymerizing gradually at temperatures far below the melting point. In addition, as the polymerization initiation by irradiation begins homogeneously all over the solid, the treatment of the reaction becomes interesting from the point of view of the kinetics of solid reactions. Polymerization in solid state is now offering an interesting topic for investigations, and research is speeding up steadily. Discussions here will be concentrated on the solid state polymerization induced by irradiation.

2. Caracteristics of rigid mediums

Various characteristics are anticipated with the process of chemical reactions in solid state. Long ago, especially in the field of biochemistry, attentions have been focussed on the characteristics of reactions occuring in rigid medium. S. AUGUSTINE, G. AUGUSTINE and R. LIPPINCOTT[1] for instance have reported that the deactivation of trypsin by X-ray radiation in solution occurs at 0.5×10^4 rep, while it needs twenty four times as much energy (i. e., 12×10^4 rep) when, by addition of about one percent agar, the solution has been transformed into a rigid gel. The chemical mechanism of the reaction however was not clear. M. DAY and G. STEIN[2] reported a sixty percent increase of the reaction efficiency

in the transformation $KI \rightarrow I_2$ when irradiation was applied in the presence of 1% agar. G. N. LEWIS and D. LIPKIN[3] found that tetramethylbenzidine undergoes ionization and radical formation on irradiation with ultra-violet light, yet only in a so-called EPA-rigid solventconsisting of five parts of ether, five parts of isopentane and two parts of alcohol. Between the ion-radical $[(CH_3)_2 \bar{N}-\langle\rangle-\langle\rangle-N(CH_3)_2]^+$ thus produced and the chemically produced ion-radical, there is a complete identity in the absorption spectra (near 6500 and 5500 Å). The normal ionization potential of these molecules in gaseous phase (8 to 12 eV) is shown to decrease to 3 to 5 eV. The difference here corresponds to the electron trapping energy on acceptor molecules and it depends on the solvation or on the rigidity of medium. If the latter were proved predominant, the significance of reactions in solid state must be unfathomed on the part of the future photo- and radiation-chemistry. In this item, recently S. MATHESON and C. VERMEL[4] reported for the polymerization of isobutene by ultra violet light that in the liquid state the ionization potential is about 1 eV smaller than in the gaseous state.

3. Molecular movements in the solid state

Supposed that chemical reactions are possible within a solid without large molecular movements, some kind of atomic group movement should be taken into consideration. In this field a recent study on nuclear magnetic resonance (NMR) has been enlightening. M. DOLE[5] introduced the results of NMR measurements on polypropylene at a certain symposium discussion, i. e., the NMR pattern of isotactic polypropylene showed six peaks at liquid helium temperature ($-269\,°C$), nine in liquid nitrogen ($-196\,°C$), and seventeen at $-140\,°C$. The start of rotational movement of the methyl radical from around $-200\,°C$ to $-150\,°C$, which had been fixed at lower temperature, is accounted for by the additional peaks in the NMR spectra. Different transition temperatures are thus proved to exist at far lower than the glass transition temperatures of solids or the melting points of crystals. C. M. HUGGINS, L. E. PIERRE and A. M. BUECHE[6] considered the possibility of a certain translational motion from the fact that the crystal size of polyethylene was

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[1] S. AUGUSTINE, G. AUGUSTINE and R. LIPPINCOTT, *J. Physic. Chem.* 64 (1960) 1211.
[2] M. DAY and G. STEIN, *Nucleonics 8* (1951) 34.

[3] G. N. LEWIS and D. LIPKIN, *J. Amer. Chem. Soc.* 64 (1942) 2801.
[4] S. MATHESON, C. VERMEL and S. LEACH, in *Second Conference of Radiation Research, Harrogate 1962*, p. 172.
[5] M. DOLE et al., in *Comparative Effect of Radiation* (1960).
[6] C. M. HUGGINS, L. E. PIERRE and A. M. BUECHE, *J. Physic. Chem.* 64 (1960) 1304.

changed by annealing for a long time below the second transition temperature. The properties of the solid state differ greatly not only with its temperature but also with the cooling rate of the preparation. S.MATHESON and A. SMALLER,[7] and J. A. GHOMLEY and A. C. STEWART[8] made measurements on the condition of the hydrogen atoms which had been trapped by ionizing irradiation of ice, using electron spin resonance and ultra-violet absorption. They found that in slowly cooled crystals far larger quantities of hydrogen could be accumulated than in quickly cooled ones. According to a report of M. EBERT and T. H. WOOD[9], a certain cell was killed at $-72\,°C$ by irradiation more efficiently when having been cooled slowly than when it had been cooled quickly. An important item must be involved here though main causes of the fact are beyond simple surmises since, in the two cases, the molecular state of the proteins shows differences and they are differently co-existent with a third material like oxygen.

4. Storage of energy in the solid state

Storage of energy in various forms takes place in a solid under ionizing irradiation. This energy can serve later to induce the polymerization reaction. According to previous reports it may be stored in free radical state to be used later for post-polymerization or graft-polymerization in the pre-irradiation method.[10]

Phosphorescence is observed with this method due to neutralization of knocked-off electrons with positive holes, while it takes a rather long time till luminescence occurs in the solid state when the particles are well oriented. H. LINSCHIZ, M. G. BERRY and D. SCHWEITZER[11] investigated this phenomenon for the first time quantitatively. Green luminescence was observed with organic compounds like acetone, β-propiolactone or trioxane when they were first irradiated in the solid state by γ-rays at about 10^7 rep, at liquid nitrogen temperature and then heated up to room temperature. E. M. HORL[12] had already reported the same phenomenon on irradiation with β-rays at liquid helium temperature. T. WESTERMARK[13] has measured the amount of stored energy in the cases of KI and polystyrene (by Fricke dosimetry with a scintillation counter) and used the values for the calculation of storage efficiency.[14] A. CHARLESBY et al.[15] describe experiments on energy storage in the case of polyethylene. In another field, namely

in medical, science an important discussion on energy storage is developing. R. T. BAYLEY, L. HOLZAPFEL and J. LEHMANN[16] discussed the phenomenon that a patient with the lung desease silicose gets worse when treated with X-ray irradiation, in connection with the assumption that energy stored on X-ray irradiation might be emitted as short waves near 4000 Å. T. WESTERMARK uttered somewhat similar ideas about this problem. At the International Conference on Solid Catalysis in the fall of 1960, M. HAÏSSINSKY described the general concept of the role of irradiation effects in solid state catalysis and stressed the importance of electron trapping and the formation of lattice defects. The same point was also emphasized at the International Conference on Radiation Research in summer 1962.

5. Influence of semi-conductor properties in solids

The first reliable report on irradiation effects on the polymerization by metal oxides was given by A. CHARLESBY, P. WORRALL and S. H. PINNER.[17] They studied the radiation polymerization of isobutylene in the presence of ZnO. Isobutylene is known to undergo cationic polymerization. ZnO promotes electron trapping which causes lengthening of the life time of cationic particles. The cationic polymerization by irradiation attracted wide attention until the same experiment was repeated. M. MAGAT[18] recognized that the accelerating effect of ZnO was a special phenomenon exclusive for isobutylene and could not be observed with other vinyl monomers. The retarding effect by O_2^-, which is a special feature found only in isobutylene polymerization, seemingly disappears through neutralization by ZnO. Recently A. CHARLESBY[19] pointed out the importance of water traces in the accelerating phenomenon of styrene polymerization by Al_2O_3. Later J. PRÉVE and R. MONTARNAL[20] recognized in the formation of phenol from benzene and water, that the production rate of phenol increased about two times by the addition of ZnO. The reason was considered to be the acceleration of the oxidation reaction by hydroxyl radicals. In our laboratory[21] anionic polymerization was ascertained to occur in low temperature radiation copolymerization of styrene and methylmethacrylate in the presence of γ-Al_2O_3. In connection with the semi-conductor theory of photosynthesis, A. TERENIN and others[22] measured the photoelectric conductivity of a safranine layer absorbed on ZnO under different wave lengths. They discuss their spectra with consideration of

[7] S. MATHESON and A. SMALLER, *J. Chem. Physics 23* (1955) 521.

[8] A. GHOMLEY and C. STEWART, *J. Amer. Chem. Soc. 78* (1956) 2934.

[9] M. EBERT and T. H. WOOD, in *Comparative Effect of Radiation* (1960).

[10] G. ADLER, D. BALLANTINE and B. BAYSAL, in *Symposium of Macromolecular Chemistry, Moscow* 1960, Session II, p. 396.

[11] H. LINSCHIZ, M. G. BERRY and D. SCHWEITZER, *J. Amer. Chem. Soc. 76* (1954) 5833.

[12] E. M. HÖRL, *J. Chem. Physics 31* (1958) 564.

[13] T. WESTERMARK, Riso Report, No. 16 (1960).

[14] T. WESTERMARK and B. GRAPENGIESSER, *Ark. Kemi 17* (1961) 139, 151.

[15] A. CHARLESBY and R. PARTRIDGE, in *Second Conference of Radiation Research* (1962) p. 123.

[16] R. T. BAYLEY, L. HOLZAPFEL and J. LEHMANN, *Naturwiss. 20* (1960) 464.

[17] A. CHARLESBY, P. WORRALL and S. H. PINNER, *Int. J. Appl. Rad. 4* (1958) 84.

[18] M. MAGAT, in *Symposium on Macromolecular Chemistry, Wiesbaden 1959*.

[19] A. CHARLESBY and J. MORIS, in *Second Conference of Radiation Research, Harrogate 1962*, p. 171.

[20] J. PRÉVE and R. MONTARNAL, *J. Chim. Physique 1959*, 1667.

[21] A. NATORI, K. HAYASHI and K. NAKAMURA, *Isotopes & Radiation* (Japan) *3* (1959) 417.

[22] A. TERENIN, *Disc. Faraday Soc. 27* (1960) 83.

the mechanism of charge transfer. The study of electron transfer between the surface of a semi-conductor and the reactant in the radiation chemistry mentioned above will provide for topics future investigation. A special procedure for the solid state polymerization of methyl-methacrylate was proposed recently by B. A. KARGIN, B. A. KABONOV and B. P. ZUBOV,[23] in which monomer vapor under a molecular Mg beam was polymerized on a cold metal surface at −100 °C. So far it has been generally admitted that the radical polymerization should produce a syndiotactic polymer and ionic poly-merization an isotactic one. Yet this co-condensation method is remarkable in that the polymethylmetha-crylate obtained here is isotactic in spite of the fact that the reaction is a radical one, as has been proved by ESR measurements. There may be a relation to the mechanism of the frozen state polymerization of acetal-dehyde, reported earlier by A. LETORT.[24]

6. Solid state polymerization

Some crystalline monomers with a comparatively rigid lattice can polymerize in solid state without any change of outer appearance. Copolymerization in solid solution may become especially important sooner or later.[25]

(a) Radical polymerization

Radiation polymerization was successfully employed for the first time in adsorption or adduct polymerization. To ascertain that cis-1,4-polybutadiene was obtained by β-ray irradiation, S. BROWN et al.[26] made an adduct of urea and butadiene. This was an ideal example of oriented polymerization. Recently I. SAKURADA et al.[27] attempted the radiation polymerization of a vinylchloride-urea ad-duct and obtained polyvinylchloride of high crystallinity. With acrylic amide (melting temperature 86 °C) radi-cal polymerization in solid state was investigated in detail.[28] Acrylic amide polymerizes in solid state with normal radical catalysts when the crystalline monomer is dispersed in liquid n-hexane.[29] R. SCHULZ, A. HENG-LEIN, H. VON STEINWEHR and H. V. BAMBAR[30] also in-vestigated the radiation polymerization of acrylic amide. They reported that monomer crystals were polymerized with loss of their original form and that the polymer was obtained in amorphous state. In many investigations since, no polymer crystal has ever been obtained. Recently G. ADLER et al.[31] examined the solid state polymerization

of acrylic amide by following the pattern of the rotation X-ray diagram. They observed a mixed pattern of crystalline monomer and amorphous polymer. It would be almost hopeless to try to make a monomer crystal polymerize so that the polymer preserves the original crystalline form with oriented polymer molecules. R. H. WILEY and D. J. PARISH[32] were to show the polyme-rizability at −52 °C of diethylfumarate, one of the 1,2-disubstituted vinyl monomers. C. H. BAMFORD and A. D. JENKINS[33] tried radical polymerization in solid state by ultra-violet irradiation on methacrylic acid crystals. They recognized that the presence of about 0.01 wt % water accelerates polymerization. C. H. BAMFORD et al.[34] also found that methacrylic acid polymerizes under dis-charges in a Tesla coil. The similarities in the reactions with high energy radiation, ultra-sonic waves, short waves, ultra-violet rays and electric discharges may bear pro-blems for future research. A. J. RESTAINO, H. MORAWETZ, D. S. BALLANTINE, G. DIENES and D. J. METZ[35] investi-gated the radiation polymerization of acrylic amide and found that polymerization was possible in solid state (melting temperature 84 °C) by heating up to 10° to 60 °C after irradiation. Later, the material in the vi-cinity of the growing ends of the chain molecules was believed to be melted away by the polymerization heat. Though the reaction appears to be a solid state poly-merization, it is therefor of no great significance from the view point of reaction mechanism. The polymerization of barium acrylate investigated by W. BURLANT and A. ADICOFF[36] was, however, apparently a pure solid state polymerization because the reaction temperature was about 250 °C below the melting temperature (about 300 °C) and also because the experiment was carried out at a very slow polymerization rate. Lately T. A. FADNER and H. MORAWETZ[37] have investigated in detail the poly-merization of acrylic amide in solid state and have made sure of the existence of a radical mechanism by ESR measurements. Yet they did not deny the existence of the following ion-radical nor consider the reaction as a simple example of normal radical polymerizations.

$$CH_2{=}CH{-}CO{-}NH_2 \rightsquigarrow \ ^+CH_2{-}\overset{\cdot}{CH}{-}CO{-}NH_2$$

$$\text{or } \overset{-}{CH_2}{-}\overset{\cdot}{CH}{-}CO{-}NH_2$$
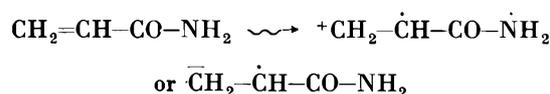
An average initiating rate was obtained by dividing the polymerization rate by the molecular weight. Thus the $G_{initiation}$ was found to be 0.5 to 0.8. Recombination of active particles in the crystalline state was considered to account for the small value of $G_{initiation}$. For aggregates of microcrystals obtained by quick cooling, $G_{initiation}$

[23] B. A. KARGIN, B. A. KABONOV and B. P. ZUBOV, Vysko. Soed. 2 (1960) 303.
[24] A. LETORT, J. Chim. Physique 57 (1960) 752.
[25] Z. ORSZÁGH, in Symposium on Radiation Chemistry, Hungary, 1962.
[26] S. BROWN, Chem. Eng. News 28 (1958) 47.
[27] I. SAKURADA and S. NANBU, J. Chem. Soc. Japan. Ind. Sect. 61 (1958) 60.
[28] R. B. MESROBIAN, J. Chem. Physics 22 (1954) 565.
[29] S. OKAMURA, A. TAKEWAKI and H. INAGAKI, in Annual Meeting of Japanese Chemical Society, 1955.
[30] R. SCHULZ, A. HENGLEIN, H. VON STEINWEHR and H. V. BAMBER, Angew. Chem. 67 (1955) 232.
[31] G. ADLER and W. REAMS, J. Chem. Physics 32 (1960) 1698.

[32] R. H. WILEY and D. J. PARISH, J. Polymer Sci. 45 (1960) 503.
[33] C. H. BAMFORD and A. D. JENKINS, Nature 186 (1960) 712.
[34] C. H. BAMFORD and A. D. JENKINS, Nature 186 (1960) 713.
[35] A. J. RESTAINO, H. MORAWETZ, D. S. BALLANTINE, G. DIENES and D. J. METZ, J. Polymer Sci. 45 (1960) 475.
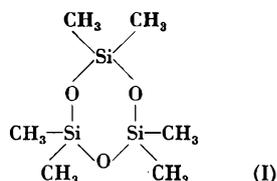[36] W. BURLANT and A. ADICOFF, J. Polymer Sci. 27 (1958) 269.
[37] T. A. FADNER and H. MORAWETZ, J. Polymer Sci. 45 (1960) 475.

values about twice as high were found. Mixed crystals with propionamide were investigated for radiation polymerization. The reaction rate was almost constant even at 50 % addition, while the degree of polymerization decreased quickly. The chain transfer constant of propionamide was calculated to be 100 times larger than in the case of liquid state polymerization. Neither cautious and slow polymerization at low temperature, nor the attempt at solid polymerization gave any polymer crystals with methacrylic acid. According to the theory of MORAWETZ et al. the interaction between lattice dislocations and activated lattice points initiates polymerization and so, in turn, the rate of polymerization is determined by the lattice conditions.

(b) Ionic polymerization

Ionic polymerization in solid state is becoming an interesting item. As A. MAGAT[18] already pointed out, hexamethyl cyclotrisiloxane[38] (I) had been polymerized. This cyclic monomer shows ionic polymerizability and therefor opens up a new possibility in solid state polymerisation.

$$CH_3 \quad CH_3$$
$$\diagdown Si \diagup$$
$$\diagup \quad \diagdown$$
$$O \qquad O$$
$$CH_3-Si \qquad Si-CH_3$$
$$\diagup \diagdown O \diagup \diagdown$$
$$CH_3 \qquad CH_3 \qquad (I)$$

The rates of polymerization show a maximum at about several degrees below the melting temperature (84 °C). Recently H. SOBUE and Y. TABATA[39] have studied the solid state polymerization of acrylonitrile at -200 °C. They recognized that the polymerization proceeded by as small an activation energy as 0.4 kcals/mole, that no induction period was observed and that no change in polymerization rates occured in the presence of a radical scavanger. A. CHAPIRO and V. STANNETT[40] carried out the solid state polymerization of styrene at -78 °C by X-ray irradiation and concluded that this polymerization is probably a cationic one. Moreover, A. CHAPIRO, paying attention to post-polymerization, is studying the behaviour of a very thin layer of solid monomer under X-ray irradiation. By this technic the separation of the polymer from the remaining monomer becomes possible by quick dissolution after the irradiation. This method, A. CHAPIRO emphasizes, may reveal a great deal about the experimental errors hither to made with the solid state polymerization. The question whether or not post-polymerization has more to do with the solid state ionic polymerization than with the solid state radical polymerization can only be answered by future investigations.

M. MAGAT, L. TER MINARSIAN and C. CHACHATY[41] investigated the solid state γ-ray polymerization of formaldehyde between -100 °C and -196 °C and found an interesting relationship between the reaction rate and the temperature of polymerization. From -100 °C to -160 °C the rate of polymerization was gradually increasing with decreasing temperature. At -160 °C it reached a maximum and then decreased on further lowering of the temperature. No remark was made by the authors on the physical significance of the rate maximum at -160 °C. In the temperature range in which the polymerization mechanism changes from the one in liquid to the one in solid state, the activation energy should be on the negative side. Later, R. H. WILEY and D. E. GENSHEINER[42] and also M. MAGAT[43] observed solid state polymerization of ethene sulfonamide and also of isobutene respectively at low temperature. The author considers the ionic polymerization in solid state by irradiation as an interesting subject for study, judging from the following three points; (i) post-polymerization is considered to be not so violent as radical polymerization, (ii) the possibility of getting polymer crystals in oriented state is greater than in the case of radical polymerization and (iii) a considerably large rate of polymerization is obtainable even at low temperature.

No convenient arrangement of the monomer molecules in the crystal has yet been brought to light, though this would be most significant in the solid state polymerization. Historically the polymerization of hexamethylcyclotrisiloxane mentioned above was the first successful instance of ionic polymerization in solid state. The crystal lattice of the monomer molecules might be especially convenient here for the polymerization reaction.

The results of these investigations lead to the problem of ionic polymerization in solid state induced by irradiation of ring compounds. Several points of this item will be discussed here. K. HAYASHI, Y. NAKAMURA and the author[44] attempted first a γ-ray solid state polymerization of trioxane (II), chosen as a compound similar to (I). When the polymerization yields at 4.4×10^5 rep were compared, the values obtained were about 1 % at 80 °C in the liquid state and 22 % at 55 °C and 16 % at 50 °C, both in the solid state.

$$CH_2$$
$$\diagup \diagdown$$
$$O \qquad O$$
$$CH_2 \quad CH_2 \qquad (II)$$
$$\diagdown \diagup$$
$$O \qquad (m.p. 62 °C)$$

When the polymerization proceeded slowly, the X-ray diagram of the polymer showed a remarkably good crystallization. Y. KITANISHI, K. HAYASHI and the

[38] E. J. LAWTON, W. T. GRUBB and J. S. BALWIT, J. Polymer Sci. 19 (1956) 455.
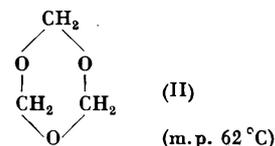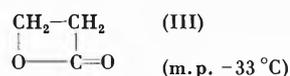
[39] H. SOBUE and Y. TABATA, J. Polymer Sci. 43 (1960) 459.

[40] A. CHAPIRO and V. STANNETT, J. Chim. Physique 57 (1960) 35.

[41] M. MAGAR, L. T. MINASSIAN and C. CHACHATY, in Symposium on Macromolecular Chemistry, Moscow 1960, p. 427.

[42] R. H. WILEY and D. E. GENSHEINER, J. Polymer Sci. 42 (1960) 119.

[43] M. MAGAT, Makromol. Chem. 35 (1959) 159.

[44] K. HAYASHI, Y. NAKAMURA and S. OKAMURA, Isotope & Radiation (Japan) 3 (1959) 416.

author[45] further carried out the γ-ray polymerization of solid β-propiolactone (III).

$$\begin{array}{c} CH_2\!-\!CH_2 \\ |\qquad\ | \\ O\!-\!\!-\!\!-\!C\!\!=\!\!O \end{array} \quad (III) \\ (m.p.\ -33\,°C)$$

Large crystals of several mm length were made by slow cooling. They were polymerized by a low dose rate of γ-irradiation at low temperature. After the extraction of monomer left over, an X-ray diagram of the polymer was directly taken. A diagram of crystalline polymer in oriented arrangement was obtained. The polyester produced is described as $-(CH_2\!-\!CH_2\!-\!\underset{\overset{\|}{O}}{C}\!-\!O\!-)_n$. Its fiber period was rather difficult to calculate.

A similar γ-ray solid state polymerization was attempted with diketene (IV).[45]

[45] K. HAYASHI, S. KITANISHI and S. OKAMURA, in *Symposium on Macromolecular Chemistry, Montreal 1961.*

$$\begin{array}{c} CH_2 \\ \| \\ C \\ O \quad\ CH_2 \\ C \\ \| \\ O \end{array} \quad (IV) \\ (m.p.\ -6\,°C)$$
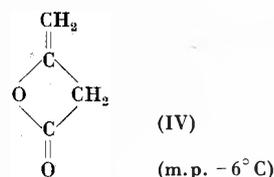
In this case too a long monomer crystal was made by slow cooling. It was then polymerized in solid state at low temperature. The X-ray diagram showed a crystalline and oriented polymer. Ionic polymerization was assum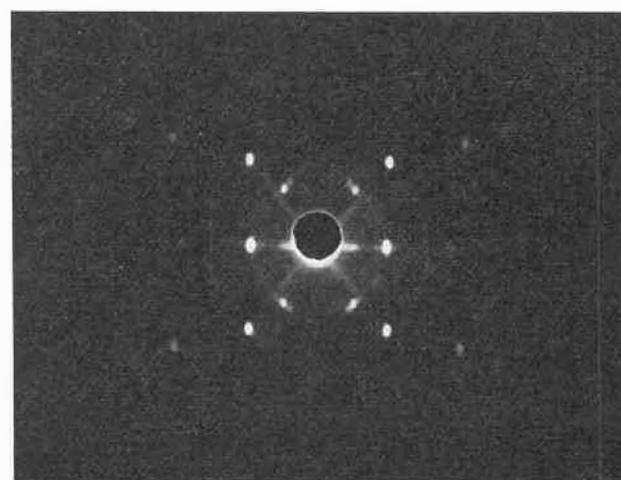ed to occur in the formation of the polyester $\left(-\underset{\overset{|}{CH_2}}{C}-CH_2-\underset{\overset{\|}{O}}{C}-O-\right)_n$. Polymerization in liquid state at high temperature produces a vinyl polymer with the formula $\left(-CH_2-\underset{\underset{CH_2}{\diagup}\underset{\overset{|}{C}}{\diagdown}CH_2}{C}-\right)_n$.
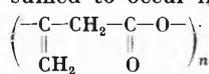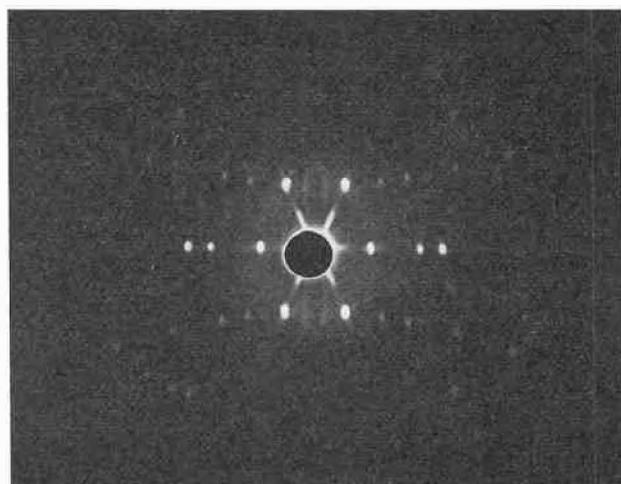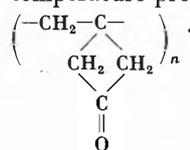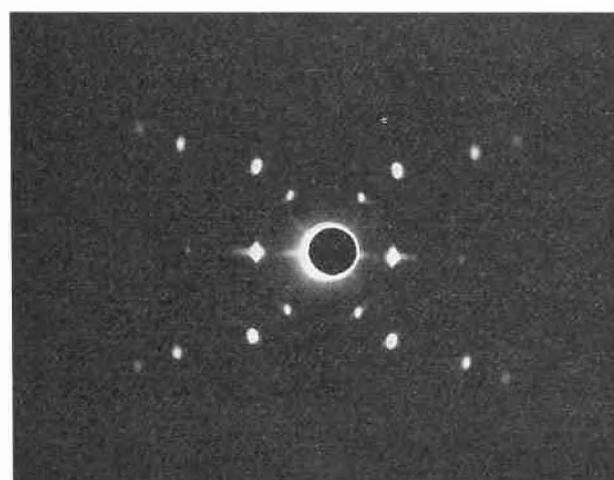

N 87 Monomer
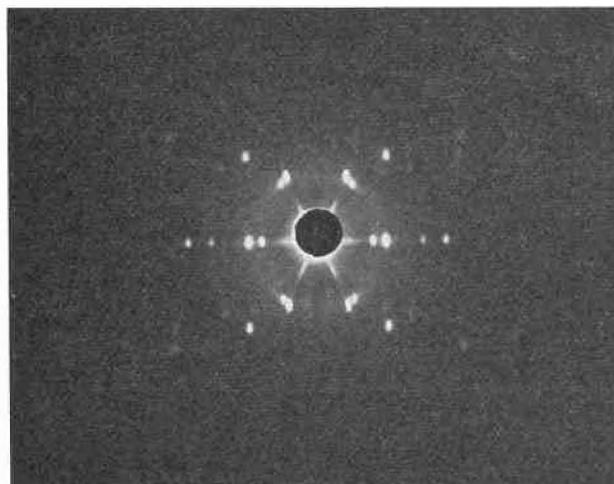
N 89 $D = 1.1 \times 10^5$ r
Polymerization yield 20%

N 91 $D = 4.2 \times 10^5$ r
Polymerization yield 80%

N 92 Polymer

Fig. 1. Rotation X-ray diffraction diagrams of trioxane and irradiated trioxane. Irradiation at 55 °C, $I = 9 \times 10^3$ r/hr
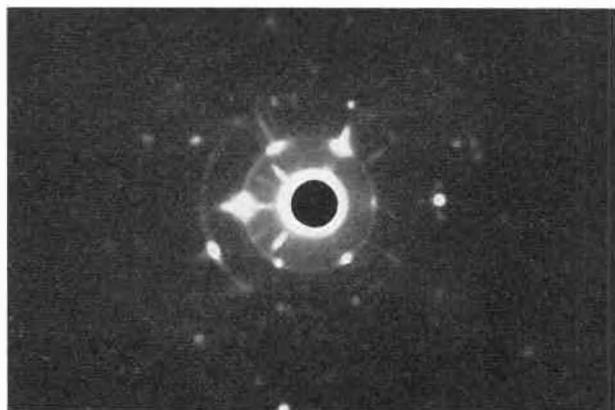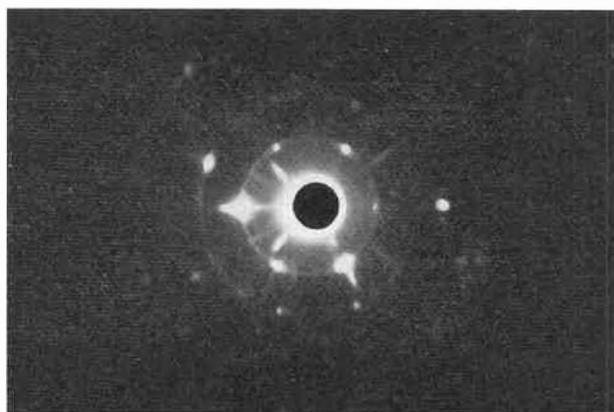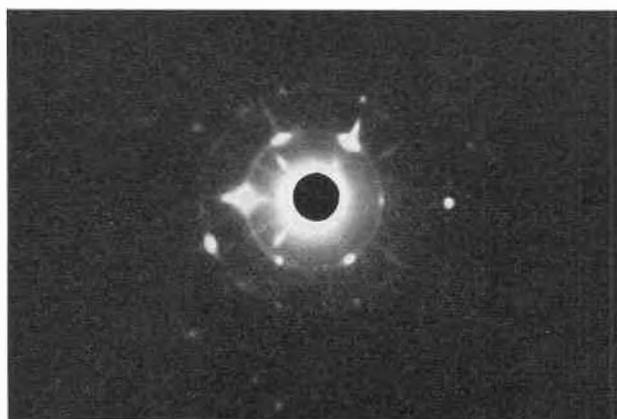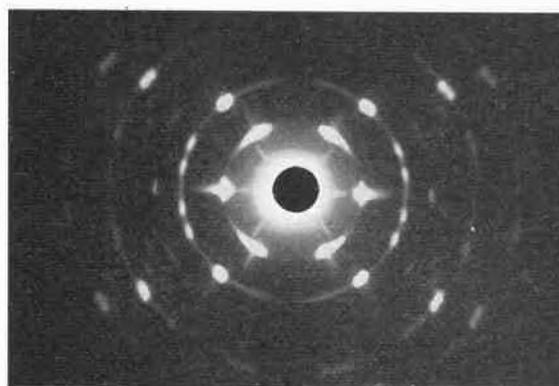
Relative angle 0°

Before heating (original)

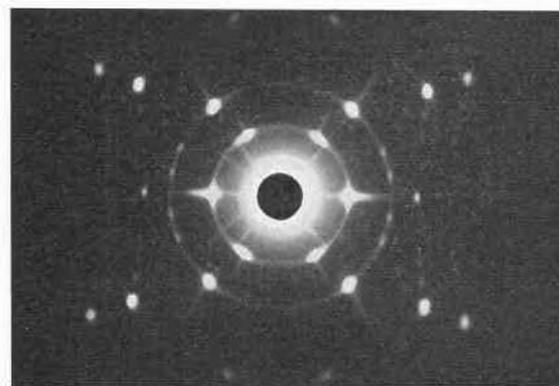60°

2 hrs heated

120°

5 hrs heated

Fig. 2. X-ray diffraction diagrams (non rotated) of poly-trioxane, polymerized at 30 °C, polymerization yield 79%. Various relative angles of rotation around the C axis

Fig. 3. Rotation X-ray diffraction diagrams of poly-trioxane and heat-treated poly-trioxane, polymerized at 28 °C, heat-treated at 170 °C

7. Polyoxymethylene in a different crystalline form
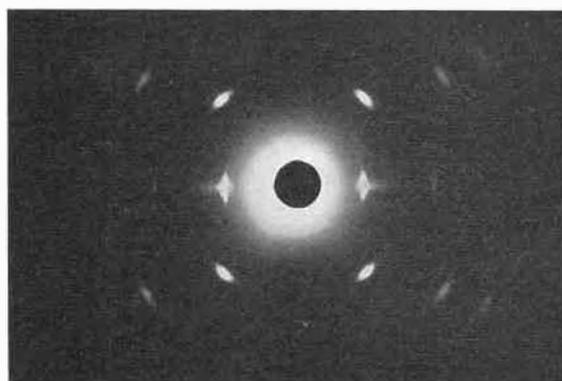
Formaldehyde (m.p. ca. −100 °C) is transformed by trimerization into trioxane with a raise of the melting temperature (m.p. +62 °C). The monomer is brought into a crystalline transparent form and then poly-merization by irradiation follows. The synthesis of poly-oxymethylene by this procedure leads to a different crys-talline form. An outline of the method shall be given here.[46]

[46] S. OKAMURA and K. HAYASHI, in *Second Conference of Radiation Research, Harrogate 1962.*
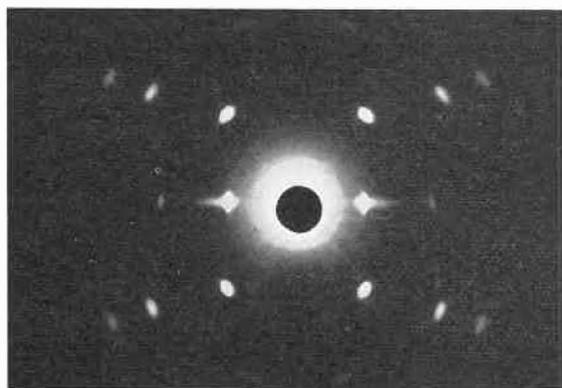
Before heating (original)

2 hrs heated

5 hrs heated

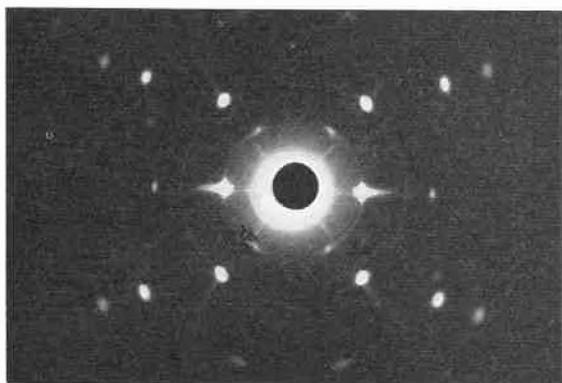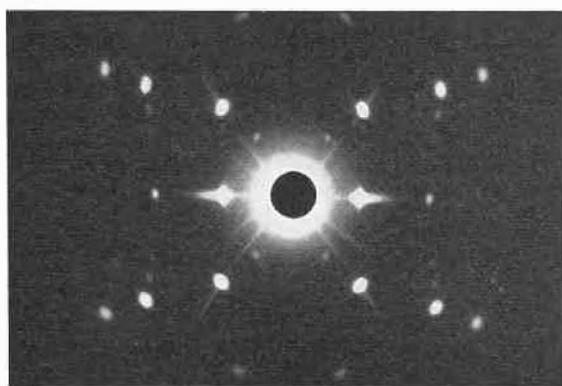*Fig. 4.* Rotation X-ray diffraction diagrams of poly-trioxane and heat-treated poly-trioxane, polymerized at 55 °C, heat-treated at 170 °C

(a) Process of crystalline polymerization

The polymerization process of formaldehyde to trioxane in crystalline form may be illustrated by the following four rotating X-ray diagrams (c.f. Fig. 1).

No disturbance of the monomer crystal could be observed during polymerization. Like the solid monomer

(c.f. N. 87), the polymer was a hexagonal crystal. This may be seen from the three X-ray photographs which were taken by rotating at angles varying 60° (Fig. 2).

(b) Characteristics of the crystalline form

In the X-ray diagram shown above as N. 92 in Fig. 1, we can see four-point and eight-point interference spots (shown also in the upper diagram, of Fig. 3) which are not observed in a usual polyoxymethylene polymer like «Delrin». These strange spots disappeared by heat treatment as shown in Figures 3 and 4.

(c) Reaction mechanism of the crystalline polymerization

When the monomer molecules are arranged in one direction as shown in H of Fig. 1, they can be polarized and then act as counter-ions in the radiation field. A rather large rate of polymerization can be expected in this case. The proposed mechanism resulted from materiallizing the theory of collective excitation evolved by N. N. CEMENOV.[47] This special case of solid state ionic polymerization may also be considered as a topochemical polymerization.[48]

Topochemical polymerization was already encountered in the case of trioxane polymerization initiated by formaldehyde vapour.[49]

$$HCHO \xrightarrow{Topo\text{-}atactic} Polyoxymethylene$$
$$\downarrow$$
$$(CH_2O)_3 \xrightarrow{Topo\text{-}tactic}$$
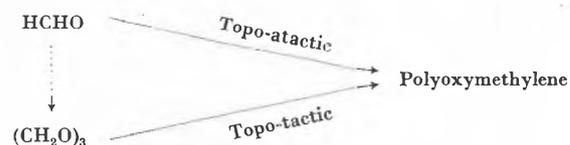
The following reaction was also investigated because it gives a connection to powder metallurgy.

$$Fe_2(NO_3)_3 \xrightarrow{Topo\text{-}atactic} \alpha Fe_2O_3$$
$$\downarrow$$
$$\alpha Fe(OOH) \xrightarrow{Topo\text{-}tactic}$$
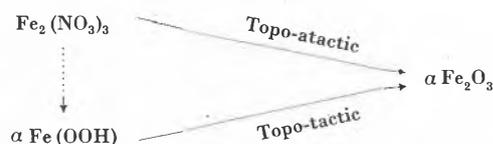
8. Conclusions

Our discussion under the title of solid state polymerization was limited to the solid state polymerization induced by γ-irradiation. Solid state radical polymerization may be achieved in different other ways. Though the subject of ionic polymerization induced by irradiation has been extensively investigated, unsolved questions are still left. A basic one is whether or not the ionic particles acting in the polymerization are the same as those in catalytic ionic polymerization. In the field of

[47] N. N. CEMENOV, in *IUPAC Conference, Montreal 1961*.
[48] S. OKAMURA, *J. Polymer* (Japan) *11* (1962) 93.
[49] H. W. KOHLSCHÜTTER and L. SPRENGER, *Z. phys. Chem. B. 16* (1932) 284.

A	**B**	**C**	**D**
Homogeneous radical	Co-ordinated, radical (KARGIN)	Adducts, radical (BROWN)	Solid state, radical
E	**F**	**G**	**H**
Free ionic	Ion pair	Co-ordinated, ionic (NATTA)	Solid state, ionic

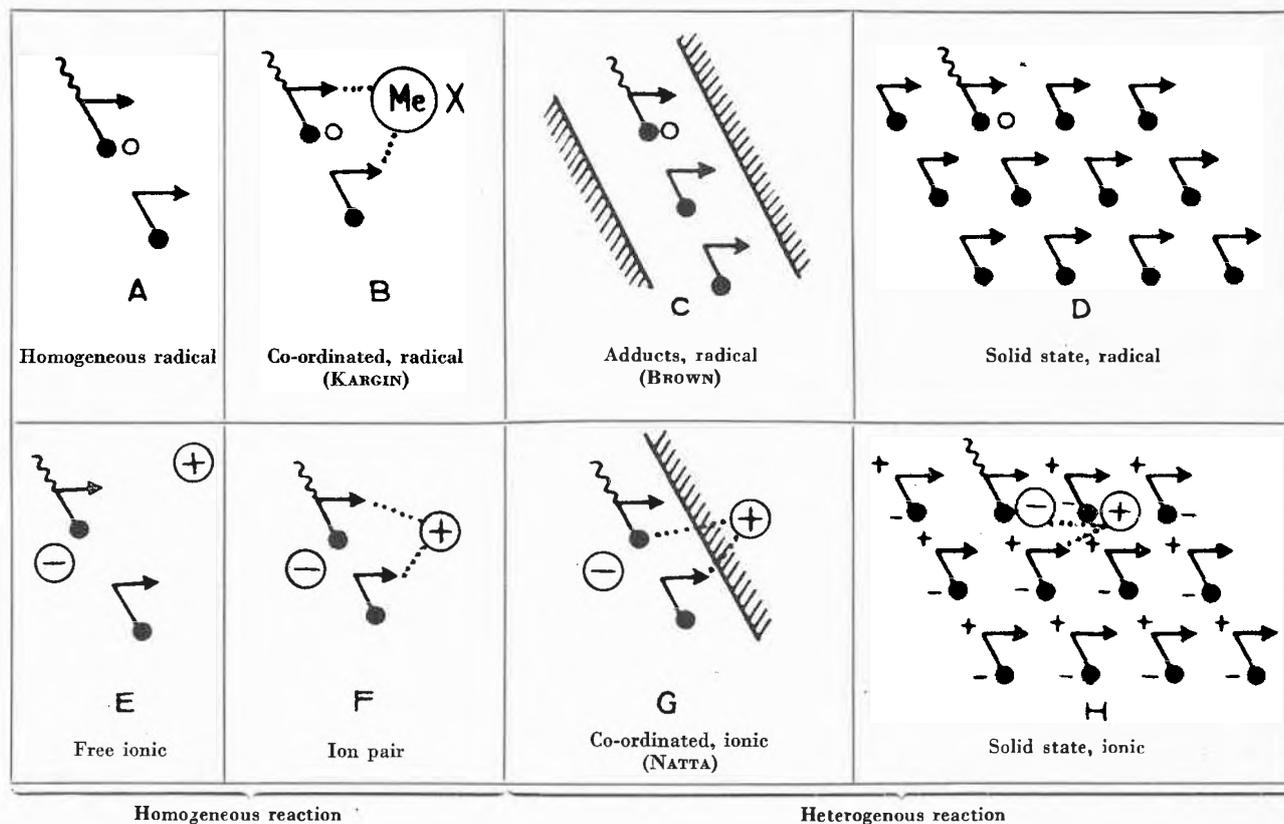Homogeneous reaction   Heterogenous reaction

Fig. 5. Schematic diagrams of polymerization mechanisms

radical polymerization ESR measurements have contributed much to enlightening the radical, a kind of activated molecule. If practical methods are further improved and reaction mechanisms clarified, then solid state polymerization will certainly play a greater technical role in the future than imagined today.

Chronique   Chronik   Cronaca

Zum 60. Geburtstag von Herrn Direktor Eugen Maier

Am 1. Februar 1963 feiert Herr EUGEN MAIER – Mitglied des Direktionsausschusses der SANDOZ AG – seinen 60. Geburtstag. Der aus Beromünster stammende Jubilar trat nach erfolgreichen Jahren der Bankpraxis 1929 in die Dienste der damaligen Chemischen Fabrik vorm. Sandoz. Dank seiner Intelligenz, seiner raschen Auffassungsgabe und seiner Fähigkeit, Kontakte zu schaffen wurde er schon 1930 mit der Führung des Textilchemikaliengeschäftes in Deutschland betraut. Von Chemnitz, wo er viele geschäftliche und freundschaftliche Verbindungen herzustellen wußte, kam er 1937 nach Basel zurück und wurde hier zum Assistenten des kaufmännischen Departementsvorstehers ernannt. In rascher Folge führte der Weg nun aufwärts. Herr MAIER wurde 1939 zum Prokuristen, 1946 zum Vizedirektor, 1949 zum stellvertretenden Direktor, 1953 zum kaufmännischen Leiter der Abteilung für Chemikalien und 1956 zum ordentlichen Direktor befördert. Seit dem 1. Januar 1963 hat Herr Direktor MAIER als Mitglied des Direktionsausschusses der SANDOZ AG die Oberleitung des Chemikaliendepartementes inne. Der Erreichung dieser Stufe gingen großer Einsatz, besonders in schwierigen Zeiten und Situationen, ausgedehnte

Reisen, Konferenzen und ständige Kontaktnahmen mit wichtigen Persönlichkeiten voraus. Immer wieder ist es erstaunlich, mit welcher Sicherheit Herr Direktor MAIER den Kern schwieriger Probleme erfaßt und richtige Entscheide zu treffen weiß.

Es ist verständlich, daß die Bewältigung dieses großen Arbeitspensums selbst einer so vitalen Persönlichkeit kaum Zeit läßt, auch im öffentlichen Leben hervorzutreten. Trotzdem stellt Herr Direktor MAIER seine Dienste der Öffentlichkeit zur Verfügung, zurzeit z. B. als Präsident der Kommission für die kaufmännische Berufsbildung des Kantons Basel-Stadt.

Erholung findet der Jubilar in seinem Heim in Riehen im Schoße seiner Familie und in seinem schönen Besitztum im geliebten Orselina. Mögen ihm noch viele Jahre der Gesundheit und der Freude in seinem so verantwortungsvollen Wirken vergönnt sein.

Dechema-Preis. Dr.-Ing. JOACHIM SCHMIDT, Langenfeld (Rheinland), erhielt den Dechema-Preis 1961 der Max-Buchner-Forschungsstiftung für seine Entwicklung der Gegenstromkristallisation als neues Trennverfahren, womit sich ein Weg zur kontinuierlichen und wirtschaftlichen Trennung bisher schwer trennbarer Stoffgemische eröffnet hat.