

SOME ASPECTS OF SOLID STATE POLYMERIZATION

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ABSTRACT

Previous investigations on solid state polymerization are reviewed, and a few examples of new experimental results are added. Radiation-induced polymerizations of methyl methacrylate in the supercooled liquid phase, and of cyclohexene oxide in the plastic crystalline phase, have been examined. Polymerizations of acrylamide and *N*-vinylcarbazole were investigated on a solid surface with initiation induced by chlorine atoms. Solid suspension polymerization of trioxane was studied with cationic initiation. Differential thermal analysis, and electron-microscope investigations of radiation-induced polymerizations of tetraoxane and acrylamide are discussed.

1. INTRODUCTION

Chemical reactions have usually been investigated in homogeneous gas or liquid phase, mainly because solid state reactions involve heterogeneous characteristics which are difficult to treat reproducibly.

In the last fifteen years, however, extensive studies have been concentrated on radiation-induced solid state polymerization in the homogeneous phase. High energy radiation can penetrate into the solid system and initiate homogeneous polymerization. Crystalline acrylamide or methacrylamide have been found to polymerize in the solid state by gamma- or x-ray irradiation into amorphous polyacrylic or polymethacrylic amide. These facts have been reported by Henglein and Schulz¹, Morawetz and Rubin², Ballantine *et al.*³, Bamford *et al.*⁴, and by others. There seemed to be possibilities for both fusion by heat and disordering by displacement during polymerization. To avoid these possibilities high melting acrylic acid salts of alkaline earths were examined in radiation-induced solid phase polymerization by Morawetz *et al.*⁵, O'Donnell *et al.*⁶, and others.

Low temperature polymerization has been studied more easily by using high energy radiation at low temperatures; at temperatures as low as that of liquid nitrogen almost all organic liquids are frozen solid. The x- or γ -ray-induced polymerization of formaldehyde and acetaldehyde, also in the solid state, has been reported by Chachaty and Magat⁷, and by others. Some vinyl monomers such as acrylonitrile, methylmethacrylate, vinyl acetate and styrene have been examined in γ -initiated solid state polymerization by Pshejetskii and Kargin⁸, Amagi and Chapiro⁹, Goldanskii *et al.*¹⁰, Hardy

*et al.*¹¹, Chen and Grabar¹², and by others. All these cases were recognized as polymerizations of crystalline monomer into amorphous polymer. Finally, crystal-into-crystal solid state polymerizations have been reported with trioxane, 3,3-bischloromethylcyclo-oxetane, β -propiolactone and diketene by Hayashi *et al.*¹³ in our laboratory.

So-called solid phase polymerization has been the subject of continuing interest and has been examined in three cases: (1) crystal-to-crystal type polymerization has been examined on tetra-oxane, pentoxane and recently hexa-oxane by Tadokoro *et al.*¹⁴; (2) Crystal-to-amorphous polymer type polymerization has been examined on the surface-initiated catalytic polymerizations of acrylamide, methacrylamide or *N*-vinyl carbazole, and this work is summarized here; and (3) glass-forming systems have been examined and reported on from radiation-induced polymerization in the supercooled liquid states of methylmethacrylate or acrylonitrile. The main results of this work are also summarized here. In order to clarify further the intricacies of solid state polymerization behaviour, I would like to report here (4) some of the preliminary work on the plastic crystal phase polymerization of cyclohexene oxide compared with its liquid and crystalline phases.

2. RADIATION-INDUCED POLYMERIZATION OF VINYL COMPOUNDS IN THE SUPERCOOLED LIQUID PHASE¹⁵

(a) Thermal measurement

A differential thermal analyser (DTA) (AGNE Research Centre Co. Ltd) was used for estimating the glass transition temperature, T_g , and other critical temperatures of the systems. For example, DTA traces of some acid-amide systems are represented in *Figure 1*. First (A in bottom figure)

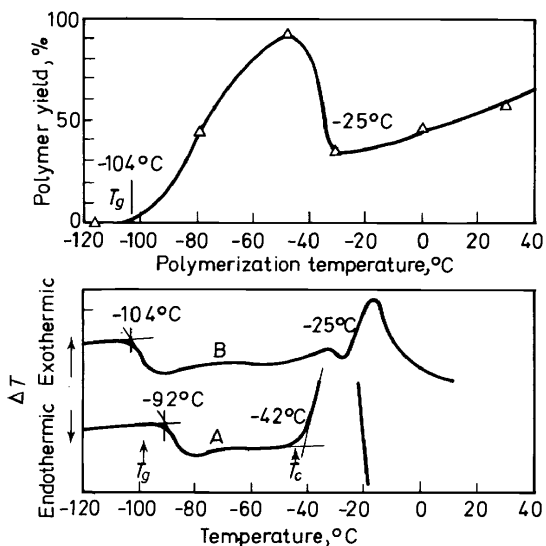


Figure 1. Polymerization and DTA of monomer-acid-amide systems indicating glass transition^{15c}. MMA-propionic acid-acetamide (13:38:49).

in a propionic acid-acetamide mixture, T_g is seen at -92°C and with the crystallization temperature, T_c , at -42°C . After adding methylmethacrylate (MMA) to the system, (B in the figure), T_g decreases to -104°C , and T_c becomes uncertain, roughly about -25°C . Between these two ($T_g - T_c$) critical temperatures, the system is said to be in the supercooled liquid state, being glassy to outward appearances.

(b) In-source polymerization

For polymerization experiments, each sample is degassed three times in glass ampoules and sealed off in a vacuum. The sample is then irradiated by γ -rays from a cobalt-60 source (90000 Ci) at the desired temperature. The polymer obtained (PMMA) is precipitated in cooled methanol and the polymer yield determined gravimetrically. The molecular weight is determined by viscometry in benzene solution at 25°C .

The rates of polymerization in a glass-forming matrix are shown in the upper part of Figure 1. It is obvious that polymerization does not occur below T_g , but proceeds rapidly in the temperature range above T_g . The rate of polymerization shows an apparent maximum value between T_g and T_c , being due to changes in the viscosity of the system. Diffusion of the molecules is restricted near T_g . With raising of the temperature above T_g , the restriction for a propagation reaction is lessened but not yet sufficiently for a termination reaction to commence. This causes acceleration of the reaction rate, as well as increase of the molecular weight. Polymerization in a supercooled liquid behaves in much the same way as solid state polymerization.

(c) Post polymerization

The samples are irradiated by γ -rays at liquid nitrogen temperature (-196°C) and then carefully heated at a controlled rate. As shown in the DTA curves of Figure 2 B, the post-polymerization reaction of the MMA-propionic acid-acetamide system does not proceed below T_g , but starts at about -92°C .

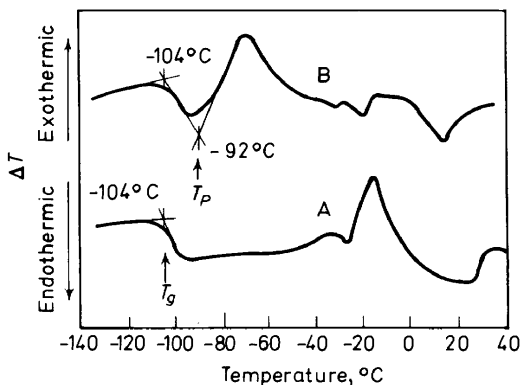


Figure 2. DTA traces of methylmethacrylate-propionic acid-acetamide system. A: Before irradiation; B: After irradiation (4×10^5 (rad/h) \times 1 (h) at -196°C)

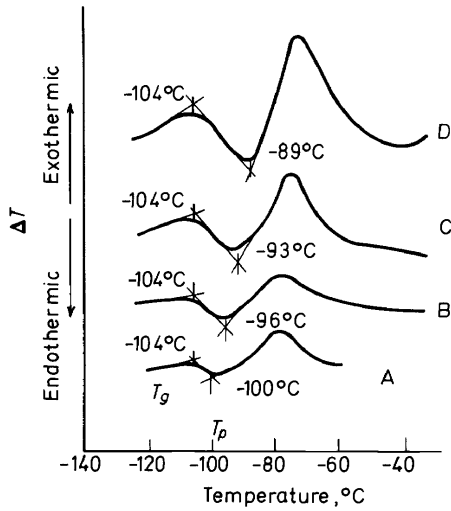


Figure 3. DTA traces of methylmethacrylate-propionic acid-acetamide irradiated system. Heating rate (mV/min) A: 0.04; B: 0.1; C: 0.2; D: 0.4 (4×10^5 rad/h) \times 1 (h) at -196°C

By increasing the heating rate, the temperature for initiating polymerization (T_p) increases, but T_g remains constant. These facts are shown in Figure 3.

As shown in Figure 4, the temperature difference ($\Delta T = T_g - T_p$) tends to zero when the heating rate is extrapolated to zero. This indicates that post polymerization starts at the glass temperature in the supercooled liquid state. Similar results are also obtained in the systems of acrylamide-itaconic

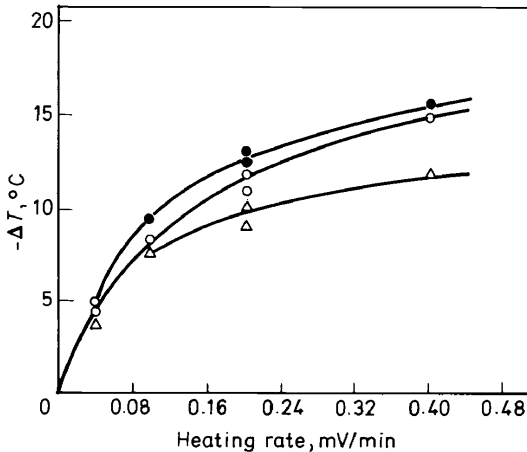


Figure 4. Temperature difference ($\Delta T = T_g - T_p$) between T_g and T_p as a function of heating rate. ○ Methylmethacrylate-propionic acid-acetamide. ● Methylmethacrylate-succinic acid-acetamide. Δ Acrylonitrile-succinic acid-acetamide

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Table 1. Molecular weight of polymer obtained in the polymerization of glass-forming systems^{15a} (acrylamide-propionic acid-formamide, 1:1:0.5, irradiation dose, 0.003 Mr)

Irradiation temperature (°C)	$\overline{DP} \times 10^{-4}$	Huggins constant (k')
-78	2.1	3.40
-63	2.4	3.00
-48	1.6	0.52
-30	1.1	0.51
-20	1.3	0.48

acid (or -malonic acid) and acrylic acid-acetamide (or -formamide). Unusually large values of Huggins's constant k' in the viscosity equation are found between T_g and T_c in the acrylamide-propionic acid-formamide system, as shown in Table 1. The reason for the large k' -value in supercooled liquids arises from increased reactivity in branch formation which chain transfer may increase by increasing the polymerization rate between T_g and T_c .

The glass-forming systems are obtained by carefully selecting the cooling rate. Acrylamide is found to form its glassy state by mixing with acids, like itaconic, malonic, or acrylic acid. Similarly acrylic acid can form glass with formamide, acetamide or propionamide. Here T_g values dilatometrically measured are set out in Table 2.

Table 2. Transition temperatures of glass-forming systems^{15b}

Systems	Composition (in volume)	Glass transition temperature. (°C)
Acrylamide-itaconic acid	1:0.8	-39
Acrylamide-malonic acid	1:1	-60
Acrylamide-succinic acid-acetamide	1:0.5:1	-74
Acrylamide-acrylic acid	1:1	-100
Acrylamide-propionic acid-acetamide	1:1:0.5	-100 ~ -105
Acrylamide-propionic acid-formamide	1:1:0.5	-110
Acrylamide-propionic acid-formamide	1:1:1	-115 ~ -120
Acrylic acid-acetamide	1:0.5	-110 ~ -115
Acrylic acid-formamide	1:1	-135 ~ -145

3. CATALYTIC POLYMERIZATION OF VINYL AND CYCLIC COMPOUNDS IN SOLID PHASE¹⁶

(a) Solid state polymerization of acrylamide initiated by a Cl atom at the solid surface

The crystalline monomer of acrylamide or methacrylamide has long been recognized to polymerize in the solid state by u.v.-, x- or γ -rays. During polymerization the solid shape of the monomer does not change in outer

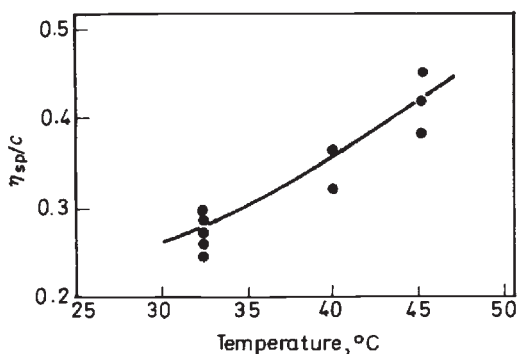


Figure 5. η_{sp}/c -values of the polymer obtained in the solid state polymerization of acrylamide and polymerization temperatures^{16a}. $[M]_0$: 1 g in 33 ml, $[Cl_2]$: 21 m moles per litre

appearance but the polymer obtained is always found to be amorphous. The essential point lies in whether the propagation occurs before or after disordering of the monomer lattice. The behaviour depends critically on the rate-relationship between the solid state reaction and the crystallization of polymer molecules. The polymerization might proceed in a highly viscous state. It depends also upon the order of disturbance by the polymerization reaction.

Now, crystalline monomers of acrylamide and methacrylamide are found to polymerize in the solid state in the presence of chlorine gas under u.v.

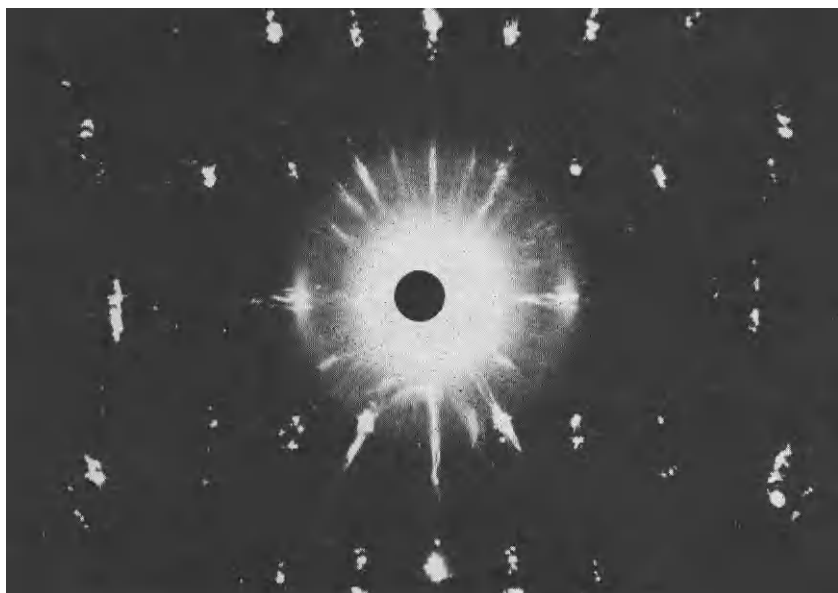
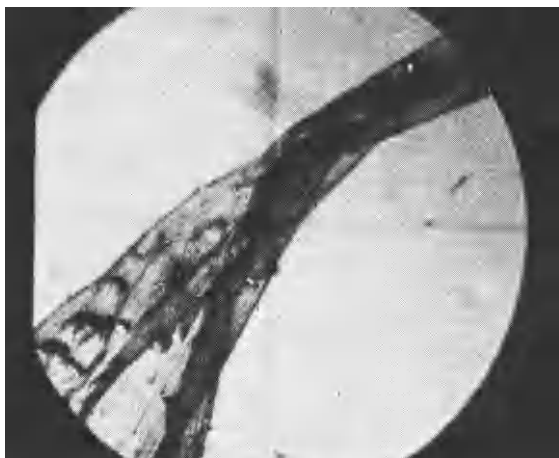


Figure 6

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radiation. As the shape of the monomer remains unchanged, the polymerization proceeds from just below the surface of the crystals. It is obvious here that the chlorine atoms produced by the decomposition of chlorine molecules initiate the polymerization at the surface of a monomer crystal. As one apparent characteristic of solid state polymerization the molecular weights of the polymers obtained are shown to increase by raising of the polymerization temperature. One of these results is shown in *Figure 5*.

After unreacted monomer was sublimed from partially polymerized crystals of acrylamide, the polyacrylamide obtained was found to be crystalline by the Debye-Scherrer ring diagram in x-ray diffraction analysis and to be somewhat oriented by polarized microscopic analysis, as shown in the following x-ray diagrams (*Figure 6*) and photographs (*Figure 7*).



Ordinary microscopic



Polarized microscopic

Figure 7

Polyacrylamide or methacrylamide as reported in radiation-induced solid-state polymerization has already been recognized to be amorphous, but here the polymer obtained in the surface polymerization was found to be crystalline.

Once Professor I. Nitta *et al.*¹⁷ examined the molecular alignment of monomer acrylamide in a single crystal and assumed that monomer molecules existing in the 'a-plane' should be easily polymerized into a polymer layer in random directions within the plane. If the sites for initiation are distributed at random in the crystal, then propagation in the direction vertical to the a-plane may also be random which will make the polymer amorphous. In the case of the surface initiation mentioned here, however, the initiation sites are concentrated, at least in the early stage of polymerization, in the surface of the crystal; in the a-plane, then, propagation proceeds step by step along each a-plane. Regularity will be obtained by slow surface-initiated solid-state polymerization at the interaction between polymer molecules probably by hydrogen-bonding at >NH and >C=O groups. Gradual sublimation of unreacted monomer was the only way of obtaining a crystalline state of the polymer, but solvent extraction by methanol or acetone destroys the polymer structure in which no birefringence shows.

(b) Solid state polymerization of *N*-vinyl carbazole initiated by redox-catalyst in the suspension

An *N*-vinylcarbazole crystal was polymerized in suspension in water using ammonium persulphate and sodium bisulphate as redox catalysts. As one characteristic of solid state polymerization, the molecular weights of the polymer obtained¹⁸ were shown to increase with rising polymerization temperature (Figure 8). Birefringence was clearly observed in the polymer layer of a partially polymerized crystal. The crystalline Debye-Scherrer rings were also observed in x-ray diffraction diagrams of the polymer.

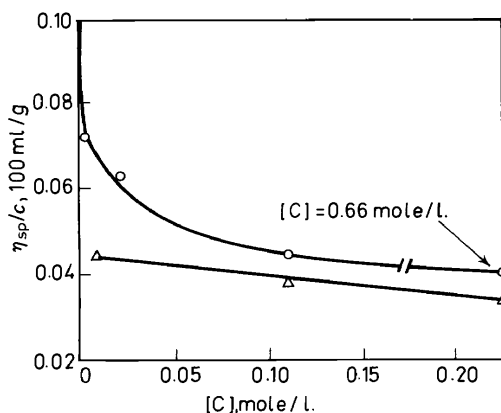


Figure 8. (η_{sp}/c) (100 ml/g)-values of the polymer and the catalyst concentration in the medium [C], (mole/l). Polymerization temperature: \circ 50°C; \triangle 40°C: at $[M]_0$: 1 g in 20 ml medium¹⁸

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These are also cases of surface-initiated solid-state polymerization. Sublimation of the monomer in this case, however, destroys the regularity of the polymer structure in which no strong bonding exists, in contrast to acrylamide.

(c) Solid state polymerization of trioxane initiated by cationic catalyst in suspension

Trioxane was polymerized in a suspension of *n*-hexane, having stannic chloride as a cationic catalyst. The effect of polymerizing temperature on the molecular weight of polymer obtained is represented in *Figure 9*. The general

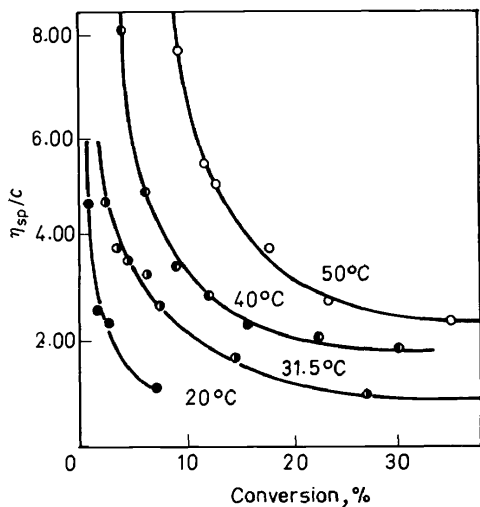


Figure 9. Effect of polymerization temperature on the molecular weight (η_{sp}/c) of polymer^{16c}. *n*-Hexane, $[M]$: 0.74 mole per litre; $[SnCl_4]$: 11.25 mmole per litre, $SnCl_4$; TAA = 1; 0.57; polym. temperature. ○ 50°C, ◐ 40°C, ◑ 31.5°C, ● 20°C

tendency for solid state polymerization as a function of molecular weight is also confirmed in these cases.

The polyoxymethylene obtained here was highly crystalline and well oriented in three dimensions as shown in *Figure 10*.

In these cases no large differences were observed between radiation-induced and surface-initiated solid state polymerization.

(d) Differential thermal analysis of radiation-induced post-polymerization of tetra-oxane and acrylamide in the solid state^{16c}

Thermal measurements were done using the Shimadzu DT-10 analyser for tetra-oxane and acrylamide. Tetra-oxane has the benefit of a smaller tendency to sublime than that of trioxane. *Figures 11(a)* and *11(b)* show DTA curves for non-irradiated (each a) and irradiated tetra-oxane and acrylamide, respectively.

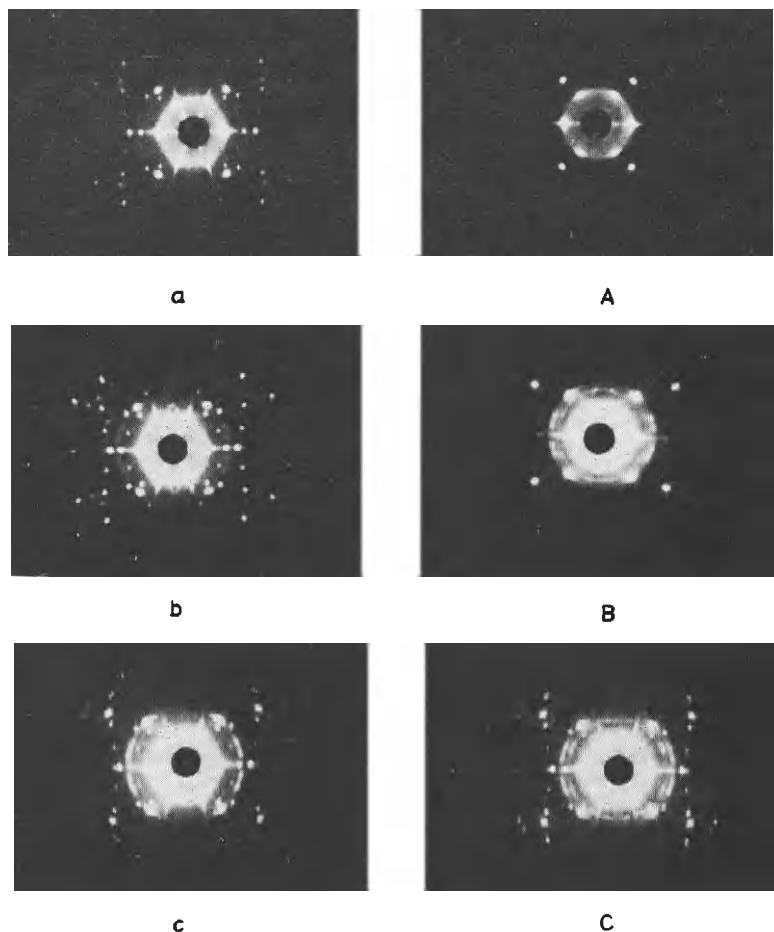
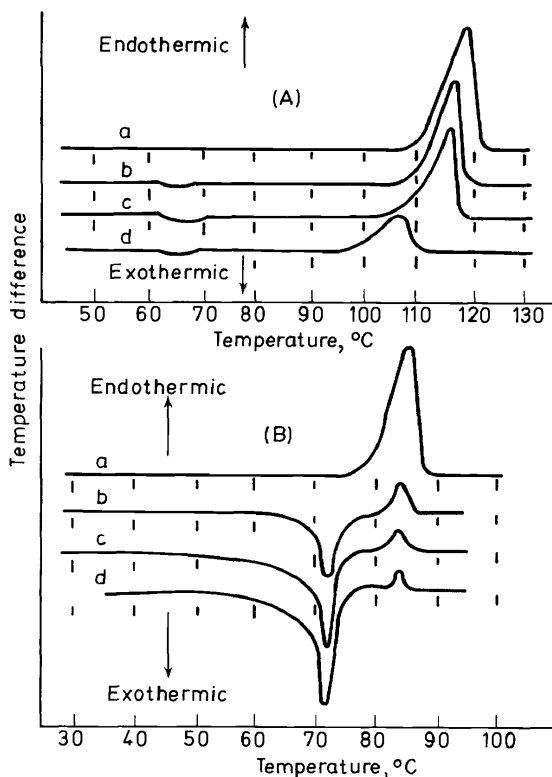


Figure 10. X-ray diffraction diagrams of POM obtained in solid state. Polymerization in *n*-hexane by stannic chloride-TCA at 50°C.

			Conv. (%)	Polym. time (min)
A.	} Containing unreacted monomer	a.	23	9
B.		b.	39	60
C.		c.	56	360

The melting point of tetra-oxane was seen at 112°C and this endothermic peak decreased by irradiation (shown in b, c and d) due to decrease of the amount of monomer remaining. In irradiated samples, exothermic broad peaks were observed to start at about 62°C. $-\Delta H_p$ was found to be 0.8 ± 0.1 kcal/mole from calculation of the exothermic heat content divided by the amount of polymer obtained. ΔH_f was similarly calculated to be 5.8 ± 0.3 kcal/mole from the endothermic heat content divided by the amount of monomer remaining. ΔH_f for pure monomer was found to be 5.2 ± 0.1 kcal/mole with which the calculated value mentioned above could well coincide.

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 Figure 11. DTA of tetra-oxane (A) and acrylamide (B)^{16e}.

	Pre-irradiation dose (r)	Polymer yield (%)		Pre-irradiation dose (r)	Polymer yield (%)	
(A)	a	0	(B)	a	0	
	b	1.0×10^6		b	2.2×10^5	39.6
	c	3.4×10^6		c	4.1×10^5	61.2
	d	6.4×10^6		d	1.2×10^5	76.7

The melting point of acrylamide was found to be 84.5°C and this endothermic peak also decreased by irradiation due to decrease in the amount of monomer remaining. In irradiated samples, exothermic broad peaks were also observed between about 35°C and 70°C, due to post-polymerization. The post-polymerization seemed to be fast as represented by the steep exothermicity. In this case, the heat of polymerization, ΔH_p , could not be obtained due to the fusion of some part of the monomer by a rise of temperature. For the calculation of ΔH_p , the extrapolation to zero heating rate was done by which ΔH_p was found to be 8.1 ± 1.1 kcal/mole. However, the ΔH_p for solution polymerization has been known to be 13.8 ± 0.3 kcal/mole. In a similar way to that for tetra-oxane, ΔH_f in solid state polymerization for the monomer was found to be 0.7 ± 0.1 kcal/mole which was very much smaller than ΔH_f for the pure monomer: 4.1 ± 0.4 kcal/mole.

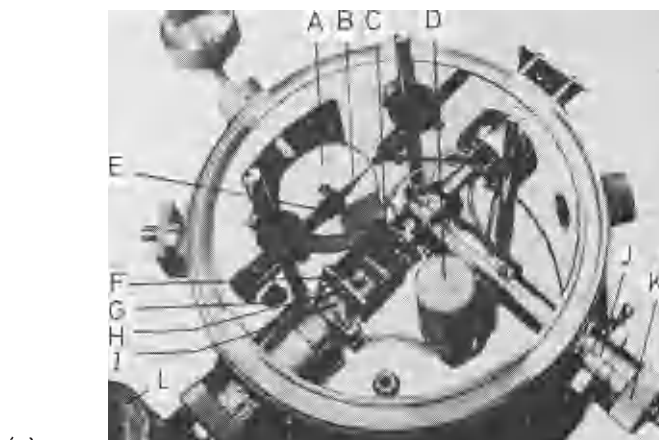
Table 3. Thermal data for post-polymerization

	Observed	Calculated
$-\Delta H_p$	8.1 ± 1.1	13.8 ± 0.3
ΔH_f	0.7 ± 0.1	4.1 ± 0.4
$-\Delta H_p$	0.8 ± 0.1	0.7 ± 0.1
ΔH_f	5.8 ± 0.3	5.2 ± 0.1

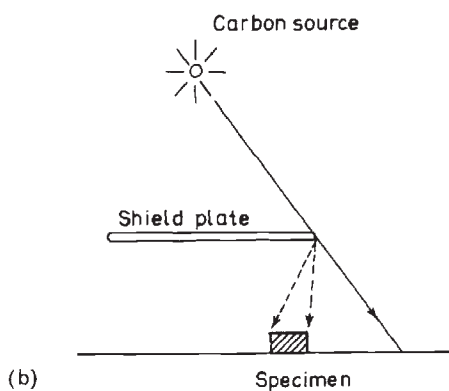
These experimental facts (Table 3) seem to be well explained by the assumption of propagation in the molten state in acrylamide and propagation in the crystalline state in tetra-oxane both in the solid-state post-polymerization.

(e) Electron-microscopic observation by low-temperature replica for post-polymerizations of trioxane and acrylamide in the solid state^{16f}

To demonstrate some differences of chain propagation between cyclic and vinyl polymerization, the replica method at low temperature was adopted with the electron microscope for observation.



(a)



(b)

Figure 12. Low-temperature replica apparatus. a: Photograph, b: Schematic diagram of a single-stage carbon replica using a shield plate^{16f}

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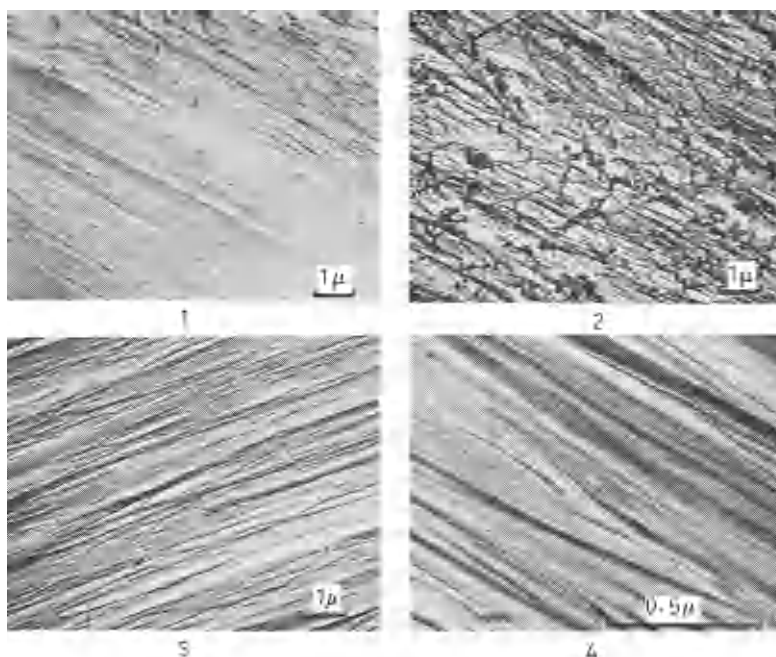


Figure 13. Electron-micrograph of trioxane. 1. Trioxane: 8000 \times ; 2. Polymerized trioxane (P: 4%) 9300 \times ; 3. Polymerized trioxane (P: 10%) 9300 \times ; 4. Polymerized trioxane (P: 10%) 67000 \times

In the radiation-induced solid-state polymerization of trioxane, crystalline polymer fibrils of 200 to 500 Å diameter and above 1 μ in length were observed in electron micrographs taken using a low temperature replica, as shown in *Figures 13 and 14*.

Table 4. Relations between intermolecular contacts in the monomer crystals and conformations of polymers produced

Compound	Intermolecular contacts (A)*	Monomer unit length (B)†	B/A
Trioxane	4.175 Å	5.80 Å	1.39
Tetra-oxane	4.160	7.73	1.86
Pentoxane	6.74	9.66	1.43
Hexa-oxane	7.913	11.59	1.46
Trithiane	5.17	6.45	1.24
BCMO	3.3	4.8	1.46
Acrylamide	3.9 ^a	2.52 ^b	0.65
Acrylic acid	3.52 ^a	2.52 ^b	0.72

* The distance between the monomer molecules along the direction of greatest chain growth.

† Occupied length of the monomer unit in the polymer chain.

a. The shortest distance between the vinyl bonds.

b. Fully-extended zigzag chain was assumed.

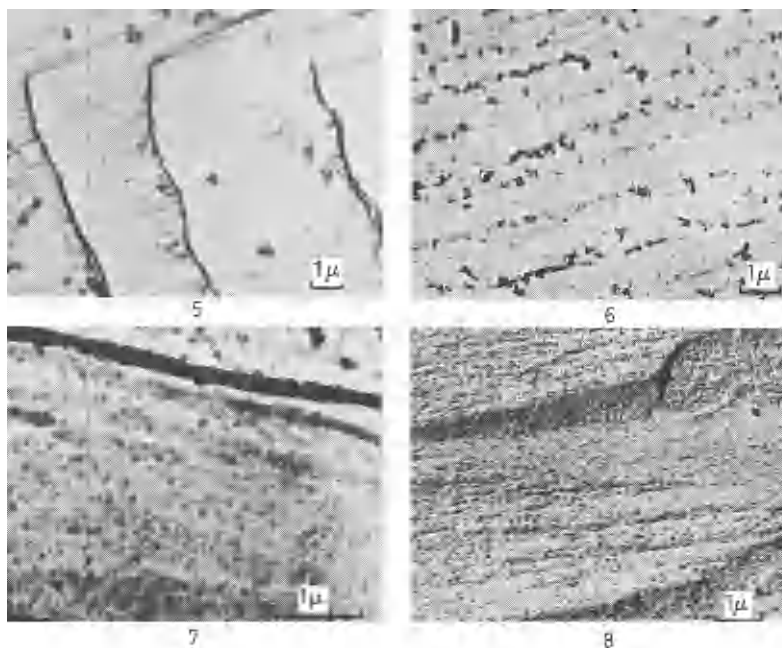


Figure 14. Electron-micrograph of acrylamide. 5. Acrylamide: 6700 \times ; 6. Polymerized acrylamide (P: 1.1%) 8300 \times ; 7. Polymerized acrylamide (P: 4.1%) 20000 \times ; 8. Polymerized acrylamide (P: 20%) 10000 \times

In those of acrylamide, amorphous globular polymer particles of 300 to 400 Å diameter were found. It has been concluded that chain propagation of trioxane was controlled by the regularities of ordered monomer molecules in the crystal lattice, but with acrylamide the reaction was not controlled.

Tables 4 and 5 summarize the displacements of monomer assumed during solid-state polymerization in ring-opening and vinyl polymerizations¹⁴.

Table 5. Cross section of monomer molecule (E) and that of polymer (Q)¹⁴

Cyclic monomer	E	Q
Trioxane	25.48	17.30
Tetra-oxane	22.7	17.30
Pentoxane	25.6	17.30

4. RADIATION-INDUCED POLYMERIZATION OF CYCLOHEXENE OXIDE IN A PLASTIC CRYSTAL¹⁹

By thermal measurements on various kinds of monomers, cyclohexene oxide has been found to have two kinds of solid phases. Solid-II (below the

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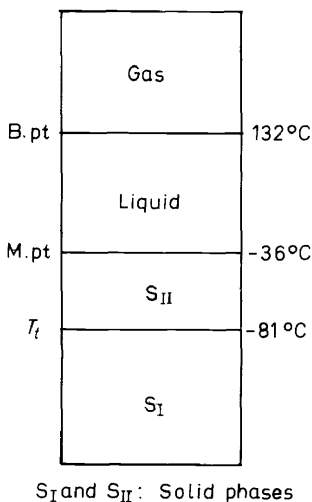


Figure 15. Phases for 1,2-cyclohexene oxide¹⁹

melting point, $T_m = -36^\circ\text{C}$, to the transition point, $T_t = -81^\circ\text{C}$) and Solid-I (below the transition point, $T_t = -81^\circ\text{C}$) (see Figure 15). Thermal data are shown in Table 6, with some compounds already known as plastic crystals.

Table 6. Transition temperatures of several cyclic compounds¹⁹

Compounds	T_t (°C)	Transition ΔS_t (E.U.)	T_m (°C)	Melting ΔS_m (E.U.)	$\frac{\Delta S_t}{\Delta S_m}$
Cyclohexene oxide	-81	7.5	-36	1.0	7.5
Cyclohexane	-87.1	8.66	6.3	2.0	3.94
Cyclohexanol	-10	7.45	25.5	1.37	5.45

Figure 16 shows the x-ray diffraction diagrams. At the phase S-II the reflections at high orders have relatively weak intensities. The vapour snake phenomenon was also observed in the S-II-phase. These facts indicate that the S-II-phase may be a plastic crystal in which the molecules in the solid are fixed at the heavy points of a crystal lattice, but can rotate freely around the lattice points.

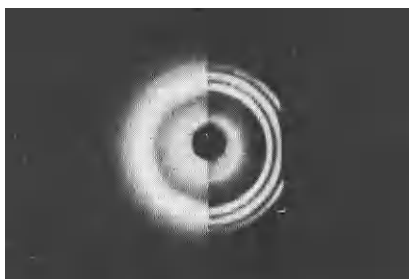
The radiation-induced polymerization behaviour has been presented in Figure 17 as the rates and degrees of polymerization. We can see that the rates in a plastic crystal are similar to those in liquids but the degrees of polymerization are nearer those of the crystal S-I.

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A Cyclohexeneoxide

Plastic crystal
 S_I at $-75 \pm 5^\circ\text{C}$

Crystal
 S_I at $-128 \pm 5^\circ\text{C}$

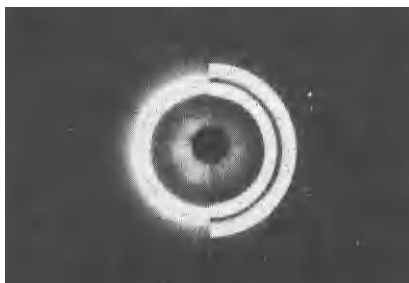


Liquid (-36°C) S_{II} (-81°C) S_I

B Cyclohexane

Plastic crystal
 S_{II} at $-81 \pm 5^\circ\text{C}$

Crystal
 S_{II} at $-130 \pm 5^\circ\text{C}$



Liquid ($\pm 6.6^\circ\text{C}$) S_{II} (-87.1°C) S_I

Figure 16. X-ray diffraction diagrams of cyclohexene oxide and cyclohexane¹⁹

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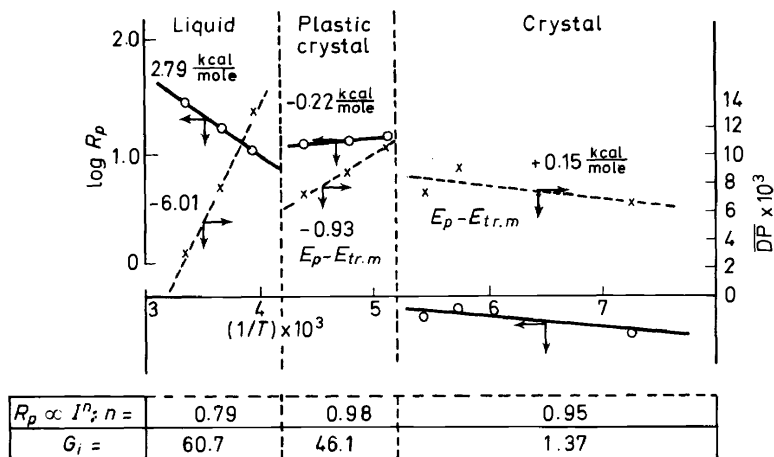


Figure 17. Polymerization of cyclohexene oxide, initial rates and degrees of polymerization at various temperatures in three phases

5. SUMMARY

Here solid state polymerizations of various kinds are reconsidered. Between the liquid and crystalline states, there seem to be supercooled liquid and plastic crystal phases, in which polymerization behaviour should also be interesting and worth more thorough investigation.

The author wishes to express his gratitude to the colleagues engaged here in this work.

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