Crystallization and Polymerization

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A. Prologue

In modern scientific writing, it is fashionable to be concerned with subatomic particles, relating the resistances of the universe to the big bang theory.

For critical purposes of the understanding of the universe, it is important to be concerned with matter: what we see and what is based on gases and solid materials. I am specifically interested in solid matter that we see on earth and nearby planets.

Matter is primarily solid, to some extent crystalline material, which is composed of silicon, aluminum, magnesium and oxygen. Eighty per cent of matter are inorganic polymers and are what we see or can detect.

On earth, life developed approximately 4 billion years ago, based on carbon, hydrogen, nitrogen, oxygen, and to some extent phosphorous and sulfur content. Life was supported and created to some extent by the presence of water. We call these materials natural materials or macromolecules, and we use the word polymer made from precursors from definable monomers. Much of what we know of natural materials concerns macromolecules – polymers.
Without going into details, the guiding principle of life is directed by nucleic acid. It is the rubberstamp, the proverb, the vocabulary and the language for the production of proteins, poly (amino acids) that are the basis of our life and existence. They are also the catalysts for the formation of our most important life substances, the polysaccharides. In practice, about 500 billion tons of cellulosics materials (~8 billion tons of useful wood) (polysaccharides) are annually produced by seasonal photosynthesis, using carbon dioxide, sunlight and usually poly (amino acids) as enzymes as catalysts and water with sufficient temperature.

About 150 years ago, a new science and technology was discovered and developed relating to macromolecules or polymers. We are producing today about 300 million tons of synthetic macromolecules and use about 4-5% of the crude oil that is annually harvested.

B. Subject

Why are we, and why should we be concerned with the problems of the Universe and the planetary system in which we live? Well, we live on a planet that has a solid surface, water, and an atmosphere with a composition of 4:1 nitrogen to oxygen and that has a gravitation force according to the mass of the planet. It has an iron core that creates magnetism, and we have magma that escapes occasionally out of the mantle in volcanic eruptions. The volcanic eruptions, when they occur, spew lava at temperatures of 2,000 to 3,000°C to the Earth’s surface. Lava composition is similar to the Earth’s crust (with some variation). The lava then cools, crystallizes, forms rock, and is weathered, creating fertile soil.
The composition of living matter is totally different. It is based fundamentally on carbon, hydrogen, and nitrogen chemistry. The existence of carbon is the most important element.

This is not the time to discuss how life was created, nor how chirality (i.e., handedness) was first introduced on Earth. We discussed this elsewhere.

In this commentary, we are only interested in the Crystallization and Polymerization and the common and differing features between the two subjects. Crystallization and Polymerization, the formation of macromolecules, is the art of the creation of the Universe and our planet Earth. This is the forming and reforming of macromolecules, inorganic macromolecules, basically oxides at high temperatures and pressures. Do we know it exactly? Probably not.

C. Crystallization

Let's take crystallization first: As I see it, the crystallization is the agglomeration in highly organized form individual molecules, neutral molecules, or molecules that assemble from solution (or melts) to organized structures.

The key to crystal formation is the nucleation. If some molecules of likeliness (in aqueous solution or melt) find each other and start a critical mass of a nucleation circumstance, nucleation and crystallization will set in. Approximately 99% of the Earth's crust consists of such materials. There is another important factor called is supersaturation.
If we now consider temperature as the other driving factor for crystallization, the picture becomes clearer. It is even easier to demonstrate when crystallization interacts with water.

When crystallization from an aqueous solution occurs, a nucleus is formed (or introduced). By crystallization, a "native" nucleation agent is formed – the molecules to be crystallized have reached a critical size. This might still be in solution. Crystallization goes through the point of supersaturation of the compound to be crystallized. If this critical saturation (quiescent) occurs slowly evaporating the solvent, large crystals will be formed. If no additional nucleating sources are available, the crystallization will continue on the surface of the large crystal.

Should the “slow” crystallization be interacted upon, for instance by breaking up the already formed nuclei (i.e., by agitation or other interference), new nuclei will be formed and many more crystal nuclei give birth to many small crystals which will further grow in the presence of water.

Although we have mentioned this trivial phenomenon in general, we have experience. For years Jan Bartus has grown pure large crystals of sodium chlorate. Those chloral nuclei when agitated will give chiral, but small crystals. Usually helped my careful chiral nucleation. When on the other hand the crystallization of sodium chlorate was carried through the state of supersaturation, it means that compound “is ready to nucleate.” And if no chiral nucleus is present normal random crystallization occurs with left and right handed crystals in equal or near equal proportions.

If we have a mixture with some accumulation of one component, it might be a reason why we find beautiful crystals instead of sandy soil on this planet and next-door neighbors. It is always the “nervy” purity of the components like in silicon dioxide, which forms near precious form quality, the nucleation and low crystallization, is the driving force. It not only forms perfect crystalline assemblies, but it is
also polymeric. Other minerals, laced with impurities, fall into the same category. Carbon as diamonds seems to be different. It forms at or below the earth’s crust under high pressure and temperature and is extruded through volcanic activity to the surface or remains at depth.

D. Simple Molecule Systems

We discussed crystallization in general but still one or two percent of the crystals on Earth are used for our life, the life that we live and love. We buy at more than reasonable prices sodium chloride and sugar. The first category represents ionic crystals the latter molecular crystals. What is important and most relevant is that they are basically three-dimensional polymers. One is based on the formation of sodium chloride crystals from sodium and chloride ions (going though the supersaturation for crystallization). The other is a molecular crystal assembly also three-dimensional, but in both cases non-bonded individual molecules and ion pairs. Every true crystal is an assembly resembling these two examples. --- Three-dimensional non-bonded macromolecules, one giant macromolecule per crystal.

E. Polymers (Macromolecules)

Polymers, on the other hand, are similar, one directional assemblies that are usually formed from monomers. We distinguish normally “addition” polymers’, polymers that derive from well defined monomers by addition reactions. The other kind (about 20% of the total polymers produced) is commonly called “condensation” polymers. They include polyamides, polyesters and similar, sometimes, for special application exotic polymers.
While nucleation is the critical point of crystallization, it is initiation that caused the formation of addition polymers. We will, for convenience concentrate in this commentary, on addition polymers because it shows also the most parallism to the formation of perfect crystals. In the modern literature and also in some older articles the words catalysis and catalyst have been used for initiation of polymerization. It is well-documented usage but we prefer the correct wording of initiation (because the initiator becomes part of the polymer chain).

F. Crystallization vs. Polymerization

Early in my scientific life I became interested in understanding how the Earth was made, how possibly fragments were pulled together. I was interested in the composition of the Earth’s crust and the volcanic eruptions based on deep-seated liquid magma that at thousands of degrees, form and reform chemical bonds that create dense liquid lava flow. His liquid is composed of silicates, aluminates and other multivalent atoms that gravity and temperature alter. Gemstones are beautiful naturally occurring crystals. They require a slow and controlled cooling as we can see in capsules that allow the capsule to crystallize slowly near the supercritical crystallization point and form spectacular crystal silicates and aluminates. When co-crystallized with minute amounts of transition metals they form fabulous gemstones of remarkable sizes and colors.

I (OV) grew up in Europe and the early history dedicated much time and space for the fabrication and transfer of the sodium chloride crystal.

I was actually directly involved. Sodium chloride crystals when exposed to high-energy radiation form radicals in the crystalline matrix, the blue sodium chloride that are stable and cannot recombine because of the crystal lattice. My physics Professor (Professor Przibram) and examiner for my final examination was an expert. I found
out and studied carefully and extensively. Would you believe he asked me that very question, and I ended up with an “A” in my physics final Rigorosum?

How does this all fit into what we are discussing? Actually, quite well. Over the years I spent quite a bit of time on the early part of the polymerization of aliphatic higher aldehydes, and especially chloral and was puzzled how long polymerization can continue when the polymer was obviously “insoluble” and had precipitated out.

Crystallization and crystalline phases always oscillated in my brain. By chance, I was introduced to the group of crystallizers at the Polychemicals Department at DuPont: Phil Geil, Ed Clark, and all the supporting brains at the Polymer Physics group. I learned the crystallization of POM, of poly (pivalolactone) and the chain folding of polyethylene and polypropylene. The later were of enormous influence when I cooperated with Montedison on polypropylene.

As a consequence, I came to the conclusion that crystallization is three-dimensional and polymerization one-dimensional, in crystals, ionic or molecular in polymers primarily based on carbon, oxygen and nitrogen.

G. Inorganic Analytic and Minerals.

First I will relate a commentary of my future at the end of my doctoral degree. Yes, Rektor (President of the University) when I formally received the degree, was a crystallography Professor and the Dean of philosophy who actually handed me the degree. Since we are talking about the final degree, I had to take what was called a
Rigorosum in psychology. I specialized in “associations” and “dreams” and the examiner was the feared nut, beloved Professor Rohracher.

Now back to the University of Vienna in 45' and how chemistry was studied. The degree of the Realschule high school diploma allowed you directly to enter the university. Liberal arts and advanced mathematics courses were taken care of. (There were no sports or entertainment in the curriculum).

As we studied chemistry, this was the only objective. The decision of “finding your-self” was finished. There were no BS, MS or other degrees.

Lectures were required but not imposed as long as you passed the required examinations. I chose the Chemical Institute to study chemistry. The chemistry program required a sequence of laboratory courses: inorganic qualitative and quantitative analyses, organic chemistry, physics and physical chemistry. After a rigorous examination on all subjects at the same day, one was qualified for selecting the thesis advisor.

I entered the inorganic laboratory in the fall of '45, was assigned a place, and this was my home at the university. The laboratory was open six days a week from 8:00 a.m. until 6:00 p.m. You could do your experiments whenever you wanted to, go to lectures when you wanted (or not). There was no examination required but it was wise to take it. Fifty six (56) students were in a laboratory and they were supervised by three scientific instructors. We were given the samples for analysis, and were quizzed by the instructor and otherwise left alone.

Interesting was the quantitative analytical laboratory, because it consisted not only of liquids to be analyzed but also real mineral mixtures. I still remember how much we feared the potassium/sodium separation as chlorides
(in platinum containers) the calcium/magnesium separation as carbonates (magnesites), and others involving iron, cobalt, nickel and antimony. We had to handle real minerals. Today this is all done with instruments by spectrographic means.

When I became a lab instructor I oversaw the laboratory on quantitative analysis with my friends Goldberger and Kainz. Kainz later became the chair professor of inorganic analysis at the II Chemical Institute of Vienna.

H. Crystallization

a. Search for Initiators and Failures of controlled. Polymer formation:

For almost two years I had been battling science. Initially it looked so obvious. Just take chloral and replace acetaldehyde for chloral and polymerize it and you had a super polymer. I read the Dutch work from 50 years ago. It was likely that the polymerization was of anionic character because of the electron deficiency of the carbonyl group. I was suspicious, because the work talked about powders or smaller shaped materials.

As polychloral was insoluble in any solvent and was not melt-fabricable, we tried syringing injection of the initiator, dropping wise addition, fast or slowing injection – the polymer was immediately formed exactly in the shape of the stream that was injected. We tried potassium alkoxides nothing, just a coating of polymer on the crystals. Then I remembered that a polymerization technique was rediscovered and name was given to the technique, “living” polymerization. – the polymerization was initiated with butyl lithium or lithium metal. The initiating species the butyl anion added to one molecule of styrene and formed an electron and formed one addition product, the (head to head) styryl (di) anion. When the polymerization was conducted properly all styryl-
terminated anions added more styrene and consequently ended up with polystyrene of very narrow molecular weight distribution. We concluded that the success of the initiation was related to the fact that the nucleophilicity of the butyl anion was perhaps 2-3 orders of magnitude stronger than the subsequent styryl (or polystyryl) anion.

\[
\text{n-butyl Li}^+ + \text{HO-R} \rightarrow \text{Li}^+ \cdot \text{O-R} + \text{n-butane}
\]

\[\text{R + cholesteryl}\]

So for chloral polymerization, I decided to go in two steps. First react butyl lithium with an alcohol and then use lithium alkoxide as initiator for chloral polymerization. The idea was good and we overcame the basicity of perhaps 2-3 magnitudes. Again, that did not work. Polychloral was just too insoluble. But this technique allowed us ultimately to make the first “good” polychloral sample.

We realized ultimately to use a highly hydrophobic tail the alkoxide of cholesterol. Not until we found the final trick, did we make respectable polymer with lithium cholesteroxide, and it was isotactic and optically active. It took us another 15 years until we could measure the optical rotation.

Ultimately and under great pressure we found how to initiate and polymerize chloral (by initiating above the polymerization temperature) in one molar solution the ceiling temperature and cooling. We called it cryotachensic polymerization and were able to fabricate final pieces by monomer casting. We had discovered the homopolymerization of chloral and shortly after we succeeded in the polymerization of chloral with p-chlorophenylisocyanate and with other isocyanates and ketenes. Now we had to find a better initiating system and turned to special lithium butoxides that were commercially available.
homopolymer  co-polymer with p-chlorophenylisocyanate

50-year-old samples of polychloral

We should not forget that one of the prettiest crystal structures that nature provides us in cold weather is the snowflake. It is formed when nucleated material passes through a supersaturated gas containing water vapor. Numerous nucleation sites provide structures of which some people have said: No two-snow flakes are alike.
b. Lithium tertiary-butoxide and its Crystallization Behavior

We defined the principles of the catalyst systems for the chloral polymerization. The one was verification of lithium alkoxides. Most of the two-step initiating systems were not practical. We therefore focused on lithium tertiary butoxide (LitBu).

In the mid ‘60s’ a group at the University of Illinois in Champaign had just published a paper in which it described a soluble sublimable portion of the LitBu.

Today one was working in academia you would just pick up the phone and ask the main author the relevant questions, but when you are working for a company, when you are working on a potentially high volume product, with ramifications for product protection, the need for patent protection is enormous – you bypass what other people have seen and published. – you work all applications out yourself.

Consequently, I purchased some commercially available LitBu (this is also important in industrial work. As much as possible has to be commercially available and can be contractually purchased.)

Now came the purification of the crude product - by sublimation.

I remembered how we separated by distillation alkaloids, after extraction from seeds. My colleague Nesvadba and I used to use the Kugelrohr distillation technique to separate the alkaloids of cytisus laburnum, the golden rain, to separate laburnine from cytisine and methyl-cytisine.
It goes without saying that I had to make Kugelrohr. The “bulb tube” had to made by myself from Pyrex glass not the "green", cheaper glass that we used in my student days. To go to a glass blower at the Experimental Station, would have taken day's even weeks and ultimately required Union permission. It was much easier to make a couple of the Kugelrohr yourself.

Now the Kugelrohr could be filled with a long spout thin funnel and the powder placed directly into the last bulb. I was surprised how easily they were filled (1/3 full). Until later, much later I realized that the particles must have had hydrophobic surfaces and allowed them to glide smoothly. The bulb tube was connected to the vacuum system capable of producing a vacuum of at least 0.1 mm (torr). The open end of the Kugelrohr was connected to the vacuum system with a thick-walled rubber tube and the last bulb of the bulb tube of the evacuated system placed into an air bath of 150°C. LitBu begins to sublime and is collected in the second bulb.

The content of the second tube is readily soluble in methylcyclohexane, the solution could be kept on a tube, closed with a silicone septum unchanged for some time. I gave a part of the sample to a friend in the instrumental laboratory for mass spec analysis. The result of the analysis is shown in the figure. It consists substantially of the tetramer
with smaller amounts of the dimer and hexamer. It seemed to be clear that our tetramer was a stable for LitBu that had a tetrahedral structure with the tightly coordinated Li and O atoms, surrounded by a surface of methyl groups. Therefore, it was hydrocarbon soluble. At the same time not stable enough that a reactant, as we later see, chloral can easily interrupt this arrangement and utilize LitBu as monomer.
Tetramer of LitBu

Ultimately the LitBu in its monomeric form must be able to further polymerize to the actual crystal of LitBu)n, or LitBu)4 is an actual “stopping point.”

One other possibility but unlikely could be that the original LitBu)n, could break down at 150°C, to the monomer which sublimes as monomer LitBu and reforms as tetramers/ LitBu)4?

c. Chiral Crystallization (Sodium Chlorate)

In the last chapter, we discussed the crystallization and formation of crystalline salts that are strongly influenced by hydrophobic interactions. We found a strong tendency to break up the crystal formation to a stable tetramer. As we will write later, this can also be a “stopping point” of our polymerizations.

Now we will address another aspect of crystallization of ionic substances, chiral crystallization. (Which also has its counterpart in chiral polymerization). This probably, has frustrated scientists for 150 years, since Hofmann discovered the optical activity of sodium chlorate crystals. Years have gone by and many scientists have tried to solve the fundamentals of this problem.
In our recent paper (/268/), we described that we have solved the problem, icy was a problem of nucleation. The fundamentals are the nucleation of control sodium chlorate crystallization. Sodium chlorate has a small sodium ion and a larger chlorate ion. Important is that the chlorate ion is asymmetric, shall we call it one-sided. Sodium chlorate with the symmetric perchlorate ion does not behave that way.

Sodium bromate behaves asymmetrically in the crystalline form as does bencil and even sodium iodide 5 H2O. And many more some might not have been discovered for their pizzazz in their optical behavior in the crystalline state.

Without going into details, which are available in the recent literature, once the crystallization starts (at supersaturation) it forms a chiral, still soluble nucleus which is chiral guaranteed after 4 units, can break up any time under agitation and produce still in solution more chiral nuclei. From 5 or 6 units of addition, probably still in solution, it starts forming branched chiral structures, always maintaining the chiral super command! As the aggregates crystallize, the chiral addition continues to form the perfect chiral sodium chlorate crystal. The size relationship between the sodium ion and the asymmetric chlorate ion guarantees that there is no inclusion of any ion of a different configuration. Consequently, the sodium chlorate crystal is chirally pure. Here is a scheme, which I think will happen:
monomer

O +
O - Cal Na
O

tetramer

+ O
Na Cl - O
O
O + + O
O - Cl Na Na Cl - O
O
O +
O - Cl Na
O
The ultimate result is the sodium chlorate crystal.

I.
J. Polymerization

a. Introduction

We are producing worldwide nearly 300 million tons of synthetic polymers. No wonder that some of us call our use of the major material, the “Plastics Age”, and this compares with the Stone Age, the Bronze Age and the Iron Age when those materials were dominant.

About 80% are made by addition reaction polymerization of small molecules, monomers that have reactive group a carbon double bond. Most prominent are ethylene, propylene, styrene, vinyl chloride, methyl methacrylate (acrylics) and their copolymers and derivatives. The remaining 20% are polyamides, polyesters, polyurethanes and other “niche” polymers.

Another group of polymers that are only 2-3 % of the total amount of polymers, but play an important part in technology, where their combination of properties are needed. Those are the polyoxymethylene (POM) who are formed by polymerization of formaldehyde and other aldehydes. Only POM itself, or polyformaldehyde is commercially produced.

We are using polyaldehyde as example for comparison of polymers with crystal formation, because they, or some of them have been more extensively studied in the early stage of polymer formation, oligomerization. And we are in this article exploring the early part of crystallization, the nucleation as compared to initiation.
There are several reasons why more is known about the earlier states of polymerization of aldehydes. They are ionic polymerizations. Addition reaction polymers so usually initiated by free radicals and are initiated way below the ceiling temperature (T_c) of polymerization. POM has a Tc of about 125°C and PE nearly 500°C. PAA has a T_c of about -40°C and Pap T_c of about 420°C, while polychloral has a T_c of 17°C.

b. Polyoxymethylenes (POM)

Aldehydes polymerize with anionic polymerization initiator to polyacetals. They all behave dependent on the substituents on the carbonyl group. Aldehydes with one hydrogen on the carbon atom polymerize below their ceiling temperature. Acetone with two electron-donating methyl groups and sterically hindered, does not polymerize (ΔG of +5) but hexafluoroacetone with two electron-withdrawing fluoromethyl groups co-polymerizes.

Now back to the aldehydes. Depending on the size and electron behavior formaldehyde in the presence of water forms a linear oligomer. The carbomethyleate (glyoxalate) forms soluble oligomers. Trioxane, (m.p. 60°C) under anhydrous conditions with acid initiators gives usually trioxane, the cyclic trimer of formaldehyde (CH₂O)₃ under different conditions formed the cyclic tetramer heptaldehyde (CH₂O)₄.

Formaldehyde and its crystalline “polymers” were first discovered by Butlerov in 1859. Staudinger made the polymerization of formaldehyde much of his life work and based much of his macromolecular thinking on the polymerization of polyformaldehyde. These polymers were of relatively low molecular weight and did not seem suitable as a commercial product because of their mediocre properties, and much attention was paid to POM as
a commercial product. It was the thrust of DuPont to re-evaluate the chemistry of formaldehyde in the early 40s that brought the possibility of commercializing POM to life. This task was undertaken under the stewards of Frank McGrew in 1952 and in 1960 POM was a commercial product homopolymer. Shortly later Celanese came out with a co-polymer based on trioxane and ethylene oxide.

Please notice the “hiccup” growth in the crystallization in the growth of the crystal of LitBu at the stage of the tetramer. Coming back to trioxane and methoxane. They also have a Tc (ring strain?) I do not remember the number but in trioxane it is much higher than the Tc of POM of 125°C, maybe as high as 200°C.

The sequence from formaldehyde with all he possible important steps in between is indicated below.

\[
\begin{align*}
\text{CH}_2=\text{O} & \quad \text{trioxane} & \text{metoxane} & \quad \text{HO-}(\text{CH}_2-\text{O})_n-\text{H} \\
1,3,5-\text{trioxane} & \quad 1,3,5,7-\text{metoxane} & \\
\end{align*}
\]

Acetaldehyde has a similar sequence

\[
\begin{align*}
\text{CH}_3\text{CH}=\text{O} & \quad \text{paraldehyde} & \text{metaldehyde} & \quad \text{HO-}(\text{C}[\text{CH}_3]-\text{H}-\text{O})_n-\text{H} \\
\end{align*}
\]
Only here the structure of the trimer is much better known because the polymerization of acetaldehyde is low. What is interesting is that the cyclic trimer paraldehyde has a specific configuration. The methyl groups are placed in all cis and equatorial positions. That means in polymeric terms isotactic. If the polymerization had continued in the same stereosequence instead of cycles, it would have formed isotactic polyacetaldehyde.

The polymerization is best known for the initiation step of any polymerization: When [LitBu]4 is added to an excess of chloral above 59°C it breaks up and adds a monomeric LitBu molecule that reacts immediately with one molecule of chloral as shown in the figure here it rests. There is undoubtedly some addition and removal of one monomer molecule.

\[
\text{LitBu} + \text{Cl}_3\text{CCH}=\text{O} \quad (\text{CH}_3)_3\text{C}-\text{O}-\text{C}(_3\text{Cl})\text{H}-\text{O}^\text{-} \quad (\text{CH}_3)_3\text{C}-\text{O}-[\text{C}(_3\text{Cl})\text{H}-\text{O}]_n\text{-H}
\]

Just like in the living polymerization of polystyrene – only in this polymerization, the step one and two was only corrected by strictly holding to rigorous temperature condition, because the polymer, polystyrene is soluble and polychloral is not.

In conclusion, we were trying to find and describe the similarities of crystallization and polymerization. We had to find extreme casein, which we could point out to the importance of group size, electronic behavior and sudden differences to show these differences of crystallization and polymerization behavior. After all, we are coming from one big branch of our tree in nature with two twigs branching from the main branch but the junction point is near to each other and came from the same spot of growth.
monomer                   dimer                                   tetramer                   linear tetramer              hexamer
Lithium tert. butoxide

HO-[-CH$_2$-O]$_n$-H
polyformaldehyde
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