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Solid State Chemical Reactions and Polymerizations: The Initial Synthesis of DNA?

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Solid State Chemical Reactions and Polymerizations: 
The initial Synthesis of DNA?

A Proposal for Covering individual Macromolecules with Macromolecules 
including a Realistic Chiral Synthesis of Nucleic Acids.

Otto Vogl (in cooperation with Frank T. Traceski)

Many polymer materials compositions consist of blends of polymers and 
copolymers\(^1\) to obtain optimal properties. Some of them are non-miscible, some 
have limited miscibility, some are miscible at the molecular level, and some are 
grafted co-polymers, such as high impact polystyrene and ABS. Noryl\(^2,3\), the 
blend of polystyrene and 2,6 dimethylphenylene oxide and the blends of 
poly(vinyl chloride) [PVC] with poly(methyl methacrylate)\(^4\) [PMMA] are typical 
examples of some of the commercially used blends. Important in polymer 
compositions are limited miscibilities in polymers like the carboxylate groups in 
carboxyl substituted olefin polymers, commercially known as ionomers\(^5\). The 
miscibility depends substantially on the efficient interaction of the functional 
groups of the polymers. At the molecular level the interaction of polymer 
molecule A with polymer molecule B, the most efficient miscibility in blends 
seems to be achieved by direct hydrogen bonding or acid/base interaction\(^6\). We 
have established some very fundamental work on individually polymerizing 
chloral with other monomers that are blends of limited miscibilities\(^7,8\). But 
fundamentally, the blends are random mixtures and the interaction is random.

We are now at mixtures at the molecular level and talking in the fashionable 
language of “nanochemistry”, more specifically nano-macromolecular chemistry. 
Ultimately, it would be desirable to control a contact chemistry – and –structural 
control on a level of individual molecules.
One aspect is to cover and protect individual macromolecules. Nature undoubtedly does this without our knowing correctly. But, we have some indication that we might be able to help and to assist such structural compositions. The question is, can we selectively cover a macromolecule individually with a sheath on another macromolecule? We can do it for a copper wire by using a PVC cover, and there are other examples of these sorts.

We had an example in our chloral polymerization that might inspire similar possibilities. Let’s explore what we know and – can we expand this “primitive” knowledge to a real proposal? Can we say, that – in our specific case of polychloral with 1/8-monomer units “stuck” irremovable from the polymer make it a “sheath” of alternating chloral-isocyanate co-polymers? Can we propose that this principle of a “stuck” monomeric unit, in this case purine and pyrimidine units with ribose sticking out, can these units be ready for connection with phosphoric acid precursors to form nucleic acids? I think it is possible under the right circumstances.

This is now not a question but it is quite essential in our molecular life and conception, now inappropriately called nanochemistry. We know that all our electronic ambitions are based on our assumption that we will finally have to approach the macromolecular level. We believe that the conducting, now on a macromolecular level, must be protected by the individual macromolecules from each other by protective sheaths. We have here a proposal that can do it. Use individually inserted polymerizable monomer units in an already formed conductive polymer and polymerize these “stuck” monomer units” in place.” Unrealistic, yes, but doable also yes.

A. Chloral polymers enveloped in a sheet of chloral/isocyanate copolymer:
In the obsession of our interest with chirality, we have been intrigued with the polymers of chloral\textsuperscript{9,10} the structure of polychloral\textsuperscript{11,12} and especially the co-polymers of polychloral\textsuperscript{13a,13b,14} (Figure 1a). Polymers of chloral are uncommon examples in polymer chemistry. However polychloral with its configurationally and stereochemically specific correct structure\textsuperscript{15} (Figure 1b) is, to some extent, an ideal model of the ultimate of helicity in polymeric structures, demonstrating macromolecular asymmetry, chiral helicity of macromolecular asymmetry.

Even perfect helical polymers with this kind of macromolecular asymmetry have some “physical” faults, grooves\textsuperscript{16}. We do not accept them in the perfect states, but in imperfect states of helicity they play important roles. Take examples of DNA structures. Barton has made a lifelong and highly publicized success story of heavy metal complexes in the grooves of DNA\textsuperscript{17}.

Even in “rigid” helical polymers grooves do and must exist, or can be accommodated. I have to come back to my life long attachment to polychloral.
We, at Du Pont almost succeeded in commercializing polychloral. There were some practical and economic problems that prevented its commercialization.

Chloral polymerized only to about 88%. The remaining chloral monomer could not be practically removed from the polymer (Figure 3). We extracted the polymer with acetone, and found that the monomer was completely removed. When the polymer (PC) was again exposed to chloral (monomer), the monomer was easily removed in vacuum. Why this behavior?

Ultimately, we have concluded that the “residual monomer” – 1/8 of the polymerization components, 2 monomer units per “repeat units” of 11/4 were bound to the polymer in some firm way, in a way that these monomer units could not be removed by traditional (vacuum removal) methods.

Two later studies clarified these strange results. First, solid state NMR analysis showed that this monomer was retained in the polymer, the trichloromethyl group of the monomer chloral was firmly bound in the polymer matrix, the polymerizable HC=O group remaining outside and capable of further reactions (Figure 3). Clear additional NMR evidence\textsuperscript{18} showed that even toluene (with its aromatic ring) (Figure 2) could be attached to the rigid polychloral matrix and be distinctly associated, the aromatic ring being held tightly and the CH\textsubscript{3} group retaining free flexibility.

Figure: Solid state NMR spectrum of toluene in PC

Figure: Solid state NMR spectrum of toluene in PC
Our earliest experiments, in attempts in stabilizing polychloral, even in our first experiments in 1963, we used phenyl-isocyanate derivatives\textsuperscript{13} (Figure 4)\textsuperscript{20} in attempts to “end-cap” and stabilize polychloral\textsuperscript{21,22}.
It was successful, by “sloshing” PC freshly prepared with the isocyanate\textsuperscript{10}. Though we were stabilizing the polymer by end-capping it, we did more. We also “neutralized” and “eliminated” the monomer that was “stuck” into the polymer.

Years later we had found and demonstrated, that polychloral had the structure of an approximately 4/1 helical structure\textsuperscript{23} as a 4/1-structure and\textsuperscript{24} as a 3.5/1 helix. It was later refined by calculations to an 11/4 structure\textsuperscript{25}. We had also found, by NMR spectroscopy, that the oligomers were soluble to about the 10-mers\textsuperscript{26} that means nearly 3 turns of the helix. We also recognized that polymerization could continue in the gel phase\textsuperscript{27}. A good chloral polymer was estimated, by end group analysis, to be a 500-mer, or 180 turns of the helix.

Now we know that polymerization or co-polymerization can continue, once the polymer is formed, as long as there is monomer with a conveniently located and flexible polymerizable groups are available for “co-polymerization”.

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**Figure 9** PC 3 Repeat Units 11/4 with Purine (adenine) and Pyrimidine inserted

**Figure 10** PC 3 Repeat Units 11/4 with Bases connected with Phosphoric Acid Units Nucleic Acid Synthesis, 1 Repeat Unit of DNA
Now we had the chloral polymer and we had demonstrated the copolymerization with isocyanates (and ketenes). I had assigned Kubisa to analyze the copolymerization of chloral and aromatic isocyanates (Figure 5) especially in the last stage of the polymerization. There was no question that chloral polymerized first and the isocyanates were consumed at the end. We were sure it ended up as shown in Figure 5a. That meant that chloral polymerized first to a helical polymer and when the chloral monomer was close to exhaustion the isocyanate became involved, ending up with a “tail” of alternating polymer of chloral and isocyanate (Figure 5a).

Figure 5a Formation of Chloral-Isocyanate Co-polymer Sheath.

It was published over 30 years ago. But was it right? Did we take all our knowledge into consideration? No I think it was not right. Yes, we carried out the “co-polymerization” in the normal manner and we did all the analyses that we thought were needed, with rat studies etc. But---
What if we had carried out the “co-polymerization” as we knew at that time and we actually carried out strictly a homopolymerization of chloral – and left the “usual” 12% of chloral stuck in the chloral polymer helix, in the groove, one monomer unit stuck tightly every two turns, two in the 11/4 repeat?

If this were the case, we would have the polychloral matrix with two monomer units per 11/4 repeat left with free flexible HC=O groups in a chiral PC helical structure? Then the isocyanates would have time and proper space to “link” the free HC=O groups to a sheet of PC-isocyanate copolymer, at the same time end-capping and stabilizing the PC polymer. Is it so unrealistic? For me it is very plausible (Figure 5b). Now let’s forget Kubisa’s calculations and estimations and instead use an alternating copolymer tail of 1/8 of the polymer length, assume that the chloral polymer is a homopolymer that has a sheath of alternating copolymer surrounding it. This would be an ideal example of what is so fashionably called today “nano-engineering.”

**B. Proposed (possible?) DNA Synthesis.**

Now to DNA and heterocyclic compounds:

I always had interest in heterocyclic compounds, after all I was hired as a post-doc at Princeton by Prof. Edward C. Taylor to work heterocyclic compounds, especially antifolic acid derivatives. With Ted Taylor’s advice, when he was abroad for the summer, three key purines were synthesized: adenine, 6-mercaptopurine and hypoxanthine (6-hydroxypurine). This was the simplest synthesis for these bases of nucleic acids at that time: Take the isonitrosomalononitril salt of malonamideamidine, malonamide or thiomalonamide and melt these salts to cause the rearrangement to the key pyrimidine intermediates.
Figure 12: a. adenine; b. adenosine; c. cytosine; d. uracil

Much later, I was involved in trying to incorporate purines by a similar reaction into polymers. But they were very insoluble and only resulted in oligomers. What I am now proposing is to use our experience and knowledge for the possible synthesis of DNA.

We are using the unlike “template” of the chiral PC. We know it is capable of “absorbing” in its grooves “attachable” molecules, including toluene, an aromatic ring-structure attracted by the “negatively charged” trichloromethyl groups of polychloral in the “groove” configuration (Figure 7a). These groups, formed from
cyanide cellesterial chemistry could be attached, like toluene or chloral with the reactive group accessible and mobile. In this case it would be the pentose with the reactive OH group available for the polymerization with phosphoric acid to form the backbone of the polyphosphoric acid of the DNA with the “bases” still attached to the chiral template polymer (Figure 7b). What after that? Who knows!

One repeat unit of DNA in helical configuration (35 Å) and conformation on a rigid chiral template polymer, 3 repeat units of 11/4! Is it completely unreasonable and how much does the model have to be modified to make it real? Obviously the template chiral polymer cannot be PC but what else fits that well?

C. Covering of Individual Conducting Polymer Molecules with a Sheet of Protective Polymer:

History;
Polychloral as I had developed it by cryotachensic polymerization techniques, directly to the product, as an attractive polymer for commercialization, had the usual deficiency of polyoxymethylene, thermal instability. That was known for polyoxymethylene, Delrin as the commercial name. – It had to be end capped for maximum and ultimate stability. Polychloral was no exception. But there was one additional problem. We had no time allowed to work out the details. We had to go directly to a commercial product or the project would be, correctly, terminated. The question was, how to “end-cap” quickly and efficiently the polymer obtained from chloral by cryotachensic polymerizing in product form. In desperation I decided that the only simple “end-capping” was by sloshing the polymer in a solution of phenylisocyanate to terminate the end group the polychloral anion. So it was done even in our first experiments in the spring of 1963. The polymers were stable, free of free chloral and workable. Samples have been produced by machining, but all are of distinct dark color.
No further work in this direction was possible because we were driving for commercialization of a non-burning colorless product. There was no question that in the process of “end-capping” some copolymerization of chloral and the aromatic isocyanate, ultimately focused on p-chlorophenylisocyanate, because it caused less color after the “capping” as the better capping agent and comonomer.

The attempted commercialization of polychloral was correctly terminated by Du Pont. It was an interesting product, but had too many flaws. But as I entered the academic arena I was free to continue the fine points that had been highly interesting but contributed to the failure of the commercialization. End-capping was one point. We, now at UMass, solved all the problems. One problem had stood up and was one of the key points that caused the failure of the commercialization of polychloral at DuPont. It was because about 12% of the chloral monomer or one chloral monomer unit per two turns of the helix, was left firmly bound onto or into the polymer. I assigned Hatada, my first post-doc from Japan to investigate these phenomena by NMR spectroscopy. He found that, indeed, the monomers were “stuck” to the polymer with the trichloromethyl group tightly held by the polymer. We assumed that they were held in grooves of the polymer structure. He found that was also the case with organic solvents (in about the same amounts) like toluene. In both cases, NMR showed that in the case of toluene the aromatic ring was held and the methyl group had remained mobile, as shown from the spectrum. In the case of chloral, the HC=O group remained mobile. This is now my argument for the notice that I have put in writing. The theorem that selected molecules can be held firmly and in “grooves” in other words, in selected places in the polymer that, if the mobile position of these molecules are “reactive” or “polymerizable” these accessibilities can be a most efficient “template” for selective polymerizations and can be either the
template for chiral polymerization as we suggest for DNA, or be a regular sheet as a copolymer sheet for individual choral, strictly helical, polymer chains as copolymers of chloral/isocyanate copolymers. They can also be templates for the "bases" of nucleic acids, which are then "hooked-up" with polyphosphates for the formation of chiral polymeric nucleic acids, the source of our life. This principle of forming a sheet of an individual molecule around a template with the key polymerizable molecules "stuck" in regular places, in grooves, could also be the key of making individual conducting polymer molecules with protective cover. We do it every day with copper wire and the plastic sheet. As we go to the ultimate computing using individual molecules, we might need the individual protection of the "active polymer molecule" to reach the ultimate degree of (macro) molecular electronics on the molecular scale. We should remember that copper wire also needs to be covered by PVC or PE.

References

1 Polymer Blends Handbook, Leczek A Utracki ed. Springer Verlag


4 [M.F. Qin, Poly(vinyl halides), Head to Head (Polyvinyl chlorides) and their Blends, PhD thesis, Brooklyn Polytechnic University (1992)]


6 [E.J. Moskala, S.E. Howe, Paul C. Painter and Michael M. Coleman, On the Role of Intermolecular Hydrogen Bonding in Miscible Polymer Blends, Macromolecules, 17(9), 1671 (1984)]


10 [P. Kubisa and O. Vogl, Chloral Polymers by Cryotachensic Polymerization, Macromol. Synth., 5, 49 (1977)].


16 [T.A. Steitz, Protein-Nucleic Acid Interaction: the Sequence-Specific Binding, Quarterly Review of Biphysics, 23, 205 (1990)]

17 [J.K.Barton and S. J. Lippard, Heavy Metal Interactions with Nucleic Acids, Metal Ions In Biology, ed. T. G. Spiro, 1, 31 (1980)].


19 [O. Vogl, Chloral Copolymers, U.S. Patent 3,668,184 (1972)],


21 [L.S. Corley and O. Vogl, Haloaldehyde Polymers. XVII. Stabilization of


27 [O. Vogl and L.S. Corley, Polymerization in the Gel Phase, Polymer Preprints, ACS Division of Polymer Chemistry, 19(2), 210 (1978)].


Footnote
'H NMR solution spectroscopy: In the late 50’s and early 60’s, when I worked at the DuPont as an organic, a polymer organic chemist, I became interested and involved with the then relatively new technique of instrumentation: NMR spectroscopy. The first instrument was a 49 MHz instrument with a permanent magnet.

In the early 60’s, DuPont authorized and subsidized Varian Instruments, to develop an entirely new idea of NMR spectroscopy, using a superconducting magnet. This experimental instrument was designed to be a 200 MHz instrument with a superconducting magnet. DuPont received this instrument in about ‘61 or ‘62. It was experimental, had no temperature probe (all room temperature). This entirely new instrument was for exclusive use for DuPont’s research for two years. Thousands of spectra, primarily of biological interest were obtained during this period. Because of all its complications and implications it was also not available for “normal” polymer research within DuPont.

I had already moved at Du Pont, from the Polychemicals Department to CRD the Central Research Department, when I got to know Ray Ferguson. He was in charge of the new instrument and very secretive and Ed Brame a Polychemcals friend and upcoming in NMR. One day I convinced Ray to run the NMR spectrum of my beloved polyacetaldehyde (rubbery) on his new machine.
This was not as simple as it is today. The experimental NMR 200 MHz instrument required a liquid nitrogen and liquid helium (for the superconductivity) filling every 4 hours, day and night, week and weekend.

**Solid State NMR Spectroscopy:** Because of my friend and close cooperator Koichi Hatada, who in 1982 was already an expert in NMR spectroscopy, I became interested in this application of NMR spectroscopy. We had become interested in the polymer structures in the solid state, with some mobility, and how to understand and harness the mobility of single molecules in a rigid polymer.

The ultimate interest was to carry out reactions in polymeric matrices where individual monomer molecules, molecules that might be capable of polymerizing to carry out reactions in this peculiar monomer/polymer matrix state. This is the purpose of the exercise in this article.

Over the next decades I was very much involved in solution NMR spectroscopy, especially with Koichi Hatada. He had become the NMR spectroscopy expert and leader and coordinator of the Japanese NMR polymer program and was substantially influencing the high-resolution NMR spectroscopy with high-
resolution instruments in Japan. In our later work we very much benefited from his advice and contributions. Koichi Hatada was my first postdoctoral research associate in PSE at the University of Massachusetts.

**Mobility in crystals:**

Polymerization, the assembly of “polymerizable” molecules to macromolecules, was first recognized as linear “strings” of very high molecular weight about two hundred years ago. Now we also know about branched macromolecules even of nearly globular structures, dendrimers or highly branched macromolecules. How are they made and with what efficiency? How much are they an important factor for industrial application and how much do they contributed to life in the world of the Plastic Age that we live in today.

We are producing polymers in many ways by inducing polymerization of monomers. It is done in solution, in the malt (PE, PET, Nylon) and in the gas phase, (PE, PP).

There is one category that I feel is not fully recognized but that exists. I commented on this subject about 39 years ago. – polymerization in the gel phase.

Why make an issue of it and why make the issue now? Reason. I feel that it has not been mentioned properly and it was largely ignored.

The reason for my continued commitment is my devotion to chloral polymerization. Just a trivial reminder, chloral polymerizes to polychloral, an amazing helical polymer structure with an 11/3 helix. Chloral oligomers, even short oligomers are helical but soluble. From about the oligomer with 10
monomer units, in structural terms it means about three turns of the helix, the polymer becomes insoluble for normal solvents. But—does it mean that it remains in the presence of chloral monomer not in a state where it can continue to polymerize? We know that “normal” chloral polymers have a degree of polymerization (DP) of 500, 100 times the molecular weight that would be expected if the (2 turns of the oligomer) would be completely insoluble and incapable of further reaction.

We must have many cases in nature and our life when reaction condensations occur “in the gel state” but with available reactive groups on the surface and anxious for the reaction to occur.

**Solid State Polymerization:** In the early 60’s an observation was made, that became the fashion in polymer chemistry at that time—“solid state polymerization.” It was described that methacrylamide in its solid crystalline state could be, with complete efficiency transferred to poly(methacrylamide) with the proper initiation.

We have opposed this simplistic and unproven principle from the beginning, but solid-state polymerization as a significant part of polymer science remained for many years as part of polymerization.

**Rigid placement of monomers in monomer crystals:** I never believed in this new proposal of polymerization, that monomer molecules, placed in a completely immobile position in a monomer crystal could be added to a polymer growing end in a rigid polymer crystal.
I had some reason to believe so. In our work on polyoxamides, one of the objectives was to prepare and check the polymerizability of c-62 and c-6262. The reason for this approach was that the desirable Nylon 62 could not be effectively melt processed because it melts at 325°C and beginning at this temperature severe degradation occurs. As a consequence, the fabrication of Nylon 62 by monomer casting of the cyclic monomers was a definite possibility – but it required the synthesis of the corresponding monomers c-62 and c-6262. The polymerization of choice was anionic polymerization with alkoxides as initiators.

We tried the polymerization not only in the melt, but also below the melting point of the monomer. The polymer, Nylon 62 was also observed when the sample was held below the melting point of the monomer. This must have been while the crystal; the individual (monomer) molecules were in torsion of oscillation.

We set up experiments and determined the amount of polymer produced in a one-hour period. As the polymerization temperature was lowered, the yield of polymer decreased until it reached 0 (zero) about 50°C below the melting temperature of the polymer. Extrapolating to zero we determined what we called the temperature of mobility of the monomer crystal.

Now the door had opened, with one problem. I was assigned to another more immediate problem. Consequently, I was restricted for this (for me) exciting problem to an hour here, an hour there after work and on weekends. We were at DuPont allowed to do that.

Since such work, solid-state polymerization and the strong opposition to a fashionable “novelty” of polymerization, should have had some common interest with a commercial product of DuPont, I chose to look at trioxane as a potentially interesting case.
Trioxane is a compound, melting at about 59°C and the source, by cationic polymerization (commercially done in the melt) of POM, of DuPont’s Delrin, called Celcon. Uncovering any weakness in the polymer as a product, incomplete patent coverage, or other “faults” were of interest and work in these areas was supported.

I undertook my private investigation of opposing the “solid state” polymerization by contacting my friend Bill Statten. He was a manager in the Textile Fibers Department, a busy man and really only interested in his own work. He studied by solid state NMR the mobility of certain sections of polyesters as a function of temperature. Some of this work was related with the then quite fashionable problem of “free volume” in polymers and section that were “kind of amorphous.” Key problems at that time were in aromatic polyesters and Nylon, their properties and strategy of preparation and fabrication.

Solid-state NMR spectra of rigid materials produced a broad peak about 10 Gauss wide. But when mobility shows up a narrow peak appears on top of the middle of the broad peak. This peak can be related to the broad peak, percentages can be taken. This way a percent of mobility can be established. Apparatus modification available at this time allowed us to quantitatively measure the percent mobility as a function of temperature.

I went to see Statton and asked him to measure not a polymer, but “my” monomer trioxane in this way, to determine the percent of “mobility” (the narrow peak) as a function of temperature.

Bill thought first my question was ridiculous but I convinced him (and prepared the proper sample) and he carried out the experiment. He measured the broad
line peak from -80°C to near the melting point of trioxane, 59°C. Lo and behold what I expected happened. From -80°C to 12°C there was only the trioxane broadline NMR peak. From thereon with increasing temperature the narrow peak indicating the mobility in the crystal lattice started to appear. With increasing temperature the percentage of the narrow increased in a linear fashion to the melting point of trioxane. We had established by broadline NMR, the temperature of mobility in the trioxane crystal lattice as 12°C. The narrow peak, representing the mobility increased to 58°C, one degree lower than the melting point.

We had established before the point of mobility relative to the melting point for the c-62 polymerization by chemical means.

The solid-state polymerization of trioxane was now carried out as a function of temperature. Trioxane polymerizes to POM with cationic initiators. We used for convenience boron trifluoride gas.

![Graph](image)

a. Trioxane: Solid-state polymerization and 230°C mobility of molecules in the crystal latex as a function of temperature.

b. Solid state polymerization of C-62 (m.p. as a function of time and temperature.

As in the case of the c-62, a temperature of mobility was established about 50°C below the melting point of trioxane, namely 10°C.
Fine needles were placed in a small tube and capped with a silicone septum. The proper amount was injected with a syringe shaken and allowed to react for one hour. The polymerization was terminated, the monomer extracted, and the residual polymer (if it had formed) we identified. From -80°C to +10°C no polymer was formed followed by increasing amounts to the melting point. As an interesting curiosity and possibly an error, the polymer formed just below the melting point of the trioxane was less than the polymer formed in the molten trioxane, 2 degrees higher.

Has anyone checked the mobility of individual water (H₂O) molecules in perfect and not so perfect ice crystals? By broad line NMR?

PMR LINE BROADENING OF SMALL MOLECULES IN THE RIGID POLYCHLORAL MATRIX. IV. HALOALDEHYDE POLYMERS*

Introduction

Chloral has been reported to polymerize to the polyacetal, polychloral. When polymerization was carried out with anionic initiators and by cryotactochromic polymerization (1,2), a homogeneous gel of polychloral was obtained even at a 2% conversion of monomer to polymer (1-3). Further polymerization proceeded by increasing the rigidity of the gel as the conversion of monomer to polymer increased. The rate of chloral polymerization could be followed by the decrease of the monomer which could conveniently be done by observing the PMR signal of the aldehydic proton of chloral (4). Since the polymer is insoluble in monomer or solvents, no high resolution PMR signal of the polymer or even of oligomers could be observed.

In earlier work on the polymerization of chloral, it was observed that some line broadening of the aldehydic proton of the monomer was noticeable at high polymer conversion. This indicated that under these conditions a lower mobility of the monomer in the polymer matrix and limited averaging caused the line broadening (3).

Chloral polymerization can be carried out in the presence or absence of a solvent. In all cases polychloral separated out as a gel which was insoluble in chloral and all solvents. Even at high concentrations of chloral, or in the case of chloral polymerization in the bulk, it was found convenient to add the initiator as a 1 M solution (1,2). It was consequently found that the solvent molecules showed some unusual behavior in the polymer matrix when observed by PMR spectroscopy.

Studies of the mobility of small molecules within a polymer matrix have been carried out before, as in the study of the effect of plasticization on polymer properties and diffusion phenomena in biopolymers. A number of microdynamic characteristics of solvent molecules in polymeric media have been studied, primarily by spin-lattice relaxation and spin-echo measurements (5-17).

In the absence of specific polymer-solvent interactions, the addition of a polymer has little effect on the motions of solvent molecules even at rather high polymer concentrations. It was reported that no detectable change was observed in the rotational correlation time of benzene from pure benzene to a 35% solution of poly(methyl methacrylate) in benzene (10). The self-diffusion constant of benzene was found to change only from $5.4 \times 10^{-5}$ cm$^2$/sec for pure benzene to $0.69 \times 10^{-5}$ cm$^2$/sec for a 70% solution of polyisobutylene in benzene (14).

In cases where specific interactions occurred between the solvent and the polymer molecule, the mobility of the solvent molecules was strongly affected as judged by PMR measurements. Liu (9) reported that the spin-lattice relaxation time, $T_1$, of methylene chloride in a methylene chloride-carbon tetrachloride mixture (20:80) changed from 29 to 13 sec upon the addition of 10% of poly(methyl methacrylate), while the addition of the same amount of polyisobutylene had no effect on $T_1$ of methylene chloride. In a similar experiment it was found that polyisobutylene influenced the relaxation of cyclohexane but poly(methyl methacrylate) had no influence.

Sato and Nishio (16) investigated the relationship between phase separation and preferential and inverse absorption phenomena by studying the proton spin-lattice relaxation.

Experimental

Materials

Chloral was obtained from the Diamond Shamrock Company and was purified by distillation (18). Triphenylphosphine (Ph$_3$P) was obtained from the Aldrich Chemical Company and was purified by recrystallization from benzene. It was usually used as a 1 M solution in the solvent selected for the mobility studies in the polychloral matrix.

Benzene, toluene, o-xylene, p-xylene, tetrahydronaphthalene (terralin), cyclohexane, methylcyclohexane, and n-hexane were purified by distillation under nitrogen.

Polymerization of Chloral

A 50-ml test tube was fitted with a serum cap and a nitrogen inlet and outlet. It was dried by flaming out under a nitrogen stream and cooled under nitrogen. The test tube was placed in an oil bath at 70°C and freshly distilled chloral was transferred with a predried hypodermic syringe from the receiver of the distillation apparatus into the test tube. After 5 min, when the temperature of the chloral in the test tube had reached 70°C, the initiator solution, usually 0.2 mole-% of initiator, and, if desired, additional solvent was injected with a small syringe. The mixture in the test tube was shaken vigorously.

A suitable portion of the initiated chloral was quickly transferred with a preheated hypodermic syringe (65°C) into the PMR sample tube which was immersed in an oil bath at 70°C. The tube was sealed and was placed into an ice water bath at 0°C. A number of NMR tubes were charged the same way, and each sample tube was taken out from the bath after the appropriate time to achieve the desired conversion of chloral to polychloral. The individual PMR tubes were subjected to the PMR measurement.

In a separate experiment it was determined that the chloral polymerization proceeded at an initial rate of 10 to 30% per min, depending on the initiator concentration when the polymerization was carried out in a 0°C cooling bath. No substantial polymerization occurred when the bath temperature was above
Fig. 1. PMR line broadening of benzene and chloral signals.

35°C. However, no significant and measurable depolymerization of the poly-
chloral sample occurred during the period of the sample tube warm-up to
35°C (which was the temperature of the NMR probe used for the PMR meas-
urement), or when the polymerized sample was held at 35°C for hours.

Measurements

The PMR spectra were measured at 35°C on a Hitachi Perkin-Elmer R-24
NMR spectrometer at 60 MHz. While the measurements were carried out, reg-
ular checks of the line width of the PMR signal were done on a 5% solution
of chloroform in carbon tetrachloride to insure the uniformity of the magnetic
field in the spectrometer.

The conversion of chloral to polychloral was calculated from the rela-
tionship of the intensity measurements of chloral and solvent.

Results and Discussion

The polymerization of chloral in the presence of relatively small amounts
of solvents was followed by PMR spectroscopy with triphenylphosphine (Ph₃P)
as the initiator. The line widths of the signals of chloral and various solvents
were measured as a function of increasing conversion of chloral to polychloral.
The solvents used were benzene, toluene, o- and p-xylene, tetrahydropho-
lene, cyclohexane, methylcyclohexane, and n-hexane.

The line widths of the solvents increased remarkably with the increase in
the conversion of polymer, but the chloral signal showed only a slight signal
broadening during the polymerization. In the case of aromatic solvents, the
line broadening is much more significant in the aromatic proton region as com-
pared to the signal of aliphatic substituents. Line broadening may be a spin-
spin relaxation process in our system, arising from time correlation functions
of magnetic dipole interactions among all hydrogen atoms. The line shapes of
the signals were close to Lorentzian, and the spin-spin relaxation time, T₂,
could be obtained from the spectral line width (T₂ = 1/π ΔH 1/2). However,
T₂ thus obtained usually includes some contribution from the inhomogeneity
Fig. 2. Ratio between line widths ($\Delta H/\Delta H_0$) of benzene and chloral.

of the magnetic field, $H_0$, which cannot be eliminated and possibly from some inhomogeneity of the polychloral gel. Since the line broadening of chloral and various solvents in the polychloral matrix increased with decreasing molecular mobility, we can relate some information from the line width to the mobility of chloral and solvents. The ratio of the line width in the spectrum of the partially polymerized matrix to that in the unpolymerized solution ($\Delta H/\Delta H_0$) will be a measure of increasing correlation times, most likely rotational correlation times.

Figure 1 shows the line broadening of the signals of chloral and benzene during the polymerization of chloral at 0°C with Ph₃P. The signal of chloral is only slightly broadened up to a conversion of chloral to polychloral of 80%. The line width of the benzene signal, however, increased with increasing amounts of polymer in the mixture, especially above 30% conversion. When the ratios between the line widths ($\Delta H/\Delta H_0$) of chloral and benzene signals were plotted against the conversion, similar curves to those in Figure 1 were obtained (Fig. 2).

Polychloral is deposited from the initiated monomer solution as a rigid and insoluble but homogeneous-appearing gel. It is believed that both chloral and benzene are entrapped in the polychloral matrix. The results in Figures 1 and 2 indicate that benzene is entrapped more strongly in the polychloral matrix while chloral is more mobile in that matrix. Because of the electron-withdrawing capability of the trichloromethyl groups of polychloral, and a possible charge transfer-type interaction between the aromatic ring and the trichloromethyl groups, preventing full mobility at high conversions, benzene appears to interact with polychloral more strongly than chloral.

Figure 3 shows the PMR line broadening of the signals of toluene and chloral as a function of increasing polymerization conversions. The polymerization of chloral was carried out at 0°C with Ph₃P at three initiator concentrations. Strictly speaking, the PMR spectra of toluene as well as aromatic solvents used in this study, with the exception of benzene, are spin multiplets and the linewidth measurements would require some correction to allow for this fact. In
this preliminary study we did not make the corrections because it is believed to be small as compared to the degree of line broadening. The line broadening of the aldehydic proton of chloral, as well as that of the phenyl and methyl protons of toluene, are not affected by the initiator concentrations which ranged from 0.1 to 0.3 mole-%. This means that the initiator, as well as the active species derived therefrom, had no effect on the line broadening process. The amount of solvents (toluene), which was varied from 9.15%, also did not effect the results of line broadening of phenyl and methyl protons.

The PMR signal of chloral also showed only a slight broadening during the polymerization. The half-width of the toluene signals in the polymerization mixture increased remarkably with increasing amounts of polymer in the mixture. The degree of line broadening more significantly affected the phenyl proton signal, but did not affect the methyl proton signal. This may indicate that the rotation of the methyl group of the toluene molecule which connects the C-atom of the aromatic ring with the methyl group is less restricted in the polymer matrix than the molecular rotation of toluene.

Experiments in this work have been carried out in a rather narrow range of solvent (ca. 12%) in the chloral polymerization. Additional work will extend this range to higher solvent concentrations in an effort to see if solvent spheres of different mobility can be detected in these polymer/solvent systems. It is conceivable that two kinds of solvents will be observed in higher solvent concentra-
Fig. 4. PMR line broadening of phenyl proton signals in aromatic compounds.

Fig. 5. PMR line broadening of methyl proton signals in aromatic compounds.
Fig. 6. PMR line broadening of signals in cyclic compounds.

ations, one representing a more interacting solvent and the other freer solvent. This could cause two different signals for the solvent as has been observed by Liu (19), who found a doublet for the resonance of benzene in highly cross-linked poly(methyl methacrylate).

Figures 4 and 5 show the line broadening of both phenyl proton signals (Fig. 4) and methyl proton signals (Fig. 5) in aromatic compounds. The degree of the line broadening of the phenyl proton signal increased in the order: benzene < toluene < o-xylene < p-xylene and tetrahydroxannaphthalene. The order roughly agrees with the increasing order of the molecular size of the compound, indicating that the molecular size strongly affects the molecular motion of the solvent in the polymer matrix, although the molecular shape also has some effect. The line broadening of methyl proton signal in Figure 5 shows that the restriction of the internal rotation of methyl groups in o-xylene is much more accentuated in the polymer matrix.

In all cases of polymerizations in the presence of aromatic solvents as well as aliphatic solvents mentioned below, the line broadening of the chorial signal could not be observed during the polymerization. It is very interesting that the monomer chorial is mobile in the polychloral matrix while the mobility of the solvent is strongly restricted. The true meaning of this phenomenon is not as yet clear. However, high mobility of chorial in the polychloral matrix is probably a major reason why chorial rapidly polymerizes in the polychloral matrix to a reasonably high conversion.
Fig. 7. PMR line broadening of signals in aliphatic compounds.

Figure 6 shows the PMR line broadening of signals of cyclic compounds. The line broadening of cyclohexane is very similar to that of the phenyl protons of toluene, again suggesting that possibly the influence of the molecular size on mobility is a very significant factor.

In the study of the PMR line broadening of the signals of aliphatic compounds, the actual line broadening could not be observed because the PMR signals of these compounds were multiplets caused by strong spin-spin coupling. Consequently, the measurements of the decrease of the signal height of the solvent were used to roughly estimate the overall line broadening of these compounds during the chloral polymerization.

In Figure 7 the line broadening of the PMR signals of n-hexane and methylcyclohexane in the rigid polychloral matrix is shown. The methylene signal of n-hexane showed a steady increase of "line broadening," although the methyl signals remained relatively unchanged. The signal of the methine and methylene protons of methylcyclohexane (which were detected together) showed increases in line broadening above 50% conversion, as did the methyl protons of methylcyclohexane, but to a lesser extent. In these experiments, as before, no line broadening for chloral was observed.

PMR line broadening of the methylene signals in tetrahydronaphthalene also was determined by estimating the change in signal height of the methylene protons (Fig. 8). Tetrahydronaphthalene has two multiplets; the benzylic methylene groups have a center of the resonance at 2.76 ppm, and the methylene groups adjacent to the benzylic methylene groups have a resonance at 1.79
Fig. 8. PMR line broadening of methylene proton signals in tetrahydro-
naphthalene.

ppm (20). The height of the methylene protons adjacent to the phenyl ring
(benzylidene protons) decreased more rapidly than those of the methylene signals
(which are farther removed from the phenyl group) which represents a lesser
effect of line broadening of the latter as compared to the former. We inter-
pret the results on steric grounds and believe there is a strong interaction be-
tween polychloral, probably the trichloromethyl groups and the aromatic por-
ton of the tetrahydro-naphthalene molecule. This leaves the methylene groups,
which are further removed from the phenyl ring and more mobile, at the end
of chloral polymerization.

According to all our evidence, chloral polymerizes directly to isotactic poly-
chloral which has a 4, helix structure (21). DSC and torsion pendulum meas-
urements have not shown any discrete glass temperatures in polychloral (1-3).
We do not know whether it is meaningful to talk about a glass transition tem-
perature in polychloral, but we believe that the system behaves as if the meas-
urements reported in this work were made below the glass transition tempera-
ture of polychloral.

Additional work is under way to study more extensively the interaction of
small molecules with a rigid polychloral matrix.

References

(2) O. Vogl. H. C. Miller, and W. H. Sharkey, Macromolecules, 5, 658
(1972).
(3) P. Kubisa and O. Vogl, unpublished results.
(15) W. G. Rothschild, Macromolecules, 1, 43 (1968); 5, 37 (1972).
(20) "NMR Spectra Catalog," Varian Associates, Palo Alto, California.

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