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MATERIALS SCIENCE AND ENGINEERING

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Synthesis, Characterization and Physical Properties of Polyphosphazenes

by

1989

J. H. Magill

University of Pittsburgh

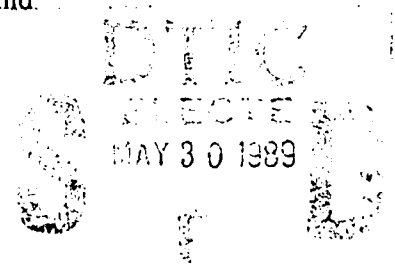
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This report summarizes work carried out under Contract No. N00014-85-K-0358 on the subject of "Synthesis, Characterization and Physical Properties of Polyphosphazenes".

A. Brief Summary of Work

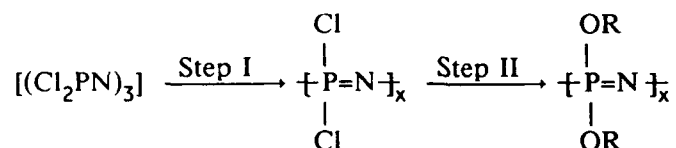
The investigation was comprised of three parts namely:

- 1) Synthesis of polyphosphazenes ;
- 2) Characterization ;
- and 3) Investigation of Physical Properties .

The results summarized here measure up to most of the objectives outlined in the original proposal; some even go beyond the original goals.

1) Synthesis of Polyphosphazenes

The solution polymerization method was "perfected" in our laboratory to produce a wide variety of alkoxy and phenoxy polymers using the scheme:



starting with polymerization grade (> 99%) cyclic hexachloromonomer which was reacted Stage I to form the poly(dichlorophosphazene) in 1,2,4 trichlorobenzene.

Many alkoxy and aryloxy substituted phosphazene homopolymers^(1,2) were made via Stage II where,

R=CH₃, C₆H₅, C₆H₄CH₃, CH₂CF₃, C₆H₄-C₆H₅, m- and p- C₆H₄F, m- and p- C₆H₄-Cl, m- and p- C₆H₄-Br, β-C₈H₁₀, Si(CH₃)₃, Si(C₆H₅)₃, (CH₂)₃ Si(CH₃)₃, OP(OC₆H₅)₂.

Sulfamic acid and ammonium sulfamate were used as catalysts. Apparently sulfamic acid functions as a catalyst in some decomposed form through its acid group. Toluenesulfonic acid and sulfobenzoic acid were new catalysts developed for solution polymerization⁽³⁾. Toluenesulfonic acid (unlike sulfamic acid) is soluble and undergoes no degradation and contains an acid group that acted as a catalyst in the polymerization. Sulfobenzoic acid likewise gave identical results in so far as molecular weight and molecular weight distribution was concerned. These catalysts exhibit advantages over sulfamic acid. The polymerization favors a cationic mechanism. Promoters were

found to speed up the polymerization reaction. Effect of different parameters including system dilution, catalyst concentration, and promoter concentration on the properties of the final polymer were investigated^(1,2). The changes in molecular weight and molecular weight distribution of the polymer as a function of polymerization reaction time were noted. The nucleophilic reaction was studied and the effect of reaction time and temperature on the properties of the final polymer were investigated.* Ring opening reactions attempted on fully substituted cyclotriphosphazenes at elevated pressures and temperatures were unsuccessful. All polymers were characterized by differential scanning calorimetry⁽⁴⁾, gel permeation chromatography, infrared spectroscopy, and ³¹P solution nuclear magnetic resonance spectroscopy^(1,2).

The effect of solvent concentration and catalyst concentration on the reaction rate was established. The catalytic activity is attributed to a decomposition product of sulfamic acid not the pure acid. The exact nature of the catalyst is still not clear at this time. The solution polymerization reaction has an induction period of an hour which is the time needed for the catalyst to become converted into its active form. The catalytic activity is associated with the acid group of the sulfamic acid, not the amine group. Molecular weights of the polydichlorophosphazenes are high from the beginning of the polymerization, indicating a chain propagation mechanism, but the exact nature of the active center for kinetic chain growth is unknown. In contrast with melt polymerization, water did not act as a catalyst when used with sulfamic acid in solution polymerization, but it had an appreciable effect on the reaction rate and on the polymer properties. Water present or released in controlled amounts from inorganic hydrates, act as an effective promoter and provides linear high molecular weight polymer with relatively narrow molecular weight distributions. Water reduced the induction period of the reaction to about five minutes, but did not eliminate it. Although the exact structure of the polymer chain ends is not known, the decomposition product of sulfamic acid must play an important role in forming the chain ends. This was evident from the fact that polymers synthesized with high catalyst concentration were of low molecular weight. The time and temperature needed for substitution in the nucleophilic reaction depended upon the strength of the

* More details are given in ONR Technical Report No. 9 and in two papers, references 1, 2 to be published soon.

nucleophile. The physical properties of the polymer can be altered adversely through branching if prolonged heating is employed.

2) Characterization

Aside from molecular weight characterization by GPC,* ³¹P solution NMR was gainfully employed to determine when and if branching took place, following specific changes in reaction conditions (see Figure 1 and reference 1). In this way, much better sample monitoring was possible than that offered by IR analysis. Besides this basic approach other physical properties were monitored. These will be mentioned in section 3. Information is to be found too in references 1 and 2.

2) Investigation of Physical Properties

In the early stages of this research, DSC analysis was heavily relied upon for the early characterization of these materials⁽⁴⁾. However, it was soon realized that this technique while very useful, alone it could lead to misleading interpretation of results if considerable care was not exercised. A background of other complementary information was required, particularly electron microscopy⁽⁵⁾, X-ray⁽⁶⁾ and electron diffraction⁽⁷⁾, were salient tools in this respect. It was soon established that polymorphism, in addition to thermotropic phase formation, featured strongly and importantly in the physical chemistry of (organo) polyphosphazenes. The conditions for which polymorphism and twinning were established working on "single crystals"^{**} using electron diffractions. Transitions temperatures were established as a function of measurement conditions⁽⁷⁾ and the proximity or coexistence of distinct phases (up to 3 polymorphs plus the thermotropic or mesostate) were documented for some polyphosphazenes. X-ray diffraction studies^{***} also supplemented this information. The coexistence of orthorhombic and monoclinic phases (where the β angle is not far off 90°) has sometimes presented analysis complications to the X-ray

* Of course there is also a problem of the true hydrodynamic radius of the diverse polyphosphazene in solution, compared to the polystyrene calibrants used.

** Hardly the correct description since these well defined lamellar shapes formed from solution were far below 100% crystalline.

*** Note that some of the early X-ray structure measurement made in this field were of dubious quality because of polymorphism.

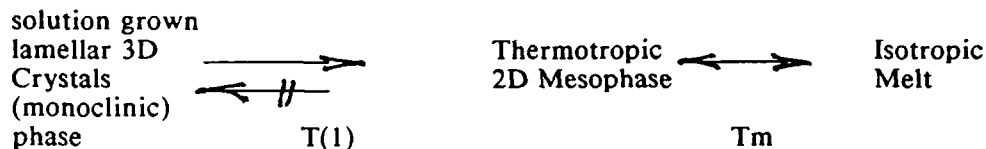
crystallographer. Polyphosphazenes are not exception here. Even now, there are very few well-defined X-ray structures established for polyphosphazenes. In fact, there is still debate over the space group of one of the simplest, i.e. the intermediary poly (bis-dichlorophosphazene) formed in stage I of the synthesis of the poly(organo) phosphazenes. According to Allcock⁽⁸⁾ the space group is a $P2_1/C$ monoclinic. Chatini⁽⁹⁾ disputes this result presenting evidence for glide type conformation of form $(T^1-C^1-T^1-C^1-)$ with $T^1 = 175^\circ$ and $C^1 = 31^\circ$. The matter remains unsettled. At this point we will leave the debate which will probably arise again as more polyphosphazene structures are examined.

Returning to the physical properties side, measurements of the glass temperature, T_g , the thermotropic transition, $T(1)$, and the melting temperature, or clearing isotropic temperature, T_m , it has been established⁽¹⁰⁾ that the side group chemistry expressed as $(T_m - T_g)/(T_m - T(1))$ scales with $T(1)/T_m$, providing a useful guideline for selection of polyphosphazenes in a predictive sense for the effect of chemistry (and to some degree group dimensions) on physical parameters.** At present, there is no theoretical basis for this correlation, but some thought has been given to an analytical approach to it. However, from the viewpoint of X-ray and limited, but continuing, solid state NMR measurements⁽¹¹⁾ further insight is provided into the role of side groups on structure and into conformational mobility through decoupling side group and main chain motions. There is a strong dependence of side group size and type on intermolecular packing of chains and it is found that separation between extended chains in the thermotropic state (above $T(1)$ and below T_m) correlates linearly with side group dimensions. However more varied work must be done to investigate some intricate crystallographic changes that take place. Interestingly, as wide angle X-ray and electron diffraction structural work has been developed, the complexity of polyphosphazene phase transitions has been classified for some polymer. For instance Figure 2 shows, for example, the somewhat complicated thermotropic and polymorphic transitions⁽¹²⁾ that exist in poly(bis-phenoxy)phosphazene). As of the time of writing poly(organo)phosphazene are known generally to

* Unfortunately many substituted poly(phenoxy)phosphazenes decompose or degrade before they melt, thus restricting work here.

** As for example in the Boyer rule connecting T_g and T_m in homopolymers!

exhibit at least two polymorphic forms and one thermotropic phase. The scenario that has been developed shows



The upper first order transition is reversible but a return to the starting crystals (usually monoclinic) does not take place, but an orthorhombic conformationally extended structure always results.

From the viewpoint of small angle X-ray scattering⁽¹²⁾ and solid state NMR⁽¹¹⁾ poly[bis(trifluoroethoxy)phosphazene] lamellar crystal mats (~140 Å thickness and ~50% crystallinity) undergo some form of chain extension upon heating the sample through the T(1) transition region. This is accompanied by a significant decrease in line width for the ³¹P MAS NMR of line width versus temperature. The ³¹C MAS ¹H decoupled NMR spectra obtained above and below T(1) were almost identical, indicative of side group mobility in the 2D thermotropic and 3D orthorhombic phases. ¹³C spin-lattice relaxation times* for CH₂ and CF₃ side groups are 1.75s. and 3.55s. with corresponding activation energies of E ~ 17.3kJ/mol and 13.7 kJ/mol respectively CH₂ for measurements made through T(1). Larger side groups will have different relaxation times and somewhat high energies of activation, but they require to be measured using a systematic series of well characterized polyphosphazenes. Information of this kind is basic to our understanding of the processing of polyphosphazenes for instance in fiber spinning, etc.

Dilatometric measurements⁽¹³⁾ are informative as to the volume changes associated with the two first order transition T(1) and T_m respectively. In PBFP poly[bis(-trifluoroethoxy)phosphazene], for example they are about comparable in magnitude at each transition (i.e. ~ 6% by volume) compared with the corresponding enthalpy results at these transitions which may ratio 10:1 or more in magnitude. A significant difference is shown here highlighting technique sensitivity as a major

* These times have a fundamental bearing on kinetic processes and the ability of phosphazenes to adopt a particular conformation subject to environmental constraints (eg. fast cooling rates, etc.).

factor between these two methods. These kinds of investigations must be extended to other polyphosphazenes to determine important physical parameters for these materials.

Crystallization kinetics⁽¹⁴⁾ are very important in regards to ability of polyphosphazenes to transform at sub T_m and sub $T(1)$ temperatures. In this field the work accomplished here also stands alone. Growth is athermal (heterogeneous) and the kinetics are well described over a significant part of the transformation range by $n = 2$. Avrami theory denotes that where $\theta = \exp(-kt^n)$. Here k is the overall rate constant, t is time, θ is the amount of untransformed polymers and n denotes the transformation mechanism whereby the change occurs. Its value may be interpreted to mean that small displacements may occur along the main chain direction (<1 repeat unit) and this is all that is required to produce transverse lateral ab growth perpendicular to the molecular chain axis. Of course, the dimensions of the side groups on the phosphorus exerts a strong controlling influence, but the temperature dependence of the transformation on undercooling is extraordinary steep (at least 5 orders of magnitude in 10°) compared to changes in homopolymers at sub T_m temperatures. More investigations are needed here to understand this behavior where morphology, kinetics and properties are closely knitted and interdependent on environmental constraints. Not only will a better understanding of polyphosphazenes evolve, but a clearer picture of thermotropic behavior for polymers generally should be established.

From the mechanical properties* made some time ago⁽¹⁵⁾ our results indicated that orientation and crystallinity determine the magnitude of the dynamic moduli and loss factor characteristics measured in polyphosphazenes. Tensile properties (modulus and strength) of polyphosphazene fibers** are currently under investigation in an attempt to relate density and crystallinity with mechanical behavior. Polyphosphazene morphology is complex. Structural and morphological investigations of polyphosphazenes with different kinds of side groups have been made in an attempt to understand the $T(1)$ thermotropic transitions. Solutions grown crystals and cast films of phosphazene homopolymers were prepared and investigated by d.s.c., electron microscopy and X-

* Torsion braid measurements only provide relative not absolute mechanical parameters.

** Activities of this kind require further funding if a better understanding of phosphazene polymer properties is to be developed.

ray diffraction. It has been established that the $T(1)$ and T_g values are roughly linearly related with the size of side groups. The interplanar distances expressed as $d(100)_{(g)}$ in thermotropic state also show a linear relation with the side group dimensions. Polymorphic forms have been found for most polyphosphazenes that exhibit a $T(1)$ temperature, the location of which is influenced by the side groups. Although our understanding has been considerably broadened through work carried out under the present contract, this research only represents a framework providing a real perspective for future more detailed investigations.

This report provides a brief summary of some of the highlights of our polyphosphazene work. More details are given in (Part B) referenced Technical Reports #1 - 11 and in current papers (Part C) also cited here.

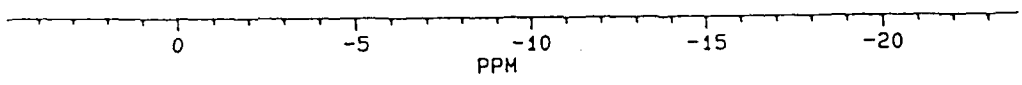
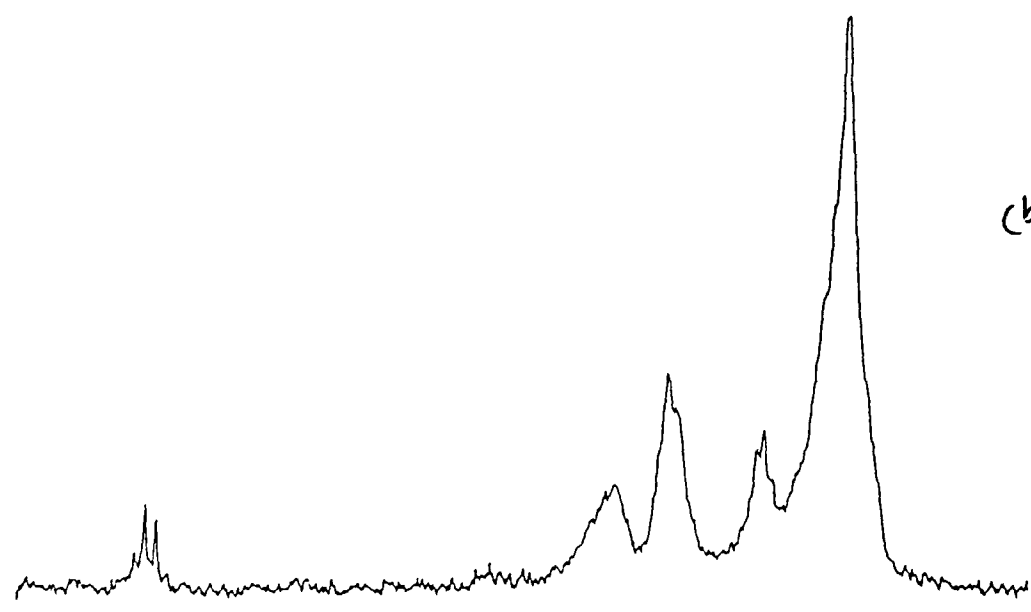
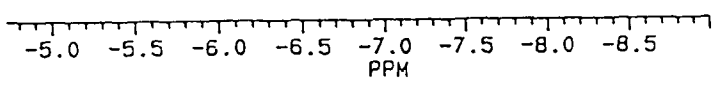
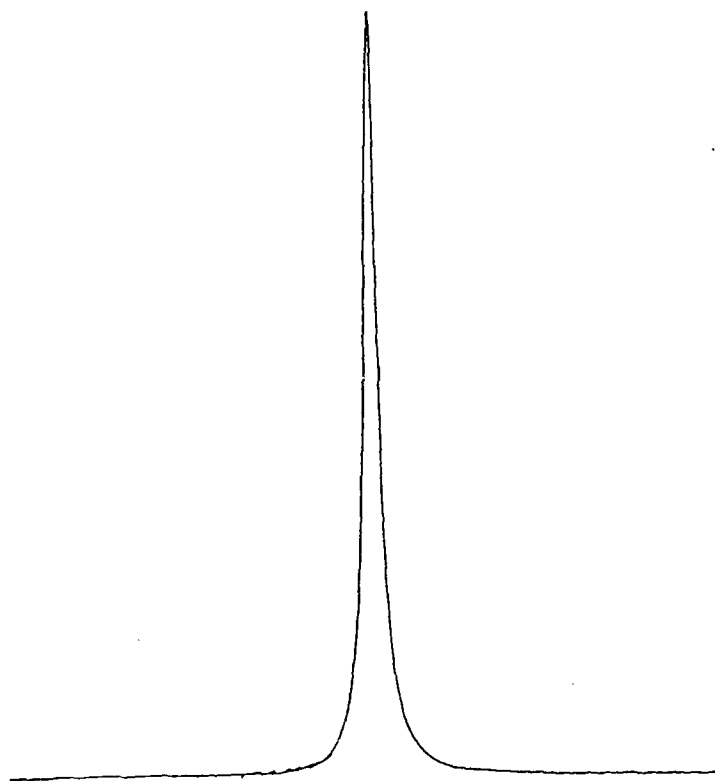
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5) Figures

Figure 1: ^{31}P Solution NMR measurements for (a) unbranched linear poly [bis (trifluoroethoxy)phosphazene] (b) branched poly [bis(phenoxy) phosphazene]

Figure 2: Transition map for phase changes observed in poly[bis(phenoxy)phosphazene].



TRANSITION MAP FOR PBPP

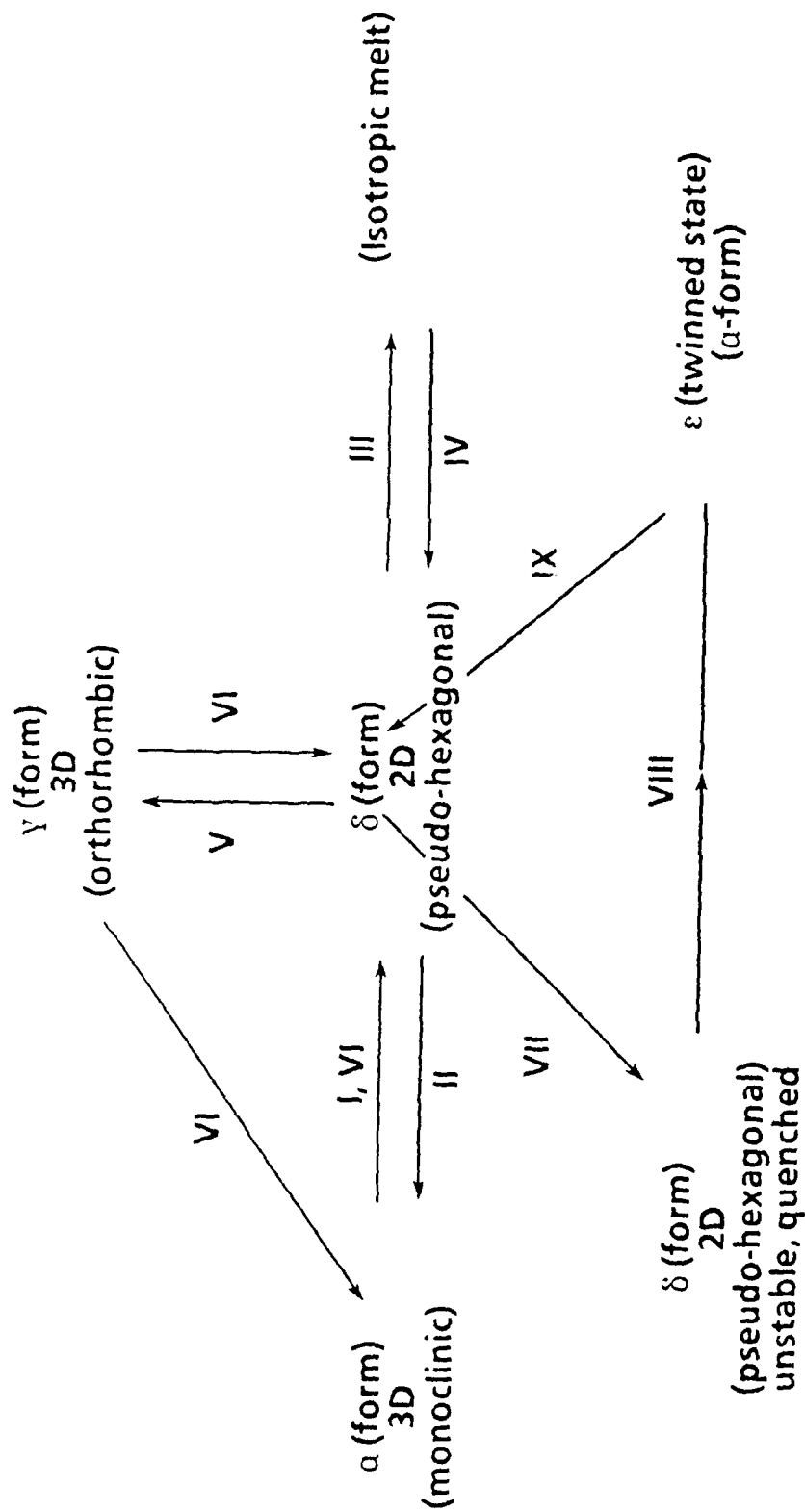


Figure 2 Transition map for PBPP for allowed transition (in arrowed directions) conditions listed:

Conditions

- I Heat above $T(1)$ and but less than T_m .
- II Slow cooling.
- III Heat to, or above T_m .
- IV Cool.
- V Fast cool to room temperature.
- VI Heat above $T(1)$.
- VII Very rapid quench into liquid N_2 .
- VIII Heat to just below $T(1)$.
- IX Heat above $T(1)$ but below T_m .

B. Index to be Completed Technical Reports

"Thermal Behavior of Polyphosphazene in Relation to Structure," D. C. Sun and J. H. Magill, Technical Report, No. 1.

"Crystallization Relationships Between Poly[bis(phenoxy)phosphazenes]-PBPP Crystals," M. Kojima and J. H. Magill, Technical Report No. 2.

"Inorganic Polymer," J. H. Magill, Technical Report No. 3.

"Isothermal Crystallization of Polyphosphazenes by DSC. Part I: Poly[bis(trifluoroethoxy)phosphazenes]," R. J. Ciora, D. C. Sun and J. H. Magill, Technical Report No. 4.

"Properties and Phase Transitions in Polyphosphazenes," J. H. Magill, Technical Report No. 5.

"Phase Transitions and Structural Modifications in Semi-Crystalline Phosphazenes," by M. Kojima and J. H. Magill, Technical Report No. 6.

"Twinned Crystals of Poly[bis-p-(fluorophenoxy)phosphazene] - PB(4F)PP," M. Kojima, T. Masuko and J. H. Magill, Technical Report No. 7.

"Influence of Side-Groups on Thermotropic Behavior of Polyphosphazenes," by M. Kojima and J. H. Magill, Technical Report No. 8.

"Polymerization Studies of Some Polyphosphazenes Using Solution Polymerization," A. J. Mujumdar, S. G. Young, R. L. Merker, and J. H. Magill, Technical Report No. 9.

"A Study of the Isothermal Crystallization Kinetics of Poly[bis(trifluoroethoxy)phosphazenes] and Poly[bis(phenylphenoxy)phosphazene]," R. J. Ciora, Jr. and J. H. Magill, Technical Report No. 10.

"A Study of the T(1) Transition of Poly[bis(trifluoroethoxy)phosphazenes] Using Solid State NMR Spectroscopy," S. G. Young and J. H. Magill, Technical Report No. 11.

C. Index to Papers (published or submitted)

Publications by the P.I. and coworkers on Polyphosphazenes supported in whole or in part by the ONR contract.

"Crystallization Kinetic of Polyphosphazenes, Part I Poly[bis(phenoxy)phosphazene]" with R. J. Ciora, Jr., *Macromolecules*, in preparation, 1989.

"Crystallization Kinetics of Polyphosphazenes, Part II Poly[bis(trifluoroethoxy)phosphazenes]" with R. J. Ciora, Jr. *Macromolecules*, in preparation, 1989.

"A Study of the T(1) Transition of Poly[bis(trifluoroethoxy)phosphazene] using Solid State NMR", with S. G. Young, *Macromolecules*, in press, 1989.

"A Study of the Isothermal Crystallization Kinetics of Poly[bis(trifluoroethoxy)phosphazene] and Poly[bis(phenylphenoxy)phosphazene]" with R. J. Ciora, Jr., submitted to NATAS's Conference, San Diego, Calif.

"Solution Polymerization of Selected Polyphosphazenes" with A. N. Mujumdar, S. G. Young, R. L. Merker) *Die Makromol. Chemie* (to be published, 1989).

"Some Properties of Poly[bis(halophenoxy)phosphazenes] with S. G. Young and M. Kojima) submitted A. C. S., *Polymer Preprints*, Miami, Fl., 1989.

"Crystallization, Morphology and Properties of Inorganic Polymers", submitted to A.C.S., *Polymer Preprints*, Miami Fl., 1989.

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"Influence of Side Groups on the Thermotropic Transition in Poly(organophosphazenes)", with M. Kojima, *Makromol. Chemie*, 190, 88, 1989.

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