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Thermal Characterizations of Inorganic and Organometallic Polymers

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ABSTRACT

This review emphasizes the breadth of metallic and metallic-like polymers evaluated as to thermal properties. Techniques usefully applied to particular systems are noted with the aim of suggesting their application to other systems.

INTRODUCTION

Generally, techniques applicable to the thermal analysis of organic polymers are applicable to the study of inorganic and organometallic polymers. The variety of bonding polarities and energies present in many metal-containing polymers often led to what has been referred to as "stability plateaus" where degradation followed by thermogravimetric analysis, TG, occurs through several somewhat distinct steps being seen as temperature ranges where little or no weight loss occurs followed by temperature ranges where weight loss is more rapid. Such stability plateaus can be divided into kinetically independent and dependent plateaus. Plateaus in the TG thermogram where no additional weight is lost if the program mode is changed to isothermal within the area are called kinetically independent plateaus.

If additional weight is lost, then that portion of the plateau can be referred to as a kinetically dependent plateau.

The discussion is divided somewhat arbitrarily into the sections Inorganic Polymers and Organometallic Polymers by the presence (organometallic) or absence (inorganic) of hydrocarbon moieties within the polymer backbone. Some divergence in this division occurs, allowing for greater continuity. Inorganic polymers such as quartz, sand, and ceramics have been omitted. Further, since volumes have previously been devoted largely or entirely to the siloxanes, the thermal aspects of siloxanes will be deemphasized to allow for a greater coverage of other topics.

As will be evident, thermal analysis of organometallic and inorganic polymers is, with few exceptions, in its infancy. Most of the studies have been carried out as one aspect of product characterization, often by those unfamiliar with many of the instrumental, procedural, and/or theoretical aspects of thermal analysis. Thus the review will lack a great deal of useful critical analysis, being largely expository and qualitative in nature. It is hoped that within the next decade this will change and a more critical, quantitative review will be possible.

INORGANIC POLYMERS

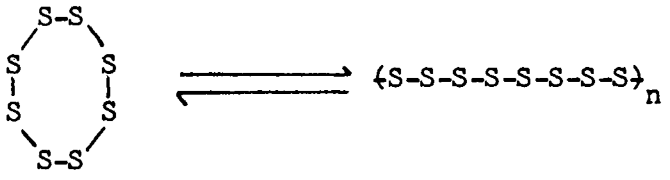
General

Elements such as phosphorus, silicon, and sulfur form catenated polymers similar to carbon, but such catenation does not usually lead to (homo) chains greater than 10. Further, such products might be expected to (and in fact do) offer poorer thermal stabilities than carbon-based polymers since their bond energies are generally significantly less (for instance the C–C bond energy for typical hydrocarbons is about 82 kcal/mol; S–S bond energy is about 58, Si–Si is 53 kcal/mol, P–P is 48, and Sn–Sn is 39 kcal/mol). The alternative of utilizing heteroatom back bones is attractive since the resultant bonds can exhibit greater bond energies than the C–C bond (for instance, P–N has a bond energy of 138 kcal/mol; Be–O is 124, B–O is 113, Si–O is 108, B–N is 106, Si–N is 104, B–C is 89, and P–S is 82, exhibiting %-ionic bond characters of ~6 for B–C to 55 for Sn–O; many of these bonds have π-bond contributions). The often relatively high ionic bond character can strongly influence polymer behavior through chain and atom interactions such as π-bond overlaps, chain stiffness, and polar bonding, and should be considered when evaluating thermal properties.

There is a wide variety of definitions utilized to define "inorganic polymers," each including and excluding certain compositions. Here "inorganic polymers" will be defined as macromolecules whose backbone or connective bridge contains largely nonhydrocarbon moieties which exhibit a sufficient amount of covalent character so as to possess directional bonding. Products not included in this review but which are considered inorganic polymers by this definition include diamond and related materials and certain silicon-containing products as sand.

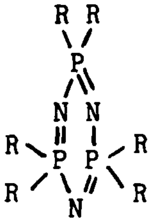
A number of degradation pathways have been identified. Some of these pathways are described briefly as follows.

Reorganization reactions include ring formation. Many inorganic monomers tend to form small, unstrained rings. Thermal degradation of products formed from such monomers often involve an equilibrium between the reactants (monomer, cyclic product, etc.) and the polymers (1):


(1)

Ia

Ib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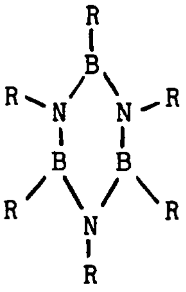
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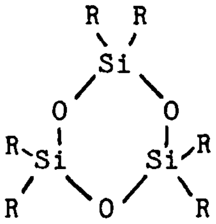
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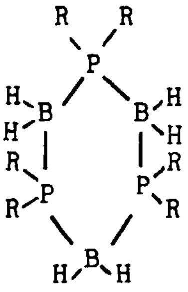

V

Other polymers degrade to highly cross-linked structures. This is directly related to the formation of the new "graphite"-polymers where mixtures of inorganic and organic polymers and monomers are "cooked" to achieve products which are highly cross-linked and exhibit outstanding thermal stability and strength [1]. Degradation to refractory oxides is fairly common among polymeric metal alkoxides, yet polymeric butyl titanate decomposes, leaving a stable titania network [2]. Borazole, Structure III where R–H, undergoes polycondensation about 500°C to form a stable, complex borazole-like structure [3]. From an industrial standpoint this degradation route could lead to a number of useful products (such as electrical or photoconductive fibers) with outstanding thermal stability.

While most typical organic polymers undergo rapid oxidative degradation within 125 to 400°C, inorganic polymers can undergo such oxidation within a much wider range (such as 20 to 800°C). Products with "oxidative resistance" above that of organic polymers should be more widely investigated as antioxidants [4].

A word of caution: A characteristic of most inorganic polymers is their susceptibility to nucleophilic and electrophilic attack. The presence of trace amounts of such impurities can give quite misleading thermal stability results. Further, because of the tendencey toward cyclization without weight loss found for many inorganic polymers, TG studies should be monitored by DSC, NMR, MS, and IR spectral analysis.

Another serious problem is hydrolysis. Proper placement of large, bulky organic groups; insertion of moieties possessing pi-bonding; tight structures with hydrophobic, largely organic "hides"; and increase in crystallinity have been used to overcome hydrolytic instability [5-8].

TABLE 1. Combinations of Group III-VA Metals Reported to Form $(M\text{-}X)_n$-Type Oligomers

Metal	Homopolymer	With nitrogen	With oxygen
B	B–B	B–N	B–O
Al		Al–N	Al–O
Si	Si–Si	Si–N	Si–O
Ge	Ge–Ge		Ge–N
Sn	Sn–Sn		Sn–O
As	As–As	As–N	As–O
Sb	Sb–Sb	Sb–N	Sb–O
P	P–P	P–N	P–O

There are a large number of inorganic polymers with few thermally characterized to any great extent. Table 1 contains a listing of reported combinations involving only the Group III, IV, and VA elements with oxygen, nitrogen, and with themselves, illustrating the vast variety and number of synthesized products. Following are brief summations of a limited number of inorganic polymer families. Reviews are given in papers by Hunter [2] and Economy and Mason [9].

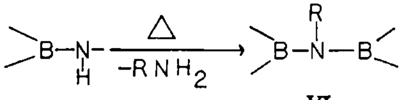
Boron-Containing Polymers

Boron-Boron Bonds

A number of polymers containing B–B bonds have been synthesized. A fusible, soluble carborane silicone-type polymer has been reported with total stability to ~425° [10]. Refractory borides with B_{12} units have been reported to be stable in air to 700°C where they begin to rapidly oxidize, forming boric oxide [11].

Boron-Nitrogen Bonds

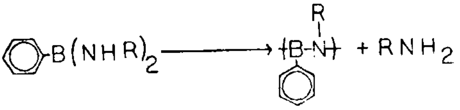
A number of products which contain only boron and nitrogen in the backbone have been synthesized from the aminoborane-amine elimination pyrolysis as shown in Eq. (2). Though most of these products were not clearly defined as to molecular weight or actual structure, their TG properties have been reported [5, 9, 12]. It was concluded that such products characteristically showed poor thermal stabilities. While such conclusions may be inferred from the thermal analysis data, it must be noted that the products were poorly defined. In fact, the poor hydrolytic stabilities of such products, possibly enhanced by the presence of residual amine formed from the pyrolysis synthesis of the products, may account for the poor thermal stability of the products. Pure products may offer considerably better thermal stabilities, particularly in light of the high energy of the B–N bond of 105 kcal/mol. Later studies with other B–N containing products show at least some products which exhibit moderate thermal stabilities.



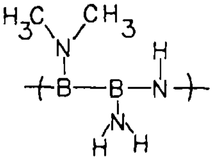
VI (2)

A number of low molecular weight polymers based on (alkylamino)-phenylboranes (VII) have been synthesized [12-14]. The products were stable in nitrogen to 350°C but were easily hydrolized.

The condensation of tetrakis(dimethylamino)diborane and ammonia gives a colorless polymer (VIII) which is stable to 500° [15]. It is reported to cross-link above 500°C with elimination of dimethylamine.



VII

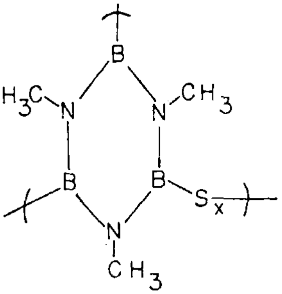


VIII

β-Trichloro-N-triarylborazines, when heated to 450°, are reported to evolve HCl and form borazine rings connected together by phenylene groups. These products are reported to be stable to 600°C in both air and N_2 [16].

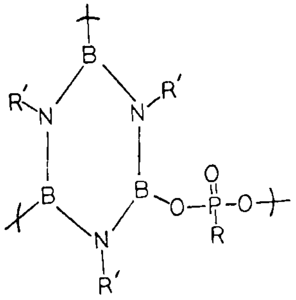
Korshak et al. made a polyborazine from the bulk condensation of β-triphenyl- and N-triphenylborazines [17]. The product retained 76% of its weight to 900°C in argon.

Polyborazylene sulfides (IX) exhibit melting ranges in the 120-200°C range and decompose in the 250-300°C range [18].



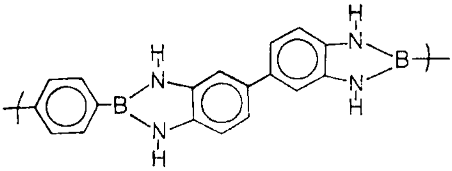
IX

Pyrolysis of monoalkoxypolyborazine phosphonates (X) at 450-500°C led to the rupture of the borazine ring with evolution of ammonia and olefins (except for R' = O–CH_3 which gave CH_4; Refs. 19-22).

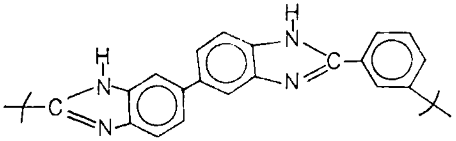


X

The boron analog of the aromatic polybenzimidazoles (XII), the polybenzoborimidazolines (XI), has been studied using TG. It offers a weight retention similar to the nonboron compound in that both show about 75% weight retention in N_2 at 800°C with initial weight loss occurring below 100°C [9, 12].



XI



XII

Silicon-Containing Polymers

Silicones or Polysiloxanes

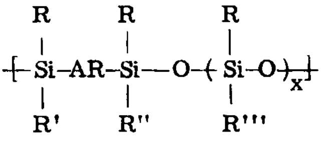
The chemical and physical, including thermal, resistance to degradation of polysiloxanes is a consequence of both the high Si–O bond energy (106 kcal/mol) and the relatively large amount of ionic character within the Si–O moiety. On the other hand, the ionic character of the Si–O bond facilitates acid- and base-catalyzed rearrangement and/or degradation reactions. Under inert conditions highly purified polydiphenyl- and dimethylsiloxanes have displayed stabilities to 350-400°C, where interchange begins to occur. In oxygen, high molecular weight dimethylsiloxane is attacked at temperatures near 200°C. Substitution of a phenyl group for one methyl group acts to increase oxidative stability to 225°C. Thus it can readily be demonstrated that thermal stability, as well as any structure-related property such as resistivity and elasticity of polysiloxanes, is dependent on the substitution on the silicon.

Extensive studies carried out on polysiloxanes show that the thermal properties are also dependent on such items as chain length, endgroup, and source (i.e., nature of synthesis). The latter is related to inclusion of impurities, pore size, amount and distribution of crystallinity, etc. This theme for precise structure/property knowledge will be repeated elsewhere to emphasize its importance.

Numerous books have described silicon chemistry and technology including their thermal behavior [23-26]. Only selected aspects will be considered here.

Several general observations can be made (exceptions are found). First, silicones possess both thermal stability and good mechanical, chemical, and electrical properties over the range of -70 to 250°C. Second, in the absence of oxygen, at temperatures greater than 350°C, many linear siloxanes degrade to give cyclic products. Degradation is believed to occur by cleavage of the Si–O bond. Third, oxidative degradation generally occurs at lower temperatures than do polymer rearrangement reactions. The greater stability of sterically hindered siloxanes and other results indicate that oxidation occurs at the silicon atom. Fourth, stability toward oxidative cleavage is dependent on both the nature of the organic groups as well as the backbone structure.

Illustrating the latter point, the thermal stability of a number of arylenesiloxanylene polymers (XIII) has been systematically studied [27-30]. Some structural changes result in little change in the thermal properties (studied by TG and DSC) of the products such as introduction in methyl-substituted polymers of one fluorinated group per silicon (namely $CF_3CH_2CH_2-$) whereas other structural changes markedly affect the thermal properties (such as replacement of methyl groups by trifluoropropyl groups in positions adjacent to the arylene moiety or nature of the arylene and alkylarylene moiety). The volatile degradation products were studied using coupled TG-MS with indications that all the volatile products were evolved in a single or interrelated process(es). Methyl siloxane fragment ions were detected for



$$\left[\underset{R'}{\overset{R}{\mathrm{Si}}}-AR-\underset{R''}{\overset{R}{\mathrm{Si}}}-O-\left(\underset{R'''}{\overset{R}{\mathrm{Si}}}-O\right)_x\right]$$

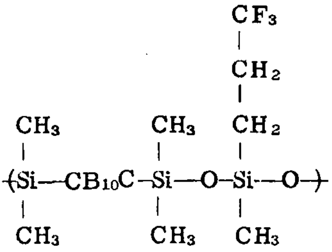
XIII

all products. Other fragments found included CF_2H^+ and CH_2^+. Degradation of these products occurs through a single decomposition (TG) curve. Such studies indicate the types of structural correlations and techniques that might be considered with studies involving other polymers.

As previously noted, siloxanes undergo extensive rearrangements at temperature in excess of 350°C, often forming cyclic products. Because of the significant mechanical, chemical, and electrical properties offered by siloxanes and modified siloxanes, great effort is still oriented toward increasing the use temperature of such products. This work is closely associated with sophisticated thermal analysis systems and is often aimed at preventing the depolymerization (reversion) reaction.

One approach often employed for preventing reversion is modification of the siloxane. Several recent attempts are described below.

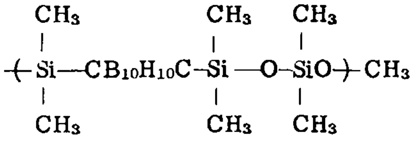
Linear D_2-m-carborane-siloxanes (XIV to XVII with one to three trifluoropropyl moieties per repeating unit) exhibit better thermal and oxidative stability than silicones and fluorosilicones [31]. Initial degradation occurs in air about 300 to 350°C, almost 100° above that typically experienced for siloxanes and fluorosilicones. The carborane-siloxanes exhibit T_g's from -50 to 0°C [31].



$$-\!\left(\mathrm{Si(CH_3)_2{-}CB_{10}C{-}Si(CH_3)_2{-}O{-}Si(CH_3)(CH_2CH_2CF_3){-}O}\right)\!-$$

Ucarsil F_1

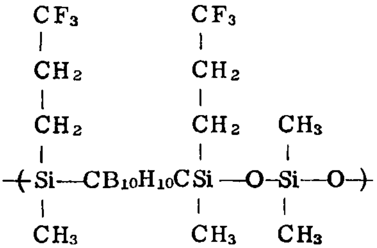
XIV



$$-\!\left(\mathrm{Si(CH_3)_2{-}CB_{10}H_{10}C{-}Si(CH_3)_2{-}O{-}Si(CH_3)_2O}\right)\!-\mathrm{CH_3}$$

Ucarsil Me_2

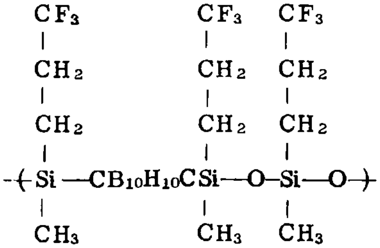
XV



$$-\!\left(\mathrm{Si(CH_3)(CH_2CH_2CF_3){-}CB_{10}H_{10}CSi(CH_3)(CH_2CH_2CF_3){-}O{-}Si(CH_3)_2{-}O}\right)\!-$$

Ucarsil F_2

XVI



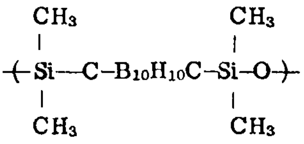
$$-\!\left(\mathrm{Si(CH_3)(CH_2CH_2CF_3){-}CB_{10}H_{10}CSi(CH_3)(CH_2CH_2CF_3){-}O{-}Si(CH_3)(CH_2CH_2CF_3){-}O}\right)\!-$$

Ucarsil F_3

XVII

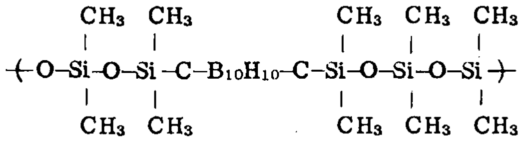
Thermal analysis of a number of linear polycarboranesiloxane copolymers and block polymers (such as Forms XVIII to XX) including TG, DTA, TBA, and TMA was made by Roller and Gillham [32]. A number of physical transitions were reported including crystallization temperature (10 to 230°C), glass transition temperature (-108 to 25°C), glassy-state transition temperature (-145 to -90°C), and melting temperature (40 to 260°C). This is one of the most complete single papers on the thermal analysis of inorganic polymers regarding the types of thermal properties cited.

A number of interesting results were found that may have otherwise gone unnoticed in briefer studies [32]. It is concluded that the cyclization mechanism of degradation which occurs for polydimethylsiloxane is not operative for polycarboranesiloxanes. At high temperatures the polycarboranesiloxanes stiffen, possibly due to cross-linking. By contrast, polydimethylsiloxane does not cross-link during degradation. In argon the polycarboranesiloxanes generally showed an increase in thermal stability of about 50°C over that of polydimethylsiloxane with many being stable at 500 to 550°C. Such integrated thermal analysis studies permit both intercorrelating of thermal measurements and a good evaluation of the expected "real" physical properties of the products.



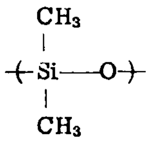
$$-\!\left(Si(CH_3)_2-C-B_{10}H_{10}C-Si(CH_3)_2-O\right)\!-$$

XVIII



$$-\!\left(O-Si(CH_3)_2-O-Si(CH_3)_2-C-B_{10}H_{10}-C-Si(CH_3)_2-O-Si(CH_3)_2-O-Si(CH_3)_2\right)\!-$$

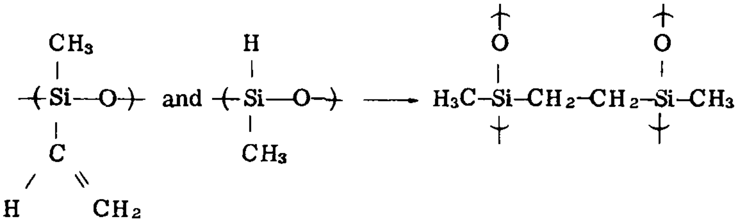
XIX



$$-\!\left(Si(CH_3)_2-O\right)\!-$$

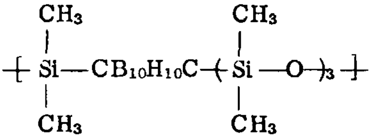
XX

Another often used approach for preventing reversion involves cross-linking of the siloxanes. For instance, a number of methyl silicone rubbers were cross-linked, about 1 cross-link per 3,000 to 20,000 units (XXI to XXIV for cross-linked products mainly composed of dimethylsiloxane; Refs. 33 and 34). DSC and TMA was utilized to evaluate the thermal properties of the products. The DSC data were acquired with the aid of an IBM System 7 computer, and kinetic data were calculated using techniques developed by Rogers and Morris [35] and by Barrett [36]. TMA was utilized to determine cross-link density along with the typical modulus properties. The cross-link density was generated by obtaining the elastic modulus. Cross-link



$$-\!\!\left(\underset{\substack{|\\ \text{C}\\ / \;\; \backslash\backslash\\ \text{H} \quad \text{CH}_2}}{\overset{\substack{\text{CH}_3\\ |}}{\text{Si}}}-\text{O}\right)\!\!- \text{ and } -\!\!\left(\underset{\substack{|\\ \text{CH}_3}}{\overset{\substack{\text{H}\\ |}}{\text{Si}}}-\text{O}\right)\!\!- \longrightarrow \text{H}_3\text{C}-\underset{+}{\overset{\substack{+\\ \text{O}\\ |}}{\text{Si}}}-\text{CH}_2-\text{CH}_2-\underset{+}{\overset{\substack{+\\ \text{O}\\ |}}{\text{Si}}}-\text{CH}_3$$

XXI XXII XXIII



$$-\!\!\left[\underset{\substack{|\\ \text{CH}_3}}{\overset{\substack{\text{CH}_3\\ |}}{\text{Si}}}-\text{CB}_{10}\text{H}_{10}\text{C}-\!\!\left(\underset{\substack{|\\ \text{CH}_3}}{\overset{\substack{\text{CH}_3\\ |}}{\text{Si}}}-\text{O}\right)_3\right]\!\!- \qquad (4)$$

XXIV

density, CD, in moles of effective network chain per cubic centimeter, is related to the elastic modulus, E, by

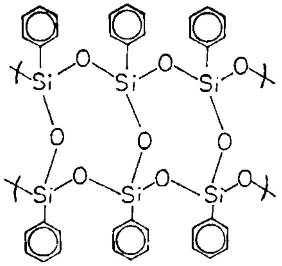
$$CD = E/3RT \qquad (5)$$

where R is the universal gas constant and T is the absolute temperature.

Experimentally there appears to be a correlation between the apparent cross-link density generated from classical swelling methods and elastic modulus determined from TMA though the correlation is not exact [34]. Which of the two approaches is better has yet to be established, but such studies show the potential for rapid determination by thermal analysis of values which are otherwise difficult to obtain.

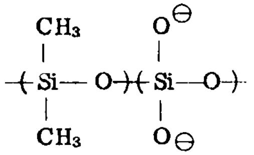
A less used approach to combat reversion is to place the siloxane or modified siloxane on an "inert" support which can assist in maintaining the original nonreverted structure. Thus Finch [37] reports the formation of a new chromatographic phase stable to 500°C based on a polycarboranesiloxane stationary phase. The system is capable of efficient separations from 50 to 500°C. In fact, TG's of the polycarboranesiloxane phase show complete weight retention to about 700°C. The meta-carborane is utilized in this study.

Siloxane-ladder polymers have been known for some time. A polymer derived from phenyltrichlorosilane (XXV), while infusible, is soluble in solvents such as tetrahydrofuran and benzene from which films can be cast [38, 39]. TG thermograms in air show no weight loss to 525°C but an upper limit for useful application is probably near 300°C [39].



XXV

There are a number of instances where thermal techniques could be effectively utilized to monitor polymer synthesis or control modification. For instance, the structure of polyorganosiloxanes (XXVI)



$$\left(\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O\right)\left(\overset{\displaystyle O^{\ominus}}{\underset{\displaystyle O_{\ominus}}{Si}}-O\right)$$

XXVI

prepared from inorganic mineral silicates can be controlled by heating high molecular weight products [40-42]. Such changes are easily followed utilizing TG. On heating to 100°C for 5 h tetrakistrimethylsiloxysilane and hexakistrimethylsiloxydisiloxane are lost from the mineral silicates, increasing the percentage of hydroxyl groups in the remaining silicate. Loss of these lower molecular weight siloxanes and increase in hydroxyl groups increases as the temperature is raised. Thus, through a judicious choice of heating times and temperatures, one is able to vary the product structure from that of a low molecular weight (degree of polymerization of about 15) slightly ionic product to a higher molecular weight product (degree of polymerization of about 60) which is highly ionic and capable of reaction with acetyl chloride, phenylisocyanate, and thionyl chloride.

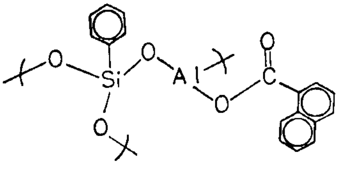
Andrianov [26] has employed a number of statistical manipulations of TG data to assist in the evaluations of the thermal stability of metal-organic polymers. For example, he calculated the extent of polyorganosiloxane degradation as follows for polymethylsiloxane. A single unit, $CH_3SiO_{1.5}$, loses weight because of removal of the methyl group (-15 amu/unit) and substitution of one oxygen for every two methyls (+8 amu/unit). The total loss is then (7 amu/67 amu/unit) or 10.45%. The half-life of polymethylsiloxane is then 5.22%. Using this, he calculated the order of thermal-oxidative stabilities of three-dimensional polyorganoxiloxanes expressed in terms of the organic substituents on the silicon to be $C_6H_5 > ClC_6H_4 > Cl_3C_6H_2 > Cl_2C_6H_3 > CH_2{=}CH > CH_3 > C_2H_5$. While such manipulations of data can lead to interesting trend generation, it must be emphasized that the desired thermal effects should be related to physical properties (such as determined by TBA and TMA). Even if 95% residue weight is retained but the necessary flexibility, etc. lost, the material must be considered thermally unstable at that temperature for a particular application requiring flexibility, etc.

Polymetallosiloxanes

Many metals form poly(elementosilanes). Elements which form poly(elementosilanes) of the form -(M-O-Si-O)- and/or -(M-O-Si)- include Bi(III), Ti(IV), Fe(III), Hg(II), Zn(II), Cu(II), Zr(IV), Ge(IV), Co(II), Ni(II), As(III,IV), Sb(III), Sn(II, IV), B, Al, and P(III).

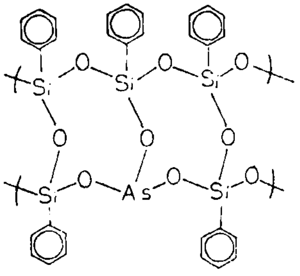
Though the number and variety of synthesized polymetallosiloxanes is wide, the number of thermal studies involving more than simple TG analyses is few, probably because more of the work associated with these polymers predates modern thermal analysis instrumentamentation. Frazer [43] has written a thorough overview of this topic. Several examples will be cited here to note the variety of products characterized.

A number of polyphenylaluminosiloxanes form brittle films which retain solubility in toluene even after 100 h heating at 150° [44]. Initial weight loss in nitrogen occur about 50 to 100°C with some loss occurring due to condensation involving free hydroxyl groups. The low mechanical strength of polymer films cast from solution (XXVII) was increased by 200% by heating the material 10 h at 120°C [45]. Coupled thermal analysis using TMA and TG should be considered in such temperature-mechanical strength studies.



XXVII

Polyorganostannosiloxanes generally exhibit TG monitored stabilities equal to or less than conventional siloxanes while ladderlike products with arsenic XXVIII offer stabilities less than that of the unmodified siloxanes [44].

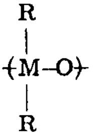


XXVIII

Compounds containing the Si–O–B linkage have been widely explored (for instance, Refs. 46-49), but most offer no advantage over siloxanes regarding weight retentions [44]. The polyorganoborosiloxanes have acquired some prominence through their use as commercial "bouncing or nutty putty" available in most toy stores.

Other Group IVA Polymers

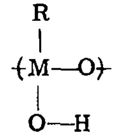
A small number of Group IVA analogs of the siloxanes (XXIX, XXX) have been formed and some thermal (TG and DSC only) properties cited [53-57]. The products are high melting or decompose before melting. Thermal stabilities resemble those of the analogous silicon products. Small endothermic regions generally occur between -30 to 100°C, possibly related to T_g [55, 57].



$$\left(\overset{R}{\underset{R}{|}} \text{M}\!-\!\text{O} \right)$$

XXIX

and



$$\left(\overset{R}{\underset{\text{O—H}}{|}} \text{M}\!-\!\text{O} \right)$$

XXX

where M = Sn, Ge

Phosphorus-Containing Inorganic Polymers

Phosphazenes and Phosphonitriles

Phosphazenes are presently the most important and most thermally characterized of the phosphorus-containing inorganic polymers. Current reports and reviews are given in Refs. 58-85. Three types of polymers based on the phosphazene structures have been developed: linear, cyclolinear, and cross-linked cyclomatrix polymers. Again, only a brief survey is made, with the interested reader pointed to articles in Refs. 61-69 for a more comprehensive literature review.

Studies on polyphosphazene thermal behavior should be monitored via spectroscopic means (such as IR, NMR, and MS) since a number of the phosphazenes (and in fact other inorganic polymers) undergo internal rearrangements and degradations without accompanying weight losses.

General. The observed low T_g's for most polyphosphazenes are consistent with the barriers to internal rotation being low and indicate the potential these polymers offer for elastomer applications. In fact, theoretical calculations based on a rotational isomeric model assuming localized π-bonding predict the lowest (~ 100 cal/mol repeating unit) known polymer barrier to rotation for the skeletal bonds for poly(difluorophosphazene) [76].

Temperature intervals between T_g and T_m are unusually small and generally fall outside the frequently cited empirical relation $0.5 \leq T_g/T_m$ (A) ≤ 0.67 [86]. This behavior could be related to complications in the first-order transition generally found for organo-substituted phosphazenes not common to other semicrystalline polymers [72, 77, 79]. Two first-order transitions are usually observed for organo-substituted phosphazenes with a temperature interval about 150 to 200°C . The lower first-order transition can be detected using DSC, DTA, and TMA. Examination by optical microscopy reveals that the crystalline structure is not entirely lost but persists throughout the extended temperature range to a higher temperature transition which appears to be T_m, the true melting temperature. The nature of this transition behavior resembles the transformation to a mesomorphic state similar to that observed in nematic liquid crystals. It appears from the relationship between the equilibrium melting temperature (heat and entropy of fusion; $T_m = H_m/S_m$) and the low value of H_m at T_m compared to the lower transition temperature, that the upper transition, T_m, is characterized by a quite small entropy change. This may be due to an onset of chain motion between the two transitions leading to the small additional gain in conformational entropy at T_m.

The absence of an as yet undetected endothermic transition at T_m for aryloxy polymers and polyarylaminophosphazenes indicates that the gain in conformational entropy at T_m for these products is indeed small [64, 79].

The lower transition is sensitive to structural changes and usually parallels T_g changes [79]. Further, these are commonly noted as T_g values. This will be done here. Changes in T_m are generally much smaller as structure is changed. Some of the literature T_m values are close to or above measured decomposition temperatures, indicating a need for caution when interpreting T_m values. Table 2 contains typical thermal data for a number of linear polyphosphazenes.

TABLE 2. Thermal Properties of Selected Poly(organophosphazenes)[a]

Product	T_g (°C)	T_F (°C)	T_m (°C)	T_d (°C)	Refs.
F_2PN	-96	-40(?)	-68	190, 270(?)	61, 87, 95
Cl_2PN	-63	-	-30		95
Br_2PN	-15	-	270		61
$(CH_3O)_2PN$	-76	-	-	100	61, 89
$(C_2H_5O)_2PN$	-84	-	-	150	61, 95
$(C_6H_5O)_2PN$	6, -8	160	390	380	60, 61, 95
$(p\text{-}Cl\ C_6H_4O)_2PN$	4	167, 169	365, 356	410	63, 73
$(p\text{-}CH_3C_6H_4O)_2PN$	0	152	340	310	79
$(p\text{-}C_2H_5C_6H_4O)_2PN$	-18	43	-	285	79
$(CH_3HN)_2PN$	14	140	-	-	61
$((CH_3)_2NH)_2PN$	-4	-	-	-	95
$(C_2H_5NH)_2PN$	30	-	-	-	95
$(C_3H_7NH)_2PN$	-92	-	-	-	61
$(C_6H_5NH)PN$	91- 105	-	-	-	64
$(p\text{-}ClC_6H_4NH)_2PN$	85	-	-	265	64
$(p\text{-}CH_3C_6H_4NH)_2PN$	97	-	-	250	64
$(p\text{-}C_2H_5C_6H_4HN)_2$	88	-	-	245	64
$(p\text{-}n\text{-}C_4H_9C_6H_4NH)_2PN$	53	-	-	253	64
$(p\text{-}FC_6H_4NH)_2PN$	-	-	-	260	64
$(C_3F_7CH_2O)_2PN$	-65	14(?)	100	270	81
$(C_2F_5CH_2O)_2PN$	-25(?)	38(?)	-	260	61
$(CF_3CH_2O)_2PN$	-66	80, 92	242	360	63, 71, 79, 95
$(C_3F_7CH_2O)(C_3CH_2O)PN$	-77	-	260(?)	-	92
$(CF_3CH_2O)(C_3F_7CH_2O)PN$	-95	-	-	572	92, 93
$(CF_3C_6H_4)_2PN$	-35	-	330	-	71

(continued)

TABLE 2 (continued)

Product	T_g (°C)	T_F (°C)	T_m (°C)	T_d (°C)	Refs.
$(m\text{-}ClC_6H_4O)_2PN$	-24	66	370	380	60, 79
$(m\text{-}CH_3C_6H_4O)_2PN$	-25	90	348	350	79
$(m\text{-}CF_3C_6H_4O)PN$	-35	-	330	-	71

[a] Where T_g = glass transition temperature; T_F = first-order transition, possibly related to a major crystal disorder process; T_m = melt temperature; and T_d signals the onset of decomposition.

From a practical point of view, polyphosphazenes are usually soft just above the lower transition, so that compression molding of films can be carried out. This suggests that the lower transition represents the upper temperature for most useful engineering applications of polyphosphazenes in an unmodified form [79].

The results indicate that organization in the mesomorphic state, as influenced by thermal history, has a great effect on the transition from a crystalline state in an unmodified form [79]. .

Following are brief reviews (containing only examples) for the three classes of polyphosphazenes.

Linear Polyphosphazenes. The thermal transition behavior of poly[bis(trifluoroethoxy phosphazene)] has been studied well [80]. Crystallization from the melt occurs at a degree of supercooling comparable to the mesomorphic-to-crystal transformation. Annealing carried out at 236°C, somewhat into the melting range, produces a higher melting component. Such thermal studies have been intercorrelated with optical microscopy and x-ray diffraction studies [87]. The results indicate that organization in the mesomorphic state, as influenced by thermal history, has a great effect on the transition from a crystalline to mesomorphic state. Optical microscopy on a solution-cast film showed that the details of spherulitic morphology persist through the transition from a crystalline to mesomorphic state (~90°C) and remain through T_m (~240°C). The apparent heat of fusion at 90°C is about 10 times greater than at 240°C.

The x-ray examination of poly[bis(trifluoroethoxyphosphazene)] shows that the lower transition at 90°C corresponds to a transformation from a crystalline to mesomorphic state (63, 71b). Above 90°C the pattern is reduced to a single sharp reflection at 11A which is interpreted as representing lateral chain packing order. Optical microscopy shows that birefringence persists up to 240°C, confirming the existence of a partially ordered state between 90 and 240°C.

This type of study (illustrated for poly[bis(trifluoroethoxyphosphazene)]) is typical of many studies concerning polyphosphazenes, making this class of inorganic polymers one of the best studied groups by thermal analysis and companion techniques.

Poly(difluorophosphazene), $\leftarrow NPF_2 \rightarrow$, exhibits by DTA a T_g of -96°C, a crystalline transition detectable at -68°C, and polymer liquification about 270°C [61]. Good correlations have been found between the thermal transitions and polymer conformational structure utilizing x-ray diffraction techniques [87].

There are both low molecular weight, end-capped poly(dichlorophosphazenes) and high molecular weight polymers. The low molecular weight polymers are stable to greater than 300°C but are quite sensitive to hydrolysis [88]. The high molecular weight polymers exhibit a T_g of -63°C, and a crystalline melting temperature near -30°C [89]. Again, good correlative studies exist between x-ray diffraction and thermal transitions [61, 90]. Further, a good deal is known about the interrelationship between thermal properties and mechanical properties (for instance, Ref. 91).

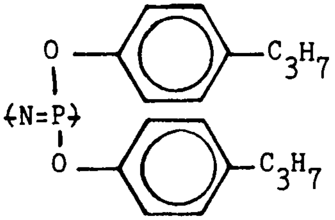
Poly(dibromophosphazene) has a T_g near -15°C and liquifies near 220°C [61].

Poly[bis(methoxy)phosphazene], $\leftarrow NPOMe)_2 \rightarrow$ shows a T_g of -76°C and has a low thermal stability with the intrinsic viscosity falling from 1.02 to 0.095 dL/g after 8 h of heating the solid at 100°C. Poly(bis(m-chlorophenoxy)phosphazene] exhibits a T_g of -37°C and a decomposition temperature of about 350°C [62]. Chain scission accompanied by weight loss occurs under isothermal conditions at considerably lower temperatures (200°C). At 165°C chain scission occurs with evidence pointing to degradation occurring by a random mode rather than by a zipper or reversion (depolymerization) mode [62]. Nevertheless, the product is more stable at 165°C in air than is polystyrene [62]. This points out the need to cross-correlate molecular weight data with thermal measurements particularly for products that undergo degradation through reversion.

The manner in which depolymerization occurred was also followed by gel permeation chromatography, an especially useful tool for studying reactions including reversion. Several mechanisms may be active, leading mainly to cyclic species through depolymerization. It is possible that many such depolymerizations occur in response to thermodynamic factors since equilibration between cyclic and polymeric species often exists at ambient temperatures in solution and at about 100°C in bulk. This thermodynamic driving force for depolymerization appears to result from intramolecular steric hindrance in the polymer which is diminished in the cyclic oligomers. It is possible that many polymeric phosphazenes are stable under a particular set of conditions only because the rate of depolymerization under those conditions is slow. This further suggests why depolymerization varies so much from state to state. In glassy and bulk situations the chains are "held" from forming cyclic structures whereas no such inhibition exists in solution. It also suggests that high temperature applications might be met by "locking" phosphazene chains into solid matrices. It would be worthwhile to evaluate a number of other inorganic and organic polymers which may undergo thermal degradation by depolymerization routes to see if, in fact, similar thermodynamic factors are in action. This would enable the development of a more rational viewpoint for synthesis and use of such materials in high and low temperature applications.

Depolymerization may not be the only thermal degradation route. Some of the interest in the polyphosphazenes is due to their variable physical properties and their high resistance to flammability [80b]. Polyphosphazenes, particularly polyaryloxyphosphazenes, are currently being considered for commercial applications as fire-resistant coatings and foams and as fire-retardant additives. Since several polyphosphazenes, including polydichlorophosphazene, have been shown to depolymerize at elevated temperatures [94], there is concern that polyorganophosphazenes might undergo similar thermal degradation at less than acceptable temperatures, particularly over an extended time period. Initial studies showed that many polyorganophosphazenes do not undergo appreciable weight loss until 300°C [80c, 92]. This does not accurately reflect their thermal stability because the weight loss was due to the distillation of oligomeric fractions and severe molecular weight reduction may have occurred at a considerably lower temperature. Several studies report that polyaryloxyphosphazenes can undergo depolymerization as low as 150°C which would severely limit their use as flame-resistant and fire-retardant materials [58, 62, 74].

Goldfarb et al. [80d] recently studied the thermal degradation of poly[bis(p-isopropylhenoxy)phosphazene] (XXXI) following a change

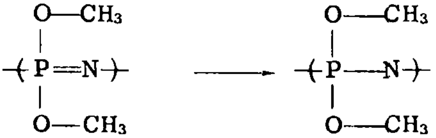


XXXI

in molecular weight by gel-permeation chromatography over the range of 100 to 300°C. While not conclusive, there was strong evidence that XXXI degrades through a scission rather than a depolymerization process with XXXIIa remaining stable to 200°C. Molecular weight began to gradually decrease even at 100°C after 96 h. Molecular weight began to decrease after 4 h at 135°C and after only 15 min at 200°C. Thus XXXI exhibits moderately useful long-term thermal stability only to about 100°C and short-term stability only to about

200°C. This may point to a clear problem in the use at least of some polyphosphazenes in high or even moderate temperature applications, and the need to study each polymer separately to determine the thermal parameters. Data were treated utilizing a digital computer, again emphasizing the desirability and usefulness of using computers to assist in the analysis of thermal and thermal related data.

Mochel and Cheng [80e] utilized ^{13}C NMR in studying the thermal rearrangement that occurs in poly(bismethoxyphosphazene) (XXXIIa) at 130°C. The migration of a methyl group from methoxy to the nitrogen also occures in the cyclic tetramer.



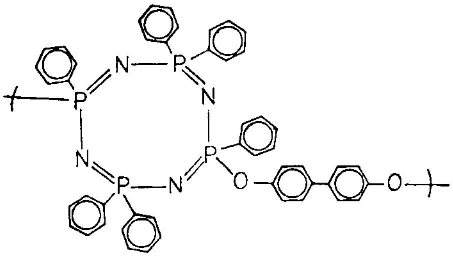
$$-\!\left(\overset{\displaystyle O-CH_3}{\underset{\displaystyle O-CH_3}{P}}=N\right)\!- \longrightarrow -\!\left(\overset{\displaystyle O-CH_3}{\underset{\displaystyle O-CH_3}{P}}-N\right)\!- \tag{6}$$

XXXIIa XXXIIb

Many other linear poly(alkoxyphosphazenes) and poly(aryloxy phosphazenes) have been evaluated using various thermal techniques—usually TG and DSC (or DTA). Most have T_g's from -84 to 20 but undergo reversion below 350°C (for example, Refs. 61, 79, 89, 92-94). Also, there are a number of good studies correlating x-ray diffraction measurements with thermal transitions [61, 77, 79].

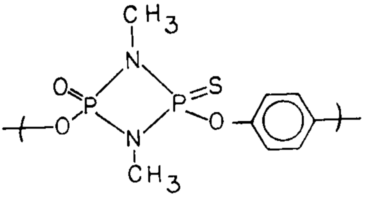
A number of linear poly(diaminophosphazenes) and copolymers have been studied (such as in Refs. 61 and 95). For instance, the presence of mixed substituents in the poly(arylaminophosphazenes) had little effect on the thermal behavior of the polymers with T_g's from 70-110°C and decomposition temperatures from 200-280°C [64, 68]. The arlyamine copolymers, like the homopolymers, show no evidence of having first-order endothermic melting points, indicating lack of crystalline nature. On the other hand, aryloxyphosphazene homopolymers and copolymers of a semicrystalline nature have been prepared [60, 85].

Cyclolinear Polymers. The development of cyclolinear phosphazene products resulted from attempts to utilize the thermal stability of cyclotetra- or cyclotriphosphazene rings while retaining flexible and elastic properties. Considerably fewer thermal studies have been reported involving cyclolinear phosphazene polymers compared to the linear polymers. Some products offer no thermal stability advantage over the linear polymers while others appear to offer significantly better weight retentions (see Refs. 96-100). Product XXXIII was stable to about 470°C whereupon benzene and oligomeric $(\phi_2PN)_x$ (where x is less than five) were detected as pyrolysis products, indicating that cleavage of the ring was the initial decomposition reaction.



XXXIII

Product XXXIV shows weight retention to 590°C [99].



XXXIV

Cyclomatrix Products. Phosphazene cyclomatrix products are generally formed from the cross-linking of cyclic trimeric or tetrameric rings yielding insoluble, rigid, high-melting resins, many with thermal stabilities equal to or greater than the linear phosphazenes (such as in Refs. 101-104). Less effort has been focused on the thermal characterizations of these cyclomatrix products compared with the linear products. Some products are stable for continuous use at 250°C and for intermittent use at temperatures to 540°C [102-104].

Polyphosphonylhydrazides, Polyphosphonylureas, and Related Compounds

Thermal analysis has been done on a number of products synthesized by the condensation of arylphosphonic dinitrile and arylphosphonic diisocyanate with diamines, hydrazides, hydrazines, thioureas, and thioureas (such as in Refs. 105-124 and Structure XXXV).

The thermal stability of P–N products has been reported to be considerably less than that of carbon analogs [43, 44] with most carbon analogs exhibiting almost total weight loss at temperatures less than 400°C. The urea linkage generally undergoes thermal dissociation about 150 to 200°C while the urethane moiety decomposes at about 225 to 300°C [43]. Polyureas generally begin decomposing at about 150 to 200°C with almost complete weight loss about 400 to 500°C while polyurethanes begin decomposing at about 260°C with degradation complete about 400°C.

Products of the classes mentioned in the subheading and illustrated by XXXV can exhibit some "resonance double bond" character throughout at least a portion of the polymer backbone. This "double bond" character appears to enhance the thermal stability of such products. For instance, most products begin decomposing about 100 to 200°C in both air and nitrogen. Nevertheless, by 400°C most show about 50% weight retention. Thus the phosphorus polymers exhibit a markedly better high temperature weight retention than the C–N analogs. Physical and chemical examination of these P–N polymers and residues should be made, in particular noting if desired properties remain within the residue. The poor low temperature stability and moderate to good high temperature stability (weight retention) is typical of many inorganic polymers and is undoubtedly due to the formation of more thermally stable residues through degradation occurring at a lower temperature. The composition and properties of such residues would be of value in evaluating the overall stability and designing thermally stable inorganic polymers.

Attempts to trap degradation products utilizing Dry Ice, liquid nitrogen, etc., proved largely unsuccessful with water being the only isolated degradation product [105]. Most systems evolved nitrogen-containing volatile products with pK_a's about 7 to 11. Several products evolved toxic volatiles, pointing out the need for thermal analysis systems to be properly vented [105].

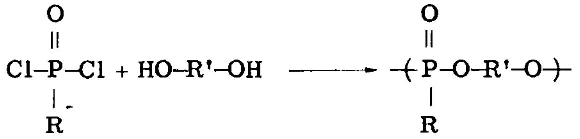
Degradation patterns are apparent when considering each polymer family with weight retention approximately independent of the nature of "R" within a diamine ($H_2N–R–NH_2$), etc. This indicates that the critical bonds involved in the chain stability are not associated with the N–R–N moiety.

The degradation of many of these products was followed utilizing infrared spectroscopy. In general, as degradation proceeds, absorptions associated with P–aryl decrease in intensity, indicating that P–aryl bond scission is one of the initial steps in the degradation. Bands associated with carbonyl groups in the ureas and urethanes also decrease, indicating that the carbonyl group is split out, giving CO in nitrogen and/or CO_2 in air. There is indication that amine moieties are formed from amide units. It would be useful to compare these spectral observations on the residue with GC-MS and TG-MS observations on the volatilized products.

Other Phosphorus-Containing Products

Again there exists a large variety of synthesized products where little thermal analysis has been conducted on the products. Examples where analysis has been conducted follow.

Diimidazolyl phosphorus and dichlorophosphorus compounds have been allowed to react with a large number of diamines and diols to yield high molecular weight products (for instance, in Refs. 125-137 and Structure XXXVI). Earlier reports are that such products (reaction with amines) melted at least 100°C lower than the corresponding

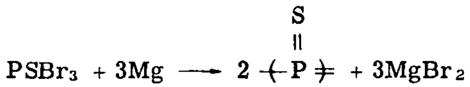


$$\mathrm{Cl{-}\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle R}{\underset{|}{P}}}}{-}Cl + HO{-}R'{-}OH \longrightarrow {+}\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle R}{\underset{|}{P}}}}{-}O{-}R'{-}O{+}} \qquad (8)$$

XXXVI

carboxylic polyamides [136] and that their thermal stabilities by TG were considerably poorer than the carbon analogs [44]. Later study indicates that at least some polyphosphates, polyphosphonates, polyphosphonamides, and polyphosphorylamides exhibit equal or greater melting points and greater high temperature (400°C) weight retentions [138].

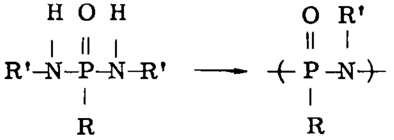
Polymeric phosphorus monosulfide (XXXVII) exists in both a crystalline form which decomposes at 240°C and an amorphous form which decomposes about 135°C [139].



$$\mathrm{PSBr_3 + 3Mg \longrightarrow 2\,{+}\overset{\displaystyle S}{\overset{\|}{P}}{+} + 3MgBr_2} \qquad (9)$$

XXXVII

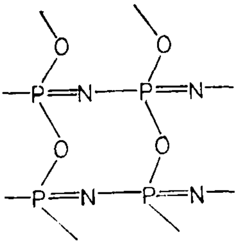
Linear polyphosphoramide resins (XXXVIII) are stable to about 300°C (R = phenyl) with the nature of R' having little effect on the thermal stability of the product [140].



$$\mathrm{R'{-}\overset{\displaystyle H}{\overset{|}{N}}{-}\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle R}{\underset{|}{P}}}}{-}\overset{\displaystyle H}{\overset{|}{N}}{-}R' \longrightarrow {+}\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle R}{\underset{|}{P}}}}{-}\overset{\displaystyle R'}{\overset{|}{N}}{+}} \qquad (10)$$

XXXVIII

Phosphorus oxynitride (XXXIX) is nonvolatile and melts above 1000°C to form a glass [141] although slow decomposition occurs to form P_4O_{10}, phosphorus nitride, and nitrogen at 750°C under reduced pressure [142]. Surprisingly, this is not reported to occur at atmospheric pressure [142]. This was done in 1937 before most of the commercial thermal tools were well developed. A restudy might be considered. This example is utilized to illustrate the need to reevaluate many older findings using modern thermal methods.



XXXIX

Polymeric Sulfur Nitride

The past several years have witnessed a remarkable growth of interest in polymeric sulfur nitride (XL) based on the findings of Labes, MacDiarmid, et al. which demonstrated that polymeric sulfur nitride exhibits some metallic properties (see Refs. 143-152). Analysis of polymeric sulfur nitride should be preceded by heating to about 75° C with constant pumping in vacuum as described by Mijulski et al. [145] to promote polymerization of oligomeric sulfur nitride and to remove traces of unpolymerized dimeric sulfur nitride. While $(SN)_x$ was prepared as early as 1910 by Burt, only recently have good preparations yielding pure crystalline material been available [145]. Thus pre-1975 thermal results should be viewed as tentative until they can be checked utilizing adequately pure polymeric sulfur nitride crystals. Since polymeric sulfur nitride crystals are highly anisotropic regarding optical and electronic properties, it would be expected that certain thermal properties (such as TMA) also be anisotropic which could lead to a number of interesting and useful applications.

$$-\!(S-N)\!- \longrightarrow -\!(S=N)\!- \tag{11}$$

XL

Polymeric sulfur nitride decomposes rapidly when heated above about 208°C. Under vacuum at 140 to 150°C it slowly decomposes to sulfur, nitrogen, and other as yet unidentified substances [145]. It can be sublimed in vacuum at 140 to 150°C without decomposition–an unusual property for a polymer [151, 152]. The polymer undergoes decomposition if exposed to the atmosphere for extended periods though no change in the x-ray diffraction pattern occurs after 2 weeks exposure [145]. Other thermal properties are given in papers by MacDiarmid et al. [151, 152].

Catenation Polymers

Polymeric Sulfur

Catenation polymers are those which contain only one element in the backbone.

Polymeric sulfur is one of the earliest, best studied inorganic, catenation polymers with Tobolsky and co-workers being responsible for most of this information [153, 154].

When heated in a sealed evacuated tube, orthorhombic sulfur melts to a pale yellow liquid of low viscosity at about 113°C. This material is largely S_8 rings. If heated to 159°C and above (preferably to 200 to 250°) and then rapidly quenched to about -20°C, a transparent elastic product is obtained. Polymeric sulfur is obtained through extraction of this material with carbon disulfide with the nonpolymeric sulfur dissolving. Equilibrium, kinetics, thermodynamics, and physical characterizations are reviewed by Meyer [153] and Tobolsky and MacKnight [154].

Both semicrystalline and elastic polymeric sulfur exhibit T_g's with T_g rising with increasing chain length to about 500 atoms where the T_g approaches a limiting value. Amorphous polymeric sulfur shows a T_g at about -30°C. Above -30°C it becomes elastic, beginning to lose its rubbery properties due to crystallization. Crystalline or semicrystalline polymeric sulfur, often symbolized by S_ω, can be synthesized in this way or by a number of other procedures (such as in Refs. 155 and 156), and exhibits an inflection at 75°C, presumably its T_g. The S_ω shows a glassy region below 75°C followed by the beginning of a transition regions. The melting point of S_ω has not been determined directly because of the transition to rhombic sulfur which becomes rapid about 90°C.

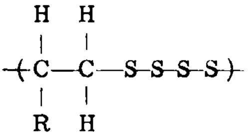
It is currently believed that the elastic sulfur is a solid solution of amorphous polymeric sulfur rings (mostly S_8), the rings acting as a plasticizer to lower the T_g from 75 to -30°C.

Particular thermal properties and polymeric fine structure correlation studies are still being conducted. Reversion is a typical mode of degradation for polymeric sulfur:

$$-\!(S)\!-_x \rightleftharpoons -\!(S)\!-_{x-8} + S_8; \qquad -\!(S)\!-_{x-8} \rightleftharpoons -\!(S)\!-_{x-16} + S_8; \qquad \text{etc.} \tag{12}$$

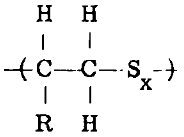
Sulfur Compounds Other Than Polymeric Sulfur

With the exception of carbon, sulfur has the greatest tendency to catenate. This leads to a wide variety of products whose properties and structure reveal a generic connection with elementary sulfur (S_1 to S_8 units). Thus, while polysulfides are not catenation polymers, they will be discussed here. The only polysulfides having commercial significance as polymers are the thiokols with most being substituted ethylene tetrasulfides (XLI).



$$-\!\!\left(\overset{H}{\underset{R}{C}}-\overset{H}{\underset{H}{C}}-S-S-S-S\right)\!\!-$$

XLI



$$-\!\!\left(\overset{H}{\underset{R}{C}}-\overset{H}{\underset{H}{C}}-S_x\right)$$

XLII

Degradation of saturated tetrasulfides at 140-150°C leads to the formation of higher and lower molecular weight polysulfides by S–S bond scission followed by recombination of different radical pairs [157]. Decomposition of unsaturated polysulfides at 170-180°C gives thiols and H_2S which probably results from hydrogen abstraction from alpha-methylene groups by sulfide or sulfur radicals [157].

T_g's are generally below room temperature (20 to -80°C) for the polysulfide polymers with crystallization occurring above their T_g's. Because the polymers are generally irregular (i.e., contain $X = 1$ to 8 for XLII), the melting region is diffuse and varies with preparation; the latter results from a varying number and ratio of S_x units according to method and conditions of preparation.

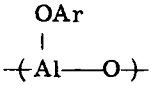
A number of copolymers of polysulfides have been synthesized and some thermal properties evaluated (for instance, Ref. 158). T_g's generally vary from about room temperature to -80°C depending on the nature of the hydrocarbon moiety and S_x [154]. A number of equations have been developed dependent on such parameters as the coefficient of cubical expansion, weight fractions of various components of the polysulfide, and stress relaxation parameters to relate such parameters with thermal properties and viscoelastic properties [154]. These studies are fairly complete regarding the parameters studied and instrumentation utilized, but an updating utilizing more modern instrumentation (such as TMA and torsional braid analysis with companion instrumentation such as x-ray spectroscopy) should be considered.

Other Compounds

Selenium and tellurium exhibit a behavior similar to sulfur [159]. Products produced by the thermal polymerization of selenium are terminated by free radicals making chain length particularly sensitive to impurities. Both selenium and tellurium products are oligomeric. Also, while germanium, tin, arsenic, antimony, and bismuth catenate, none forms stable high polymers.

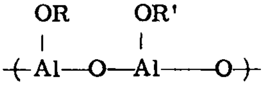
Aluminum-Containing Polymers

A number of aluminum-containing polymers have been prepared by various techniques. Arloxy polyaluminum oxides (XLIII) all showed poor thermal stability, disproportionating on heating [160]. Related products (XLIV) showed somewhat better stability but generally lost about 30% of their weight by 500°C (in nitrogen) [44, 161].



$$\left(\overset{\displaystyle OAr}{\overset{|}{Al}} — O \right)$$

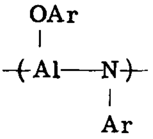
XLIII



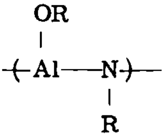
$$\left(\overset{\displaystyle OR}{\overset{|}{Al}} — O — \overset{\displaystyle OR'}{\overset{|}{Al}} — O \right)$$

XLIV

Aryloxy (and alkyloxy) polyaluminum amines (XLV and XLVI) all showed poorer thermal stabilities than the Al–O counterparts with decomposition beginning below 200°C and major decomposition occurring at 300°C with the formation of modified alumina [161].



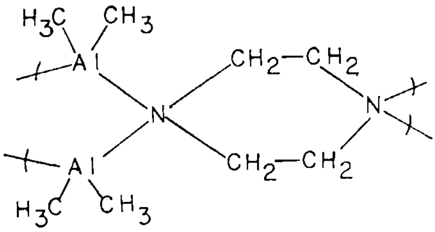
$$\left(\overset{\displaystyle OAr}{\overset{|}{Al}} — \underset{\displaystyle Ar}{\underset{|}{N}} \right)$$



$$\left(\overset{\displaystyle OR}{\overset{|}{Al}} — \underset{\displaystyle R}{\underset{|}{N}} \right)$$

XLV XLVI

Bridged alkyl polyaluminum amines (XLVII) decomposed in air above 200°C [162].



XLVII

ORGANOMETALLIC POLYMERS

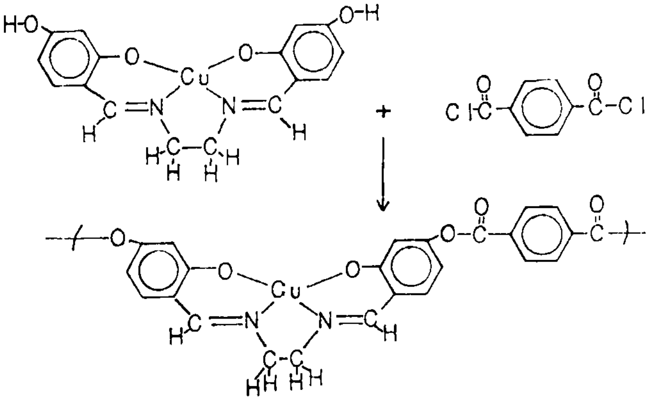
Coordination Polymers

General

Coordination polymers have been used for many years though they have not been recognized as such until fairly recently [163a]. Much of both the synthetic and thermal characterization occurred from the late forties to the late sixties. Most of this work was supported by the U.S. Air Force and other military associated organizations aimed at finding polymers that would be stable to 500°C. This program drew attention to the possibility of utilizing polymers formed from the coordination of metal ions to organic materials containing Lewis bases. Some success was experienced. Martin and Judd [163b] synthesized a number of metal derivatives of thiopicolinamides with several of the zinc compounds showing stability in the absence of air to 400°C.

The variety and types of coordination polymers synthesized and briefly characterized thermally (before 1970s mainly through the use of TG alone utilizing a modified revision of a TG described by Winslow and Matreyek [164]) is large. Coordination polymers are typically formed utilizing one of three general routes as follows:

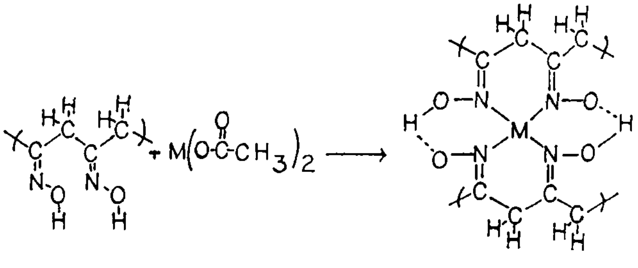
1. Polymerization of a coordination compound:



(13)

XLVIII

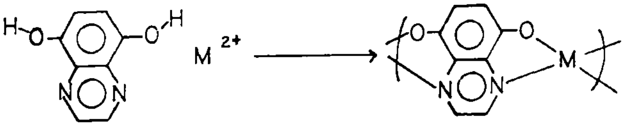
2. Use of a preformed inorganic or organic polymer to which metal ions can be chemically bound:



XLIX

(14)

3. Use of ligands which can simultaneously attach to two or more metal ions:



L

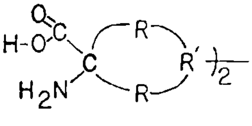
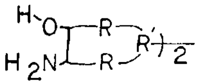
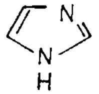
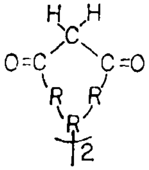
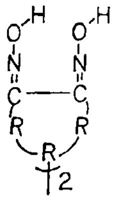
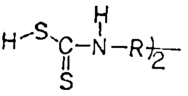
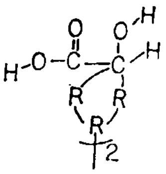
(15)

Polymers formed from Routes 1 and 3 usually contain the metal arranged in a systematic order whereas products derived from Route 2 contain the metal atom present in a somewhat disordered fashion. Polymers used to complex chelate metal ions using Route 2 include polyvinyl alcohol, polyethyleneimine, polysodium acrylate, cellulose, and protein. Ligands utilized in Route 3 are given in Table 3. Little can be gained from covering each coordination polymer since there is such a variety of compounds and results. Several examples will be reviewed illustrating this diversity. Additional specific examples are found in Refs. 165-171.

Situations involving products formed from simple binding such as Cu(II) to poly(methacrylic acid) [172], Cu(II) to poly(acrylamide) [173], effects of metal oxides on poly(vinyl chloride) [174], and metal-containing cross-linked polyesters resins [175] will not be covered in this review. The topic of ion binding in ionic polymers was recently reviewed and will not be covered here [171].

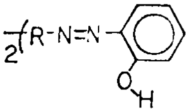
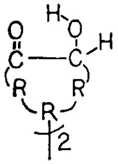
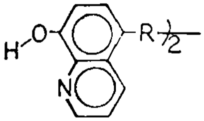
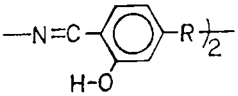
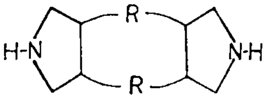
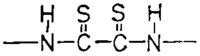
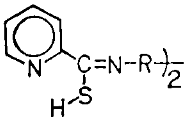
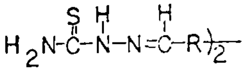
It has often been reported that organic molecules are usually stabilized with respect to hydrolysis, thermal oxidation, and thermal degradation through coordination with metal ions [176-178]. Following are results which illustrate the actual complexity betwen metal complexation and thermal stability. Thus 8-hydroxyquinoline (XLVII) sublimes rapidly at about 25°C in vacuo, while the nonpolymeric zinc sublimes at greater than 250°C [180]. Complexes of XLVII with Ni(II) and Cu(II) decompose in air at 230°C [181]. Nonpolymeric zinc-salicyclaldehyde-o-phenylene diamine loses less than 5% weight after 24 h in air at 250°C whereas the related Schiff base coordination polymer shows a 12% weight decrease after only 3 h in air at 250°C.

TABLE 3. Chelates Utilized in the Synthesis of Coordination Polymers through Chelation with Metal Ions

Chelate group	Representative structure
Bis-1,2-amino acids	
Bis-o-aminophenols	
Bis-diamines	  ETC.
Bis-β-diketones (bis-1,3-diketones)	
Bis-1,2-dioximes	
Bis-dithiocarbamates	
Bis-α-hydroxyacids	

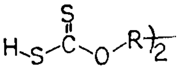
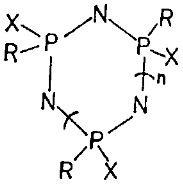
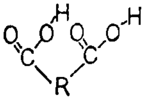
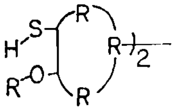
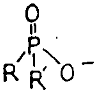
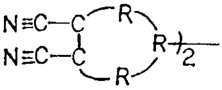
(continued)

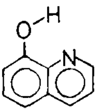
TABLE 3 (continued)

Chelate group	Representative structure
Bis-o-hydroxyazos	
Bis-1,2-hydroxyketos	
Bis-hydroxy nitrogen heteroaromatics	
Bis-o-hydroxy Schiff bases	
Bis-imides	
Bis-thiooxamides	 $-\overset{\text{H}}{\text{N}}-\overset{\text{S}}{\text{C}}-\overset{\text{S}}{\text{C}}-\overset{\text{H}}{\text{N}}-$
Bis-thiopicolinamides	
Bis-thiosemicarbazones	 $\text{H}_2\text{N}-\overset{\text{S}}{\text{C}}-\overset{\text{H}}{\text{N}}-\text{N}=\overset{\text{H}}{\text{C}}-\text{R})_2-$

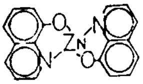
(continued)

TABLE 3 (continued)

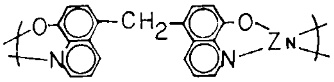
Chelate group	Representative structure
Bis-xanthanes	
Cyclophosphazenes (with chelating groups)	
Dicarboxylates	
Dimercaptodiethers	
Phosphinous anions	
Bis-o-nitrites and 1,2-dinitriles	



LI

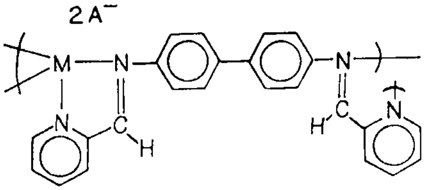


LII



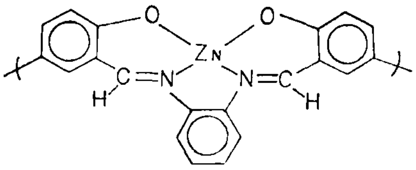
LIII

Most of the polymeric metal complexes of bis(2-pyridinal)-biphenylene-4,4'-dimine (LIV) are less stable than the metal-free organic molecule itself. The organic complexing agent itself less than a 1% weight loss at 250°C in 12 h whereas products where M = Fe(II), Co(II), Ni(II), Cu(II), Hg(II), and Zn(II), (for A = NO_3) all showed greater weight losses under similar conditions [183].



LIV

Thus there appears to be no general trend with respect to metal complexation stabilization and each polymer must be studied separately. This is true for even first row divalent transition elements. For instance, for product LIV the overall order of heat stability for the chloride-containing complexes is Cd ≅ Ni > Cu ≅ Co ≅ Hg ≫ Fe whereas the order of the nitrate containing complexes is Cd ≫ Co > Ni > Hg > Zn ≫ Cu ≅ Fe (all plus two metal ions; Ref. 183). For products of form LIV, the stability (weight retention) is Fe > Ni > Zn > Co > Cu [182].



LV

Much of the lack of clear trends with respect to metal ion may be due to either the actual wide diversity and importance of the organic complexing agent employed or the inadequate structural characterization of the individual products. The mechanisms for thermal degradation are largely unknown. If a zippering decomposition is operative, then endgroup characterization would be especially useful in discerning stability trends. The method of synthesis and purification, reagents utilized, etc. should be considered particularly important for proper stability evaluations of coordination polymers. Since this has not been usually done, the results thus far cited in the literature should be viewed as tentative. It would be useful if the (supposed) same products could be synthesized utilizing several techniques [certain products could be prepared by aqueous solution, melt, nonaqueous solution, and interfacial techniques (for instance, in Ref. 184)]. Extensive thermal analysis of the products could be carried out after adequate structural characterization of the products.

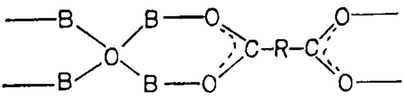
One should be continually aware of the meaning of weight retentions, particularly with metal-containing products which can oxidize at lower temperatures leaving not a desired moldable and/or flexible product but rather a powdery metal oxide. Even in an inert atmosphere the metal-containing moiety generally is one of the last to volatilize. For instance, the Schiff base coordination polymers of 5,5'-p-phenylene-bis(methylidynenitrilo)di-8-quinolinol show reasonable weight retention to 400 to 500°C with only about 15-35% weight losses, but on considering the metal content this represents 50 to 75% loss of the organic portion of the polymer [177].

Further there exists considerable difference in trends with respect to the atmosphere utilized. Utilizing air as the atmosphere, coordination polymers of 5,5'-[p-phenylene-bis(methylidylnenitrilo)]di-8-quinolinol and 5,5'-[methylene-bis(p-phenyledeenitrilomethylidyne)]-di-8-quinolinol of form XLIX exhibit the stability order Mn $<$ Co $<$ Ni $<$ Cu $>$ Zn whereas in vacuo the trend is Mn $>$ Co $>$ Ni $>$ Cu $<$ Zn [179]. This is not unexpected since stability of products studied in vacuo probably depends most on inherent bond strengths whereas the stability of products studied under oxidative conditions depends primarily on the tendency and accessibility of the metal toward oxidation.

Finally, TG thermograms of coordination polymers generally show the characteristic stability plateaus with some of the plateaus continuing onto 1000°C with over 30% weight retention. Characterization of the degradation product is seldom pursued, probably due to a greater interest in the overall stability of the products rather than the degradation products.

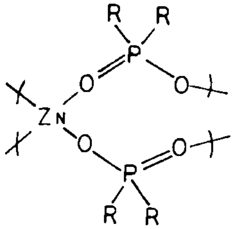
Alkoxide and Carboxylate Bridge Products

Beryllium carboxylated products (LVI) appear stable to 400°C utilizing TG weight retention but actually disproportionate even at room temperature [185], again emphasizing the need to utilize other analysis techniques in tandem with TG.



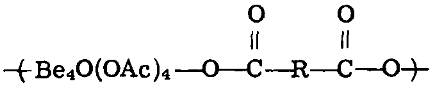
LVI (possible structure)

Inorganic spiro compounds of Type LVII formed from zinc acetate and diphenylphosphonic acid show good thermal stability in nitrogen with no weight loss to 550°C [186].



LVII

Because of the good thermal stability of basic beryllium acetate, a number of attempts have been made to incorporate it into polymers. Low molecular weight polymers from adipyl and terephthalyl chloride (LVIII) are stable to 400°C in nitrogen [185].

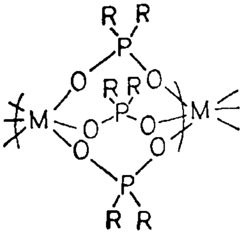


$$-\!\left(\mathrm{Be_4O(OAc)_4{-}O{-}\overset{O}{\overset{\|}{C}}{-}R{-}\overset{O}{\overset{\|}{C}}{-}O}\right)\!-$$

LVIII

A number of inorganic coordination polymers have been synthesized by Nannelli, Gillman, Block, and co-workers [186a-186j], including a number of poly(metal phosphinates). One of the most studied families is the chromium(III) trisphosphinates which give brittle or flexible films depending on the preparation of the chromiun(III) bisphosphinate precursor. The films contain mainly triple-bridged chains (LIX).

Gillham [186d] reported the thermomechanical behavior of a number of chromium polymetalphosphinates using TBA. Towle and Nannelli [186h] studied the shear and friction strength of selected films of LIX while Scott et al. [186i] reported on the magnetic properties of these films. More recently Nannelli, Gillman, and Block [186c] reported on thermal properties (TG) of LIX. Thermal



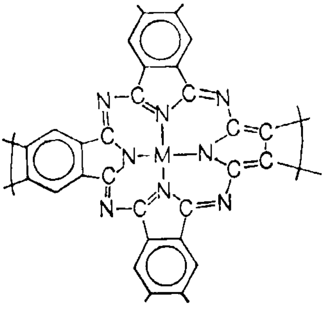
LIX

degradation of the films proceeds in air through oxidation and cleavage of the organic side groups with a degradation inception temperature around 200°C. The gas chromatograms of the volatile decomposition products of $Cr[OP(CH_3)(C_6H_5)O]_2OP(C_8H_{17})_2O$ showed at least 14 products of which 2-octane, acetic acid, and n-butyric acid are among the most abundant. Decomposition does occur at 200°C for long exposure times with a 13% weight loss for an 18-h exposure time. Addition of antioxidants such as distearyl thiodipropionate increases the longevity of the polymer films flexibility at 200°C.

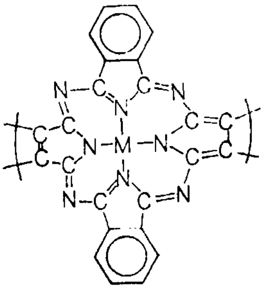
Caution should be exercised whenever any weight loss is involved if long-term applications are desired. For such situations, initial loss temperature may be a more accurate parameter of the product's true stability.

Polymeric Phthalocyanines

A number of phthalocyanines have been synthesized and thermally characterized (such as in Refs. 186h-191). Product LX is stable to 350°C but begins slow decomposition about 400°C in air [188, 189]. Products of Type LXI are crystalline, noncombustible materials which withstand prolonged heating at 500°C [190, 191].



LX (where M = Cu^{2+}, Fe^{2+})



LXI (where M = Cu^{2+}, Fe^{2+})

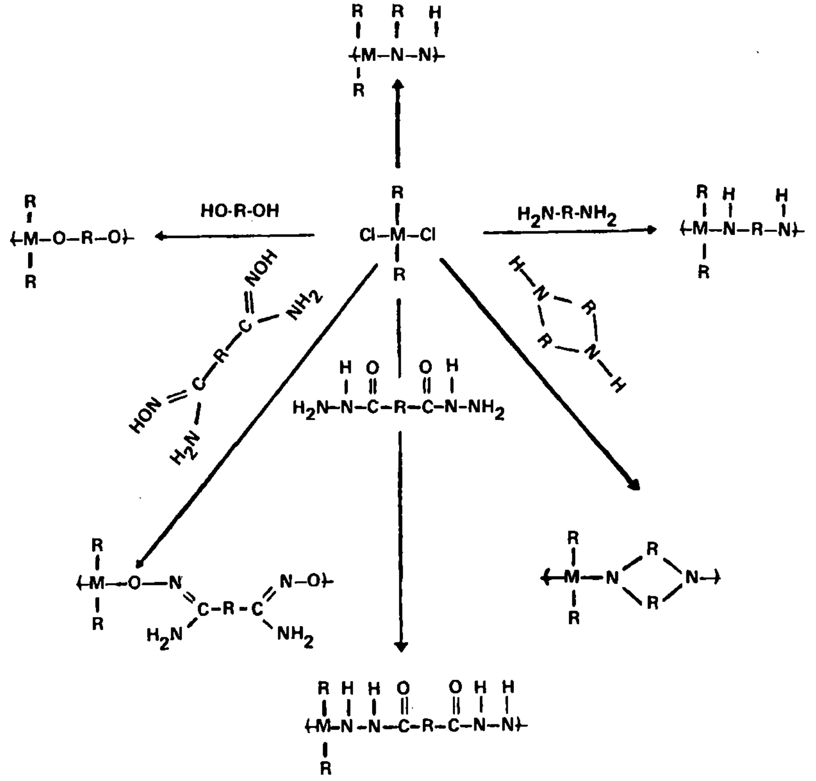


FIG. 1. Representative structures of condensation polymers.

Tin phthalocyanines polyamidoximes have recently been synthesized. These also show good stability in both air and nitrogen, exhibiting the usual thermal stability plateaus [192].

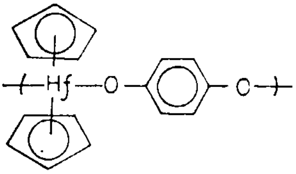
Organometallic Condensation Polymers

Here we will consider condensation products that contain both the metal atom and a hydrocarbon moiety in the polymer backbone. Again a wide diversity of products exists and are described in Refs. 193-273. Specific examples will be utilized to illustrate general trends. Figure 1 contains structures for some of the synthesized products showing the variety of compounds synthesized.

Most of the products exhibit moderate to high melting (or softening) ranges with many decomposing before melting occurs. The T_g's for most of these products are probably associated with a mildly endothermic region occurring, below 200°C, generally at or below 100°C. Infrared spectra for many of these compounds change only in the hydrogen bonding regions below 100 to 200°C [255] in agreement with a phase change such as a T_g occurring in this region. The ΔH's for these transitions are generally small, being in the order of magnitude of 10^{-2} cal/g (such as 250). Degradations above 100 to 200°C in inert atmospheres are typically endothermic with ΔH being about 10^{-2} to 10^{-1} cal/g.

Degradations in air are generally exothermic and more energetic ($\sim 10^{-2}$ to 10^{1} cal/g).

Actual thermal stability should be evaluated knowing at least some structural content of the residue. Most of the products considered here degrade in air to give the metal oxide which can be used as a quantitative determination of the metal content. Principal exceptions include the Group IVA products where each system must be studied separately since for some the metal oxide remains, while for others the metal-containing moiety is volatilized below 800°C and for some both occur. Thus a value generally referred to as minimum organic content (that is, the weight which would be present if only the metal oxide remained) should be included in weight retention reports assisting in the actual interpretation of such data. Thus for LXII there exists 40% residue at 900°C which may appear significant, yet it is all hafnium oxide, HfO_2 [243].

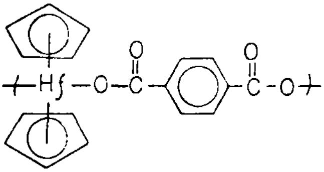


LXII

The products often exhibit what can be referred to as poor low temperature stability but moderate to good high temperature stability. Thus many products begin to degrade in both air and inert atmosphere (normally nitrogen and argon) within the 50 to 200°C range but retain adequate organic moiety content to greater than 500°C. Thus LXIII begins undergoing degradation in air about 200°C but retains 70% of its weight (25% minimum organic content) to 800°C whereupon it degrades to HfO_2 [252].

Almost without exception degradation occurs through a series of exothermic, oxidative paths in air, and occurs through a series of endothermic paths under inert conditions.

Color changes often accompany degradation in both air and nitrogen. In general, the products turn to a dark brown or black in the 300 to



LXIII

600°C range, normally becoming white by 800°C. The coloration probably results from the formation of conjugated intermediates. Spectra of products in the 300 to 600°C region generally show band broadening (compared to the original product) with a few new, sometimes sharp, bands formed about the 600 to 900 cm^{-1} region.

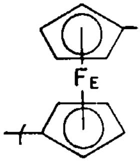
Stability in air is generally less than that in inert atmospheres probably because of the preferential oxidation at the metal site—particularly with transition metals and other metals with "low-lying" "d"-orbitals through which oxygen has entrance to the polymer backbone.

Thermal properties of a number of organometallic condensation products appear to be approximately independent of molecular weight beyond the oligomeric range. This probably results from the presence of a large amount of polar interchain interaction and is different than that observed for some vinyl organometallic and more classical polymers where thermal properties often vary through 100 units and more. Thus low molecular weight poly(ferrocene imine) degrades about 350°C whereas a higher molecular weight fraction was reported to be stable to 500°C [307-309].

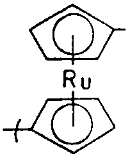
DSC appears to be a more precise indicator than TG when comparing degradation routes. Thus many TG thermograms appear similar in air and under an inert atmosphere yet the DSC thermograms are markedly different. Further, TG thermograms for many similar products, where the metal-containing moiety is held constant, can appear to be similar or quite different yet the DSC thermograms (particularly in air) often show similarity. The similarity with DSC thermograms is much less or missing when the metal moiety is varied [216]. This "similarity" in DSC thermograms is normally only a similarity in shape, number, and magnitude of "thermo peaks" and is not always observed. Thus the similarity in DSC responses for a given metal is only a general guide. This may be due to the metal bond in the polymer backbone generally being at least one of the "thermally controlling" sites dictating gross thermal stability. Thus the general temperature range of degradation and energy (whether exothermic or endothermic and general magnitude) related to degradation are mainly dictated by the metal bond sites which are sensitive to a lesser degree on the "organic" moiety. In terms of energy, oxidation in air appears to be the predominant reaction, with the (exothermic) energy related to oxidation overriding lesser energies associated more with the backbone "fine structure."

Tentatively then the mode and mechanism of degradation appears to be related directly to both the family type (polyether, polyester, polyamine, etc.) and the metal atom.

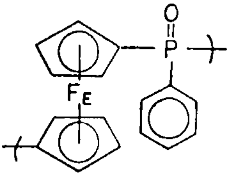
As a general rule polymers containing metallocene moieties within their backbone show only moderate thermal stability with degradation beginning about 300° C or below. For example, poly(ferrocenylenemethylene) (LXIV) begins to degrade in air about 300°C [275]; 1,1'-ferrocenylene-bridged polybenzborimidazoline in argon degrades about 100°C [276]; ferrocene poly(phenylphosphine oxide) (LXVI) in argon begins about 300°C [277-279].



LXIV

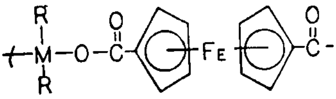


LXV

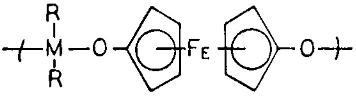


LXVI

Products containing a carboxylate unit connected to a ferrocene moiety (as LXVII) appear to degrade splitting out CO_2 and the ferrocene moiety–intact or fragmented. Degradation in air generally occurs about 250°C. The degradation is markedly rapid, possibly explosive, with sometimes as great as 70% weight loss occurring over a 10°C range [262]. [Such rapid weight losses suggest potential use as a solid (propellent) fuel.] On the other hand, products connecting the ferrocene moiety through another type of linkage (such as LXVIII) undergo degradation through a less rapid (weight loss-wise) route(s) as do polymers containing the cobalticinum moiety, including products containing the carboxylate moiety [225, 226, 231, 268, 269]. It would be of interest to note if this difference between the ferrocene polyesters and the cobalticinium polyesters (LXIX) is more related to the metallocene or the charged (salt) nature of the cobalticinium moiety.

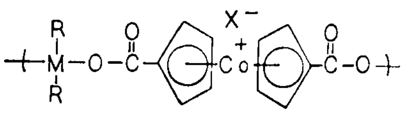


LXVII



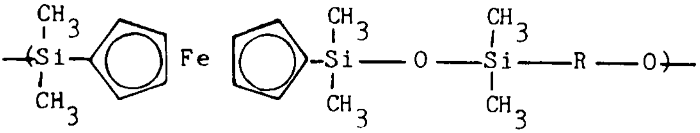
LXVIII

Pittman et al. synthesized a number of ferrocene-containing siloxane polymers condensing ferrocene bis(dimethylamino)silane



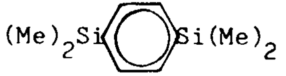
LXIX

with disilanols to evaluate the effect of the ferrocene moiety on the physical properties of the organosiloxane polymers [284b, 284c]. TG and DSC data in both air and nitrogen showed that many of the polymers formed from 1,1'-bis(dimethylaminodimethylsilyl)-ferrocene showed equal or greater thermal stabilities than polydimethylsiloxane and arylene siloxane polymers, which differed from the ferrocenylsiloxane structure LXX only in the replacement of the ferrocene moiety with a p-substituted phenylene linkage. The T_g for these products ranged from -2 to 37°C using torsional braid analyses (TBA). T_g values for a number of other oxysilane polymers were reported from both TBA and DSC with the two values generally within 5 C° of one another, showing the close correspondence of these two thermal analysis techniques for determination of thermal transition temperatures.

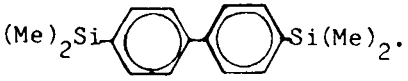


LXX

where R = Ø_2Si,

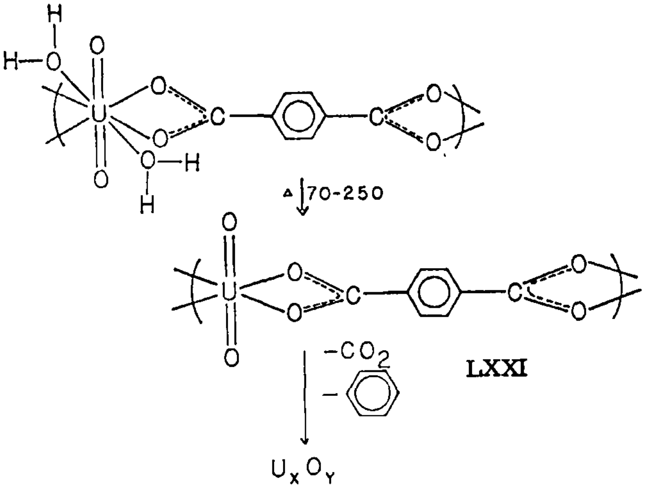


or



We recently began investigating the thermal stability of a number of condensation organometallic polymers utilizing TG-MS employing a Hewlett Packard 2116 Minicomputer for evaluation of the data [285a, 285b]. Such studies are supplemented with infrared studies of the residues at different temperatures. Two examples are given to illustrate the usefulness of this approach.

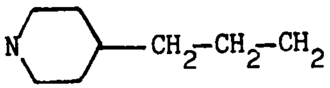
Uranyl polyesters were synthesized as part of a model project for uranium recovery and enrichment [264]. Polymer LXXI degrades at about 150°C to give mass bands at 18 and 17 amu, consistent with the evolution of water. This is verified by the disappearance, in the infrared region, of band about 3200 cm^{-1} characteristic of water. Further, the weight loss corresponds to within 0.2% to that of H_2O calculated based on LXXI. At about 450°C there is another weight loss and the appearance of mass units of 44, 16, 12, and 45 amu characteristic of CO_2 evolution and mass units at 76, 50, 51, and 38 amu in the proper proportion to be identified as originating from the phenylene moiety. The resulting residue consists of uranium oxides. No U-238 or other associated bands are found within the MS data consistent with the uranium remaining within the residue.



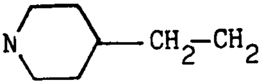
LXXI

(16)

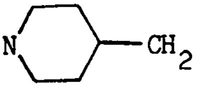
In our approach of using organometallic polymers as drug control release agents, we synthesized a number of manganese containing polymers including LXXII [285b]. Mass bands at 79, 52, 51, 50, 78, 53, and 39 amu, in the proper proportion to be identified as originating from the pyridinyl moiety, accompany the initial weight loss around 250°C. Infrared spectra of the residue are consistent with a decrease in the pyridine moiety. At 350 to 700°C other fragmentations appear, the intensity of which maximize at 445°C. Thirty-eight mass bands (all assigned) are then present in a relative abundance greater than 0.7%. Bands at 79, 52, 51, 50, 78, 53, and 39 amu are characteristic of the loss of pyridine. Mass bands at 18 and 17 amu are characteristic of the loss of water. The remaining bands are characteristic of the fragmentation of the piperazine backbone. Thus mass bands about 124-121 amu are characteristic of the



moiety; bands about 110-107 amu are characteristic of the

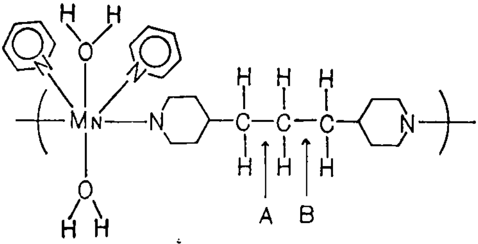


moiety and 96-93 amu are characteristic of the



moiety.

If bond scission is random, then the ratio of many of the mass bands should be predictable. For instance, if bond scission occurs at A or B (LXXII) generating mass units of 96-93 and 110-107 amu, then the ratios of these two fragments should be the same. After correction for the variation in weight of the two fragments, the abundance of the two ions is within 1.5% of one another.



LXXII

Thus initial degradation occurs with expulsion of about only 10% of pyridine, giving a somewhat thermally stable residue which subsequently degrades, reaching a maximum rate about 450°C with evolution of fragments from the piperazine portion of the backbone as well as water and additional pyridine.

We are also relating TG data with atomic absorption data by utilizing a carbon rod assembly and controllable ramp temperature for determination of both metal content and total organic as a function of temperature. Preliminary studies indicate that this approach is workable and that the AA data correlates with TG-MS data.

Vinyl Organometallic Polymers

Metallocene-Containing Products

The interest in the thermal properties of vinyl organometallic polymers stems from the observation that biscyclopentadienyliron is stable to 470°C. The major activity thus far with vinyl organometallic polymers has involved ferrocene-containing polymers, but much diversity has been evidenced within the last several years with efforts aimed at applications other than high temperature performance. The performance of ferrocene polymers in a high temperature environment has yet to match initial expectations. The topic of polymetallocenylenes has been recently reviewed by Neuse [280a].

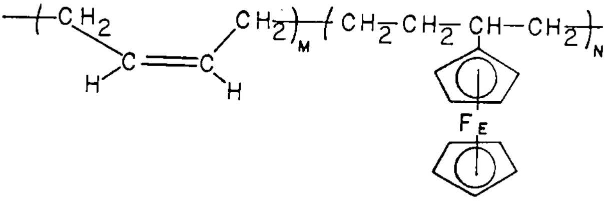
If degradation occurred by simple bond scission of the backbone, then the degradation of linear vinyl organometallic polymers should occur within approximately the same temperature range through a simple TG-weight loss curve. This does not occur. In fact, such a wide variety of results are currently available as to obscure any general trends if present. Thus only broad, general trends will be presented where possible.

Low molecular weight polyvinylferrocene exhibits a high T_g [280]. DSC shows two endothermic transitions, one at 170-190°C and the second at 225-250°C [282]. Assignment of the T_g is difficult because decomposition is fairly rapid (in nitrogen) at 240°C. The higher endotherm of about 220-250°C is probably the correct glass transition temperature [281, 283]. The activation energy for degradation between 270 and 430°C was determined using DSC to be about 8 to 9 kcal/mol [283, 284].

High T_g's are common for ferrocene-containing vinyl polymers. Examples follow: poly(ferrocenylmethyl acrylate), 197 to 210°C [280]; poly(ferrocenylethyl methacrylate), 210 to 215°C; poly(ferrocenylethyl acrylate), 160°C [280]; poly(ferrocenylmethyl methacrylate), 185 to 195°C [286].

Inclusion of a metallocene moiety into a polymer also tends to increase the T_g of the copolymer over that of the homopolymers. For instance, cis-1,4-polybutadiene exhibits a T_g of -91°C whereas LXXIII shows a T_g of 30°C with 18 mol% ferrocene inclusion [287].

Introduction of ferrocene groups in polymers generally results in an increase in T_g (see Refs. 288-291). This results in an accompanying increase in the brittleness of the materials which decreases their fabricability. Thus it is particularly desirable to gain quantitative data on the effect of the ferrocenyl group on the mechanical properties of such materials. This can be done using TMA or TBA. The latter was utilized effectively to evaluate a number of vinyl-ferrocene polymers and copolymers [291].

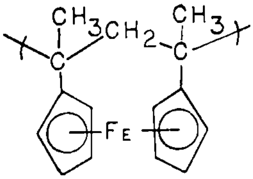


LXXIII

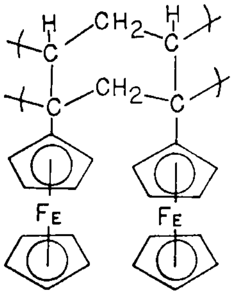
A wide variety of cyclolinear homo- and copolymers have been synthesized and briefly (thermally) characterized (see Refs. 292-302). Many of these products also show high T_g's.

Products from 1,1'-diisopropenyl ferrocene (LXXIV) are reported by some to soften about 280-300°C; others report extensive decomposition by 260°C [299]. A number of other cyclolinear products, where the ladder linkage does not directly involve the metallocene, decompose at lower temperatures.

Product LXXV degrades at 330°C in N_2 and 270°C in air [292].



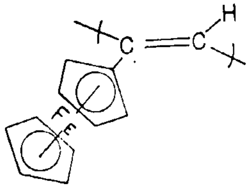
LXXIV



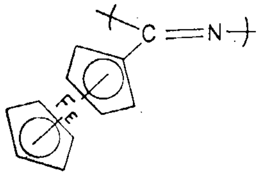
LXXV

Products containing pendent metallocenyl groups generally exhibit only moderate thermal stability with degradation often beginning about or below 350°C. Thus poly(dimethacryloyltitanasene) degrades below 220°C [303]; polyvinylferrocene decomposes below 240°C [280].

Exceptions are known. Paushkin et al. [304-307] obtained poly(ferrocenylalkenes) (Form LXXVI) which were infusible to 500°C. The analogous polyimines also showed moderate thermal stabilities [307-309]. The low molecular weight polymer was stable to about 350°C whereas high molecular weight polymer LXXVII did not melt to 500°C. (Conclusions based on the aforementioned structures should be viewed with caution since many of the structures are not well documented.)

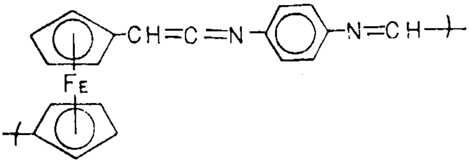


LXXVI



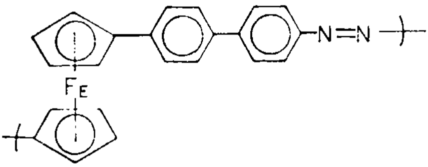
LXXVII

Polyazomethines (LXXVIII) in argon are stable to 400°C [310]. In such situations it would be of interest to determine if the products are truly stable to 500°C or if cross-linking involving the backbone occurs.



LXXVIII

Possibly related to the above are the following: Neuse et al. [310, 311] report that pure polyferrocenylene is stable to 300°C whereas ferrocene recombination products of imperfectly aromatic composition are considerably less stable [311], and azo products of Form LXXIX presumably lose molecular nitrogen below 600°C giving a cross-linked product stable to 700°C [312, 313].

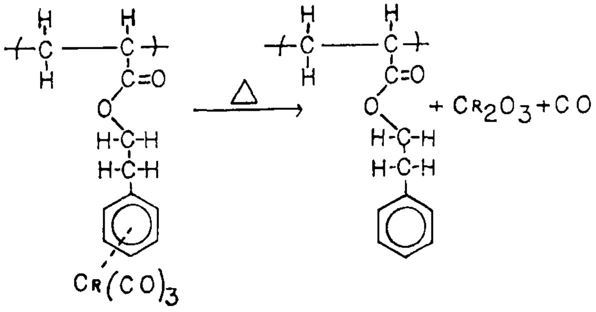


LXXIX

Degradation normally occurs giving kinetically controlled stability plateaus. The fate of the metallocene moiety is difficult to predict with studies showing the metallocene moiety being evolved during the degradation (either in total or fragmented) and other studies showing the metal remaining as the metal oxide (particularly in air). Both probably occur depending on the system.

Poly(vinyl alcohol), poly(acrylic acid), and the amidoxime of poly-(acrylonitrile) have been modified through reaction with metallocenes of Group IVB of form Cp_2MX_2 [314-316]. The products are all cross-linked and generally show equal or greater thermal stabilities in air and nitrogen compared with the unmodified polymer. The residue derived from heating in air is (quantitatively) the MO_2. Initial degradation occurs beyond 200°C. Degradation occurs through an exothermic oxidative route(s) in air and through an endothermic route(s) in nitrogen. Endotherms occur about 100°C which could coincide with a T_g.

The thermal decomposition of organometallic moieties contained as parts of polymers results in the formation of metal oxides (for electrical conductive purposes, etc.) in small particle size and homogeneous throughout a polymer film. Thus η^6-(2-phenylethyl acrylate)-tricarboxylchromium and styrene copolymers (LXXX) can be cast as films on glass. Thermal decomposition of the films at 150°C results in a homogeneous mixture of chromium oxides embedded in the cross-linked film (LXXXI) [317].



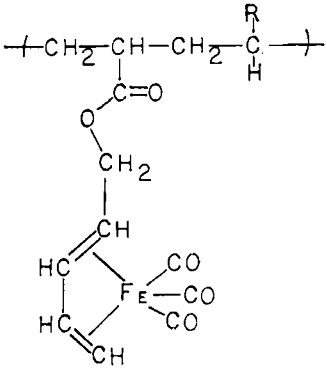
LXXX LXXXI

Copolymers of (2,4-hexadiene-1-yl acrylate)tricarbonyliron deposit iron(III) oxide when heated to 200°C in air (LXXXII) [318].

Other Vinyl Polymers

A number of vinyl polymers have been modified utilizing nonmetallocene-containing metal reactants. A general overview is given in papers by Carraher and Tsuda [319]. Modified polymers include polyvinyl alcohol [320, 321], polyacrylic acid [322-324], the amidoxime of polyacrylonitrile [325-328], polyethyleneimine [329, 330], and cellulose [319a, 331] through condensation with such reactants as Cp_2TiX_2, Cp_2ZrX_2, Cp_2HfX_2, R_3AsX_2, R_3BiX_2, R_2PbX_2, R_2SnX_2, R_2GeX_2, and R_2SiX_2.

Below or about 200°C, endothermic regions, which probably



LXXXII

correspond to T_g's, are typically present. Degradation in air occurs through a series of exothermic, oxidative reactions whereas degradation in nitrogen generally occurs through a series of endothermic reactions.

Most show better weight retention in nitrogen than air, presumably because of preferential oxidation of the metal in air. Most show better stabilities than do the unmodified polymer. Thus polyvinyl alcohol retains only about 20 to 30% residue at 350°C in nitrogen whereas the modified products from polyvinyl alcohol with Cp_2TiCl_2, Cp_2ZrCl_2, and Cp_2HfCl_2 all show better than 80% weight retention in both air and nitrogen at 350°C [316].

An interesting system to illustrate the diversity of thermal stabilities observed for such products is the modification of polyvinyl alcohol with R_3SnX and R_2SnX_2 [321]. As little as 7 mol% inclusion of tributyltin chloride results in 80% weight retention to 900°C in both air and nitrogen. In contrast, the product from triphenyltin chloride offers the same or lesser stability than does the unmodified polymer.

Within a family (such as polyvinyl alcohol or polyacrylonitrile modified by Cp_2TiCl_2, Cp_2ZrCl_2, and Cp_2HfCl_2; Refs. 315 and 316), degradation appears to occur through similar routes as indicated by the similarity of DSC thermograms in both air and nitrogen as only the metal atom is varied. On the other hand, there appears to be some divergence as the metal is held constant but the nature of the groups about the metal site is varied [321].

CONCLUSIONS

Only three of the areas reviewed in this article are in reasonably good "health" regarding thermal analysis—polymeric sulfur, siloxanes, and linear polyphosphazenes. Most of the remaining areas are in great need of research.

There are few if any definitive thermal analyses studies involving organometallic and inorganic polymers. This lack of definitive studies is due to a mixture of reasons including 1) wide variety of polymers; 2) newness of interest in the area; 3) wide variety of applications (both potential and actual) of inorganic and organometallic polymers not requiring thermal stability or thermal analysis (uses as anchored metal catalysis, control release agents, electrical and photochemical applications, speciality adhesives); 4) insufficient description, identification, of the products; 5) wider variety of degradation routes and other thermal behavior in comparison to organic polymers; and 6) many products were sythesized and briefly characterized before the advent of modern thermal instrumentation.

It must be remembered that we have just begun to look inside "Pandora's Box" (which retained "hope") regarding applications and synthesis of metal-containing polymers. The analysis, including thermal analysis, has just begun on a small fraction of the already known organometallic and inorganic polymers.

The thermal techniques that have already been utilized on more classical polymers are generally directly applicable to organometallic and inorganic polymers. The thermal analysis of inorganic and organometallic polymers is both more and less difficult in comparison to studies performed on organic polymers. On the negative side there are 1) a much wider variety of products with many polymers showing a great dependence of the thermal properties on the presence and nature of impurities; 2) general lack of definitive thermal studies and experience upon which to build; and 3) added difficulty associated with defining thermal responses such as the unusual transformation to a mesomorphic state between the T_g and T_m for most polyphosphazenes. On the positive side the wider variety of bond energies present in organometallic and inorganic polymers can allow (for certain products) a clearer isolation and definition of particular thermal transitions, such as T_g's and degradation pathways. Further, the wider variety of thermal response permits increased potential usefulness of such compounds showing unusual (either in extent, range, or actual thermal response) thermal responses. The latter is illustrated by the "mesomorphic state" found for many polyphosphazenes which is related to liquid crystal phenomenon and could be utilized in liquid crystal associated applications.

Of the potential vast array of both thermal and other characterization instruments and techniques, only TG and DSC (note that throughout this article, DSC and DTA have been typically utilized interchangeably) have been applied appreciably to the study of the thermal charactertistics of organometallic and inorganic polymers.

RECOMMENDATIONS

Following are brief descriptions of recommendations associated with the thermal characterization of organometallic and inorganic polymers in general. There is a need both for studies involving a wide variety of products and in-depth studies of several of these systems. The "survey" studies can indicate potentially interesting polymers such as products showing unusual and/or potentially useful thermal responses.

The correlation of bonding group, metal atom, and fine and gross polymer structure with such factors as degradation pathway, bonding energies, inherent stabilities should begin.

There is a need to evaluate, by newer thermal analysis instrumentation and techniques, polymers previously only briefly characterized, emphasizing those products which show potential industrial application or other meritorious property. Such products should be well characterized with regard to such factors as chain length, molecular weight distribution, endgroup, purity, nature and amount of impurities, and actual morphological structure of the polymer. For some polymers, such as many condensation organometallic polymers, thermal properties appear to be largely independent of chain length and distribution, endgroup, and purity, but for most of the other organometallic and inorganic polymers care should be made to control such parameters since there is a good likelihood that even gross thermal responses will be dependent on these variables. Even the observation regarding independence of endgroup, etc. for most condensation organometallic polymers should be more fully tested before general acceptance.

The increased application of modern thermal techniques and companion techniques must occur if the thermal characterization of organometallic and inorganic polymers is to progress. A number of companion techniques have been shown to be useful and merit further use. These include NMR, IR, MS, GC-MS, AA, x-ray microscopy, and GPC. ESR has not been appreciably utilized as a companion technique but may be considered, particularly with polymers containing ESR sensitive metals. Gel permeation chromatography (GPC) should be considered as a companion tool for thermal degradation evaluations where depolymerization is suspected. There is a need for a number of well-chosen thermal analysis studies of both the volatile products by TG-MS, etc. (for both chemical and toxicological purposes) and the residue. Such studies should occur throughout the studied temperature range rather than just at the room and final temperature.

Most of the present studies have been with "pure polymers." This needs to continue but some investigations of organometallic and inorganic polymers with added plasticizers, etc. needs to begin both because of the simple need for such studies and also because of the potential for some interesting interactions between added materials and the metal-containing polymers.

Finally, there is a need for the thermal characterization of products to occur both as a general routine characterization technique and by in-depth studies by those particularly aware of thermal responses and instrumentation. The former will contribute to previously noted "survey" studies.

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