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Polydichlorophosphazene Polymerization Studies

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ABSTRACT

Polydichlorophosphazene $(NPCl_2)_x$ is unique as a synthetic precursor for poly(organo)phosphazenes [1-6] and presents special problems in polymerization studies because of branching, crosslinking, and cyclization reactions and in characterization due to the polymer's hydrolytic instability. This paper reviews the literature and discusses problem areas and recent advances relating to polydichlorophosphazene polymerization. Melt, solution, and irradiation polymerization reactions and mechanisms are discussed. Previously unpublished results are presented, and current research efforts and areas for future investigation are considered.

BACKGROUND

In 1897, H. N. Stokes [7] first reported high temperature reactions of cyclic chlorophosphazenes forming an insoluble "inorganic rubber" which was later recognized as being crosslinked polydichlorophosphazene. Early workers such as Schenck and Römer [8], Ficquelmont [9], and Schmitz-Dumont [10,11] investigated the polymerization reaction; but the first detailed studies were not made until the 1950s by Patat and coworkers [12-15]. Since then, techniques for high temperature, melt and solution polymerizations and for irradiation polymerization have been developed; and the

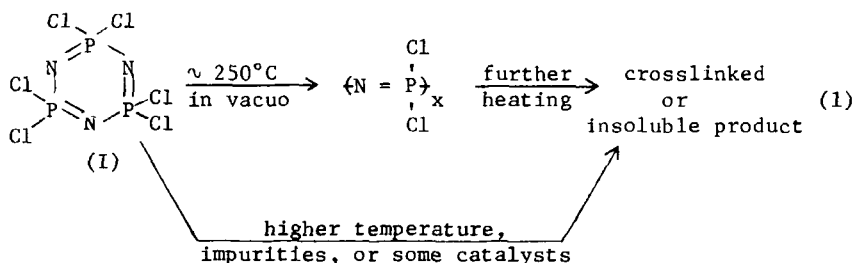
effects of temperature, pressure, catalysts, etc. have been studied [16-37]. Also, a number of polymerization kinetics studies have been reported for both catalyzed and uncatalyzed reactions [18-20, 22, 27]. The most significant advance relating to the development of technologically useful polymers was made in 1965 when Allcock and coworkers developed methods for preparing soluble, open-chain polydichlorophosphazene [1, 2]. Unlike the crosslinked or insoluble polymer, linear or branched polydichlorophosphazene is soluble in a variety of solvents (e.g., benzene, chloroform, and tetrahydrofuran) and therefore is amenable to subsequent substitution reactions where the chlorine atoms are replaced with organic nucleophiles to yield stable, high molecular weight poly(organo)phosphazenes.

HIGH TEMPERATURE, MELT POLYMERIZATION

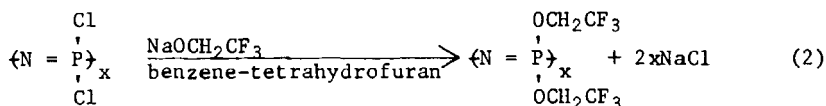
The high temperature, melt polymerization reaction of hexachlorocyclotriphosphazene (I) to polydichlorophosphazene has been most widely studied. Trimer (I) is the principal product obtained in the synthesis of chlorocyclophosphazenes [8, 38-40]. The cyclic trimer (I) is a white, crystalline (mp 112-114°C) solid that sublimes in vacuum and is soluble in organic solvents. Thermal polymerization proceeds at a faster rate and at lower temperatures with the trimer (I) than with higher molecular weight cyclic homologs [18, 25]. Also, melt polymerization has been preferred because solution polymerization generally is slower and tends to yield insoluble or low molecular weight products [12, 19, 36]. Melt polymerization reactions are usually run in sealed, evacuated glass tubes. Below 230°C, the uncatalyzed polymerization is quite slow and may not proceed at all if the trimer is extremely pure [18, 29]. Between 230° and 350°C, the rate of polymerization increases with temperature [18]. With increasing polymerization time and as the temperature is raised, the rate of crosslink formation increases. Crosslinking is unpredictable and is greatly enhanced by the presence of impurities. Also, as the temperature

is increased, depolymerization reactions occur such that at about 600°C, ring-polymer equilibrium reactions prevail and the polymer degrades to low molecular weight cyclics $[\text{NPCl}_2]_{3-7}$ [10, 14, 15, 25]. Finally, there is a large number of materials which behave as polymerization catalysts or accelerators and promote polymerization at temperatures as low as 200°C. Additives or impurities which are able to extract chloride ions from phosphorus tend to accelerate the rate of polymerization [18-20, 22, 25, 27, 29, 30, 32-34]. Unfortunately, such catalysts also tend to promote crosslinking [18-20, 27, 30, 33].

To obtain soluble, high molecular weight polymer, the polymerization is best run using highly pure trimer (I) at temperatures between 240 and 255°C in clean, glass tubes sealed under vacuum (0.005 to 0.010 mm Hg). Procedures for purifying polymerization grade trimer have been published [2, 16]. The highly pure commercial cyclic trimer/tetramer mixture, Phosnic 390 [41], may be used without further purification [37]. As polymerization proceeds, the contents of the polymerization tube become increasingly more viscous. When the reaction mixture becomes so viscous that little or no flow occurs, usually within 1-7 days, the reaction should be terminated by reducing the temperature below 200°C. Sealed polymerization tubes may be kept at ambient temperature for years without effecting further reaction. Depending on trimer (I) purity, polymerization temperature, and reaction time, polymer yields up to 75% may be obtained. However, if polymerization is allowed to continue beyond the time at which flow ceases, excessive branching and crosslinking may occur.



Recently the uncatalyzed, high temperature, melt polymerization [Eq. (1)] was investigated in considerable detail [42]. Two batches of trimer (I) were obtained from different manufacturers and purified extensively. Purified trimer (I) from each batch was placed in pyrex tubes, sealed under vacuum, and polymerized in an aluminum block oven at 250°C. Tubes were removed from the oven periodically to terminate polymerization at various stages; and the reaction products were converted into hydrolytically stable trifluoroethoxyphosphazenes by nucleophilic displacement of chlorine on the phosphorus atoms.



Mild reaction conditions were used to preserve the polyphosphazene chain backbone structure and solution precipitation techniques were used to separate the polymer from unreacted trimer [42, 43]. Polymer yields were determined gravimetrically. The polymer was then thoroughly characterized using liquid size exclusion chromatography, viscometry, membrane osmometry and light scattering. Polymer yield is plotted versus polymerization time in figure 1. The polymerization behavior of the two trimers, designated A and B, is quite different. After 7 days, polymer prepared from trimer A contains 2% crosslinked product; whereas no gel is evident in polymers prepared from trimer B. No induction period is evident. Polymerization starts almost immediately; however there are great differences in the rates of polymerization of trimers A and B. The polymerizations autoaccelerate after 1 day and 6 days for trimers B and A, respectively. Changes in the intrinsic viscosity $[\eta]$ of the stabilized polymer correspond to changes in polymer yield with polymerization time [Fig. (2)]. Molecular weight tends to increase with polymerization time and, as shown in figure 3, significant changes in the molecular weight distribution take place. The polyphosphazene has a bimodal molecular weight distribution

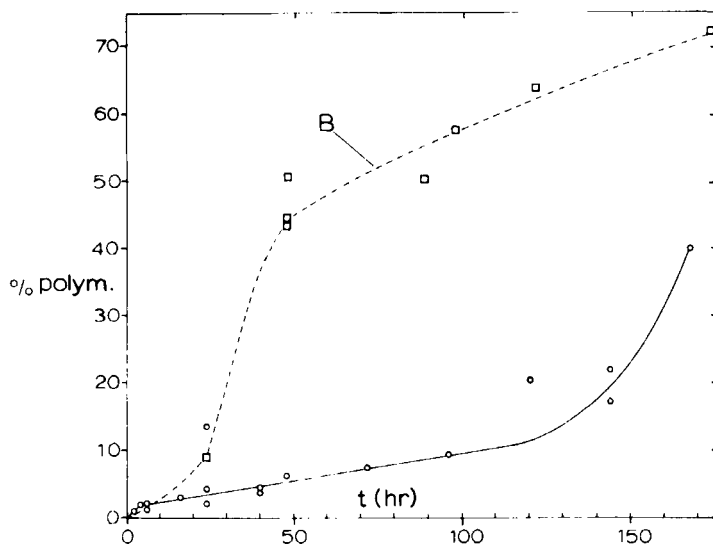


Figure 1. % polymerization of trimer A (—) and trimer B (---) versus polymerization time at 250°C.

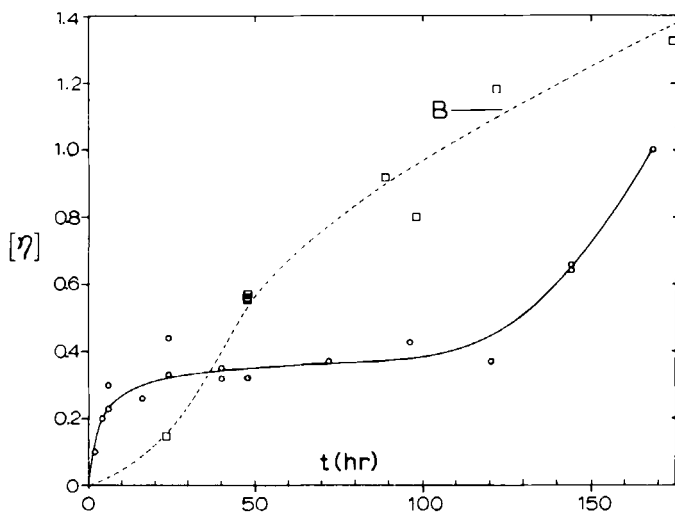


Figure 2. Intrinsic viscosity of polymer from trimer A(—) and trimer B(---) versus polymerization time.

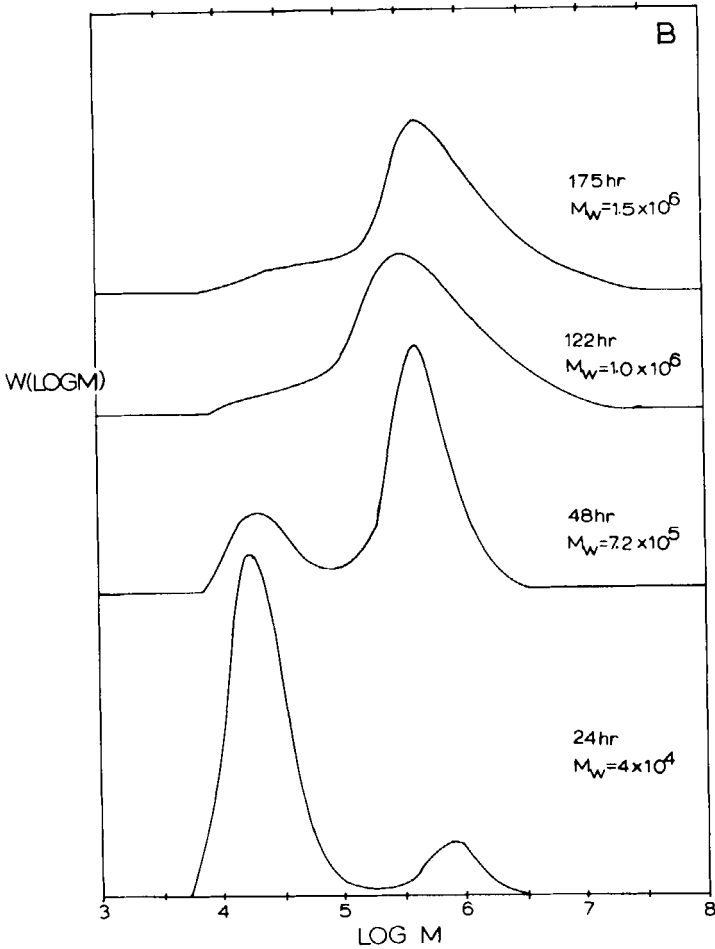


Figure 3. Weight differential molecular weight distributions of poly[bis(trifluoroethoxy)phosphazene] products from the polymerization of trimer B.

with peak maxima at 2×10^4 and at 1×10^6 g/mol. In the early stages of polymerization, the main product is low molecular weight polymer; but as polymerization proceeds, increasingly larger amounts of high molecular weight polymer are produced. The molecular weight distributions of polymers prepared from trimer A are also bimodal but not as broad as the B polymers. Finally, the

analyses suggest that polymers prepared from trimer A are relatively linear during the early stages of polymerization; but after 6 days, branching and crosslinking reactions set in. All the polymers prepared from trimer B are branched to some extent but there are no insoluble products, suggesting the absence of a high degree of crosslinking.

The quality of trimer (I) has a profound effect not only on the rate of polymerization but also on the nature of the reaction products [37]. For example, different batches of commercial trimer [41], designated LJ-3 and IL-22, and of highly pure trimer PN-1 were melt polymerized in sealed, evacuated glass tubes at 250°C. Special techniques were developed for the separation and dilute solution characterization of the dichlorophosphazene reaction products. The commercial trimer samples contained 9% cyclic tetramer, octachlorocyclotetraphosphazene; however, in both cases, the trimer/tetramer mixtures were free of apparent impurities. Polymerization times, yields, and characterization data are shown in Table 1. Intrinsic viscosity $[\eta]$, absolute number- and weight-average molecular weights, and the z-average radius of gyration $\langle S^2 \rangle_z^{1/2}$ were measured for each polymer in dilute toluene solution at 25°C. Liquid size exclusion chromatography was used to analyze nonpolymeric components in the reaction mixtures and to characterize molecular weight distributions of the polymers. It is noted that the cyclic tetramer concentration does not change and that no insoluble products are formed. Seemingly, the tetramer plays no active role in polymerization; however, there may be an indirect benefit in that the tetramer tends to keep the viscosity of the reaction medium from increasing too rapidly as polymerization progresses and thereby reduce the likelihood of crosslinking. The commercial samples give comparable polymer yields to the high purity trimer but with shorter polymerization times. Also, side reactions occur during polymerization producing high and intermediate molecular weight oligomers, particularly with the commercial samples. The intermediate MW oligomers are cyclic

TABLE 1. Analysis of Polymerization Products

SAMPLE	PN-1	IJ-3	IL-22
Polymerization Time (hours)	100	45	21.5
% Polymer	30.8	26.0	31.4
% High MW oligomers	1.8	12.4	4.0
% Intermediate MW oligomers	2.4	18.4	7.8
% Yield	35.0	56.8	43.2
% Cyclic tetramer	0	9.0	9.0
$[\eta]$ (dl/g)	1.35	0.94	1.68
\bar{M}_w (10^{-5})	24.5	8.96	18.1
\bar{M}_n (10^{-5})	4.30	3.24	4.15
\bar{M}_w/\bar{M}_n	5.7	2.77	4.36
$\langle S^2 \rangle_z^{1/2}$ (A)	874	570	774

with molecular weights up to 1000g/mol and the high MW oligomers are cyclic and linear species ranging between 1000 and 8000 g/mol. The polymers have high molecular weights and broad molecular weight distributions; and the $[\eta]$ and $\langle S^2 \rangle_z^{1/2}$ values suggest that there is little, if any, polymer chain branching. Upon comparison, there may be a relationship between the somewhat lower molecular weight and narrower distribution of sample IJ-3 and the relatively high concentration of high and intermediate MW oligomers formed during its polymerization.

The presence of trace impurities may explain why different batches of trimer (I) purified in an identical manner or obtained from the same manufacturer should polymerize at different rates and form products with different structures. For example, small amounts of water (0.02 to ~0.1 mol %) increase the rate of polymerization; while larger amounts of water (>0.2 mol %) tend to retard polymerization [33]. Trace amounts of phosphorus pentachloride (<0.10 mol %), a reagent used in the synthesis of chlorophospha-

zenes, tend to retard polymerization and lower polymer molecular weights [33]. Hydrogen chloride, formed when chlorophosphazenes react with water, in trace amounts (<0.083 mol %) also reduces the rate of polymerization and lowers molecular weight [33]. Indeed slight differences in the surface treatment and volume of the glass polymerization tubes or in the amount of air and oxygen trapped in the trimer may have a catalytic effect on polymerization [29, 32, 42].

A variety of compounds are reported to catalyze the melt polymerization of the cyclic trimer (I) and tetramer. Alcohols, ethers, ketones, esters, carboxylic acids, peroxides, nitromethane, and metals, like tin, zinc and sodium, enhance the rate of polymerization at 200° – 235°C when added in catalytic amounts [18–20, 25, 27]. At higher temperatures water [27, 33, 34], sulfur [30], oxygen [29], and the surface treatment of the walls of glass polymerization tubes [22, 32] have a catalytic effect on polymerization. In the past, most attempts to catalyze melt polymerizations resulted in the formation of products which were partly or wholly insoluble and therefore unsuitable as precursors for the synthesis of poly(organo)phosphazenes. However recently, soluble, high molecular weight polymers have been prepared in catalyzed, melt polymerizations by using highly pure chlorocyclophosphazenes and limiting conversions to about 50%. For example, at temperatures between 200° and 300°C , very low concentrations of water (0.005–0.10 mol %) catalyze polymerization [33, 44]. Catalysis of trimer (I) polymerization at 231°C with a Lewis acid (0.024 mol % $\text{Et}_3\text{Al}_2\text{Cl}$) yields 78% polymer after 6 hours reaction [45]. The polymer has a high molecular weight as indicated by its intrinsic viscosity ($[\eta] = 1.46$ dl/g) with only 0.79% insoluble gel [45]. Other Lewis acids, such as AlCl_3 , EtAlCl_2 , and Et_2AlOEt , also have proven to be effective catalysts producing soluble polymer with little or no gel and polymerization times ranging from 60 hours at 175°C to 1.5 hours at 245°C [46–48]. Melt polymerization with Ziegler catalysts containing TiCl_3 and Et_3Al yielded 50% polymer after 12 hours at 220°C [49].

SOLUTION POLYMERIZATION

Solution polymerization techniques have been applied in attempts to prepare high molecular weight polydichlorophosphazene [12, 13, 19, 36]. The potential advantages of solution polymerization include lower viscosity and better control of polymer chain structure as compared with the melt polymerization. Conceptually, it should be possible to completely polymerize the trimer and obtain high molecular weight, fully soluble polydichlorophosphazene. Initiation, termination, chain transfer and branching reactions should be controllable to the extent that catalysts and solvents in conventional solution polymerizations are effective. In practice, however, solution polymerizations have not been so successful. At the high temperatures required for polymerization (200–300°C) many solvents react with the chlorophosphazenes to form oily or insoluble residues [12, 13, 19, 36]. Trimer (I) polymerizations at 270–300°C with carbon tetrachloride as the solvent and 5–30% solution concentrations resulted in higher yields than obtained by melt polymerizations run at similar temperatures and times; but, although polymer fractions with molecular weights as high as 130000 were analyzed, less than half of the products were soluble [12]. For trimer (I) polymerizations at 210°C, only crosslinked products are obtained in cyclohexane; mixtures of soluble and crosslinked products are formed in chlorobenzene with the highest yields of soluble polymer (ca. 40%) and the least amount of crosslinked product (ca. 5%) produced in the 40–60% concentration range; and soluble, low molecular weight (<10000 g/mol) products are formed in benzene over the 20–80% concentration range [36]. Soluble fractions from the chlorobenzene polymerization have molecular weights of 2.6×10^6 g/mol which is similar to values of melt polymerized polymers and, upon comparison with results using benzene and cyclohexane as solvents, suggests an effect relating to the polarity or electrophilicity of the solvent [36].

Trimer (I) solution polymerizations at 210°C with benzene as the solvent are catalyzed by benzoic acid, ethyl ether, and ethyl alcohol but yield only soluble, low molecular weight (ca. 1300

g/mol) products [19]. A more promising polymerization uses polyphosphoric acid (1%) as a catalyst and is run at 200°C using 50% trimer (I) solutions with 1,2,4-trichlorobenzene [50]. The polymerization yields soluble polymer which is amenable for use in substitution reactions but has a somewhat lower molecular weight and broader molecular weight distribution than polymers obtained by melt polymerization [5]. Metal or quaternary ammonium salts of carboxylic, sulfonic, picric, or phosphorus acids are also effective catalysts for solution polymerization of chlorocyclophosphazenes in 1,2,4-trichlorobenzene [51]. For example, a stirred solution consisting of 1 part cyclic trimer (I), 1 part trichlorobenzene and 0.01 part $(\text{CH}_3\text{SO}_3)_2 \text{Hg}$ and blanketed with nitrogen at 217°C for 3 hours produces soluble, high molecular weight polymer [51]. There is also evidence that the presence of certain fluorine compounds, sulfur, or sulfur-donors prevent gelation in the solution polymerization of chlorocyclophosphazenes at temperatures in the range 140-225°C when solvents are used that dissolve the chlorocyclophosphazenes and have dielectric constants $\epsilon \geq 2$ [52, 53]. An amazing 94% yield of soluble polymer and no insoluble gel is obtained when a 50% solution of cyclic trimer (I) and 0.5 mol % sulfur in tetralin is heated for 70 hours at 205°C [52]. In the absence of sulfur, insoluble products with concentrations as high as 15% are found [52].

SOLID STATE POLYMERIZATION

The cyclic trimer (I) polymerizes in the solid state when irradiated with 50kV X-rays [23]. The rate of polymerization increases with temperature to a maximum of 0.8% per hour at the melting point of the trimer and drops to zero above the melting temperature [23]. The presence of water, oxygen, solvent, and even cyclic tetramer decreases the polymerization rate and the polymerization appears to terminate after about 10% conversion [23, 26]. Finally, it is noted that the cyclic tetramer does not polymerize in the solid state [23].

Properties of polymer prepared by solid state irradiation are identical to those of crosslinked polydichlorophosphazene prepared by high temperature, melt polymerization. The polymer is insoluble, exhibits elastomer behavior, and crystallizes when stretched to give an x-ray diffraction spectrum identical to the melt polymerized polymer [23, 26].

POLYMERIZATION MECHANISM

The mechanism of the polydichlorophosphazene polymerization is not known with certainty. Attempts to study the polymerization kinetics have been plagued not only with experimental difficulties due to the high polymerization temperatures and hydrolytic instability of dichlorophosphazenes, but also with the problem of reproducibility caused by trace impurities. Additionally, there are problems of interpretation where the reaction mixture includes cyclic and linear oligomers, soluble linear and branched polymers, and insoluble, crosslinked products. For uncatalyzed, melt polymerization, second-order polymerization kinetics are reported with activation energies of 42, 51.3 and 57 kcal/mol [12, 22, 27]. However rate constants determined at 250°C differ by almost an order of magnitude, probably as a consequence of trace impurities. The actual rate constant may be appreciably smaller than reported if impurities are entirely eliminated [29]. Catalyzed, melt polymerizations follow first-order kinetics and are reported to have induction periods which decrease with increasing temperature [18-20, 27]. Other investigators find no indication of an induction period for either catalyzed or uncatalyzed polymerization [12, 22, 29, 33, 34, 42]. For melt polymerizations catalyzed with benzoic acid, the activation energy is 24.3 kcal/mol in the range 200-220°C and the rate increases exponentially with catalyst concentration [27]. Finally, it is noted that insoluble products were formed in most studies and recent findings indicate that the polymerization is too complex to analyze as simple first- or second-order kinetics [37, 42].

Polydichlorophosphazene polymerization reactions are exothermic [10, 11, 24] and the extent to which the polymerization is exothermic decreases with increasing size of the cyclic oligomer [25]. This is also indicated by the fact that the rate of polymerization of the cyclic tetramer is much slower than for the trimer [18]. As mentioned previously, the rate of polymerization increases with increasing temperature [12, 18, 19, 22, 26, 27, 29] and with certain impurities or catalysts present [18-20, 22, 25, 27, 29, 30, 32-34, 44-51]. Other compounds lower the rate of polymerization and reduce polymer molecular weight [33]. Increasing temperature and the presence of impurities or catalysts also increase the rate of crosslinking [2, 18-20, 27, 30, 33]; while other compounds inhibit crosslink formation [52, 53]. Compounds, such as phosphorus pentachloride, cause polymer chain degradation [33] and may promote side reactions during polymerization of the cyclic trimer to produce high molecular weight cyclic and linear oligomeric chlorophosphazenes [37, 54]. At high polymerization temperatures, especially above 300°C, polymer chain depolymerization reactions occur and consideration of ring-polymer equilibria becomes important [16, 55]. Increasing pressure between 10 and 70 kbars favors the formation of polymer; however the rate of polymerization decreases as the pressure is raised [24]. This suggests that the rate determining polymerization step has a transition state that occupies a larger volume than the reactants and argues in favor of a ring-opening chain propagation mechanism. Of course, there are ample spectral, chemical and physical property data supporting that polydichlorophosphazene is an open-chain polymer and not a series of linked cyclic units [3, 16].

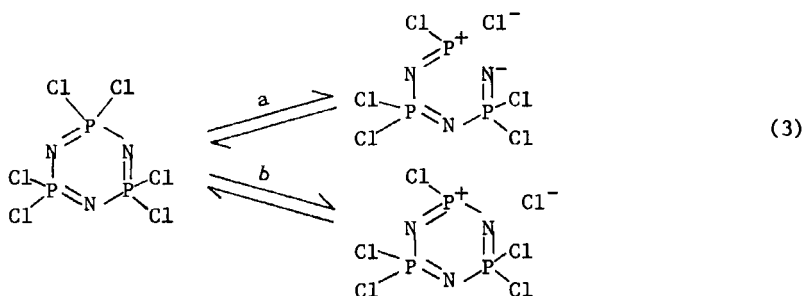
Since high molecular weight polymer is formed at the very onset of polymerization [12, 42], there is little doubt that a chain growth polymerization is involved; however there are questions concerning the exact nature of the active center for kinetic chain growth. Free radical mechanisms have been proposed for both high temperature, melt and solution polymerizations

[12-14, 22, 30]. Of the compounds that are sufficiently stable to be used as free radical initiators at elevated temperatures, sulfur has a powerful catalytic effect at 250°C [30] and oxygen appears to be an active initiator above 300°C [29] for melt polymerizations. In fact the exceedingly slow polymerization of highly pure trimer at 300°C may be a thermal polymerization involving free radical formation and initiation of the trimer [29]. However most evidence suggests, at least for temperatures below 300°C, that a free radical mechanism is unlikely. Melt polymerization of trimer is not initiated at elevated temperatures by ultraviolet irradiation [18], X-rays [17], or accelerated electrons [56]. A different mechanism involving bond interchange may explain why irradiation with X-rays induces trimer polymerization in the solid state [23, 26]. And finally, during melt polymerization at 250°C, no free radical species are detected by electron spin resonance spectroscopy [57].

Most evidence favors an ionic mechanism for polymerization. Compounds which typically catalyze ionic polymerizations are also observed to accelerate polymerization of the trimer [18-20, 25, 27, 33, 44-51]. It is also noted that the reaction of a 5:1 molar mixture of cyclic trimer and phosphorus pentachloride at 250-300°C proceeds by an ionic mechanism to form low molecular weight, linear products of the type $[Cl(PCl_2 = N)_{3x}PCl_3]PCl_6$ [28]. And during melt polymerization of the cyclic trimer, both the conductance and dielectric constant of the reaction mixture increase rapidly as the temperature is raised from 203° to 253°C and continue to increase with time at 253°C [57]. When the temperature is lowered from 253° to 202°C, the reaction mixture's dielectric constant value remains high which can be attributed to the presence of polymer, and the fact that part of the conductance is reversible is indicative of ionization equilibria [57]. Conductance data indicates that ionization of the trimer is the primary initiation step and that ionization occurs concurrently with polymerization. Finally, an ionic mechanism is consistent with solvent effects reported in the uncatalyzed, solution polymerization of trimer

[36]; i.e., to produce high molecular weight polymer the dielectric constant of the solvent must be high. In an ionic polymerization a high dielectric medium is effective in shielding or solvating the active center from its counterion to achieve higher rates of polymerization and high molecular weights, whereas free radical reactions generally are insensitive to their environment.

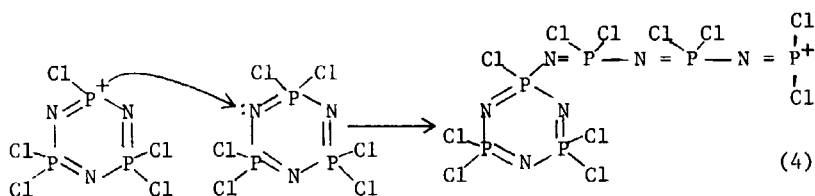
Two types of initiation processes are proposed [57] involving (a) heterolytic cleavage of a phosphorus-nitrogen bond or (b) dissociation of a chloride ion from phosphorus.



Mechanism (a) is unfavored since the cyclic trimer $[\text{NP}(\text{OC}_6\text{H}_5)_2]_3$, which has a phosphorus-nitrogen bond strength similar to that of the chlorophosphazene trimer (I), neither polymerizes nor shows large irreversible increases in conductance or dielectric constant over the temperature range 120–350°C [57]. Mechanism (b) is consistent with the conductance behavior of the trimer and the low conductance of $[\text{NP}(\text{OC}_6\text{H}_5)_2]_3$ at 350°C, since the phosphorus-oxygen bond in $[\text{NP}(\text{OC}_6\text{H}_5)_2]_3$ is quite stable to ionic reactions [16]. The chloride ionization mechanism (b) is also consistent with the facts that catalysts for the polymerization are generally those which also are able to extract chloride ions from phosphorus [18–20, 25, 27, 32–34, 44–51] and that hydrogen chloride is found in reaction tubes after polymerization [18, 20, 27, 32–34]. Furthermore, the decrease in the rate of polymerization and reduction in polymer molecular weight upon adding small amounts of hydrogen chloride during the melt polymerization of

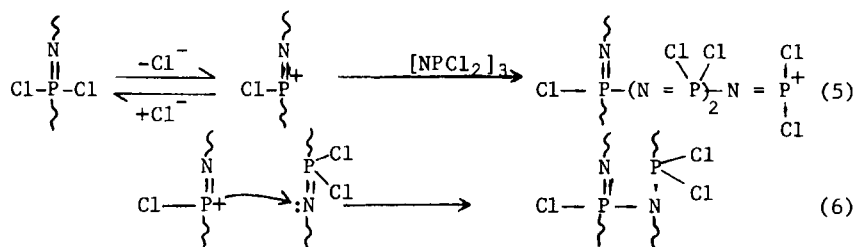
trimer [33] agrees with mechanism (b) in Eq. (3) and a mechanism for terminating chain propagation.

The high conductivity of the reaction mixture during polymerization argues against the chloride ion being the initiating species [57]. Because of the greater electropositivity of phosphorus, the electrophilic center of the initiating species is probably located on phosphorus rather than nitrogen and propagation can be envisioned as the electrophilic phosphorus center attacking another ring and inducing ring-opening.

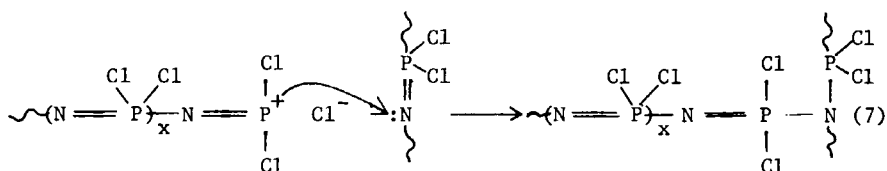


Eq. (4) is in accord with conductance and dielectric data and with the observed pressure dependence of the polymerization rate [24] which suggests that the rate determining step has a transition state occupying a larger molar volume than the sum of the reactant volumes. The high molecular weight, linear polymer found at low conversions implies that the active center for propagation is quite stable [42]. In fact the uncatalyzed, melt polymerization of highly pure trimer at 250°C has many of the characteristics of a "living" polymer polymerization [42]. If initiation were controlled and side reactions could be avoided, high molecular weight, linear polymer having a narrow molecular weight distribution probably could be realized.

Eq. (3) and (4) suggest mechanisms for polymer chain branching and crosslinking. Ionization of a chloride ion from chlorophosphazene units within the polymer chain could generate an active center for cationic chain propagation and thereby cause branching [Eq. (5)] or the active center may attack a nitrogen atom on the backbone of another chain resulting in crosslinking [Eq. (6)].



An active chain end also may produce a branch unit by attacking a backbone nitrogen atom [Eq. (7)].



A phosphorus atom in the polymer chain backbone is probably not highly prone to ionization when one considers that, in comparison with the cyclic trimer, the molecular structure and chemical behavior of an NPCl_2 chain unit and higher cyclic chlorophosphazenes $[\text{N} = \text{PCl}_2]_n$ ($n = 4, 5, 6, \dots$) are quite similar and that the higher cyclics polymerize slowly, if at all, at temperatures below 300°C . Indeed, for the uncatalyzed, melt polymerization of a cyclic trimer/tetramer mixture at 250°C , the tetramer concentration does not change with polymer yields as high as 50% [37, 54] demonstrating a resistance both to ionization and to attack by an active center. Under the same reaction conditions polymer with no apparent polymer chain branching or crosslinking is produced [37, 54]. One may conjecture that units within the polymer chain behave similar to the tetramer and inherently are more resistant than the cyclic trimer to ionization and attack by an active center. Perhaps this resistance reflects a greater degree of shielding of both the phosphorus to inhibit an active center and the nitrogen for protection against electrophilic attack in higher cyclics and chain units. It is also noted that

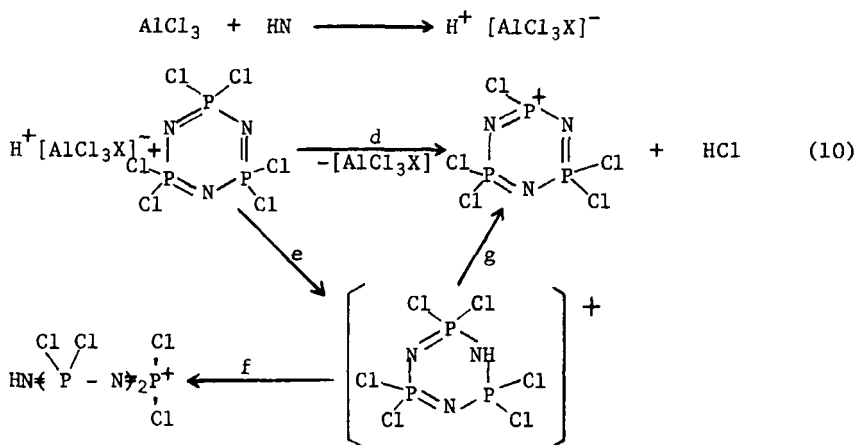
the active center generated by the equilibrium in Eq. (5) is less electrophilic than the active end in Eq. (4) and therefore probably less likely to attack a nitrogen atom.

An increase in ionization, as shown in Eq. (3b) and (5), and a reduction in steric barriers may explain both the higher rate of polymerization and the increase in branch or crosslink formation with increasing temperature above 250°C. Autoacceleration effects, as noted in the section High Temperature, Melt Polymerization, may also be interpreted in terms of the ionic mechanisms. Autoacceleration occurs at 10-15% conversion of trimer [Fig. (1)] and is accompanied by a rapid rise in molecular weight. In the early stages of melt polymerization, the viscosity and dielectric constant ($\epsilon \approx 2.5$) of the reaction mixture are relatively low; but as polymerization proceeds, the mixture becomes more viscous and its dielectric constant increases ($\epsilon \rightarrow 3.29$) [57]. Envisioning melt polymerization as an ionic, solution polymerization where the solvent medium is changing from trimer to trimer plus increasing amounts of polymer, a state of reaction (ca. 10-15% conversion) is achieved where, because of increases in the dielectric constant, the solvent effectively shields the active center from its counterion resulting in an increased rate of polymerization. Low molecular weight products formed early in the reaction, where the dielectric constant is lowest, may be a consequence of poor dissociation of the ion pair. Viscosity of the reaction medium may also be important in that charge transfer or perhaps chain backbiting mechanisms are more effective for terminating chain growth in the early stages of polymerization when the molecules are most mobile. The enhanced rate of polymerization of trimer with added tetramer [37] may be the result of the tetramer being more polarizable than the trimer and presumably, therefore, raising the dielectric constant during polymerization.

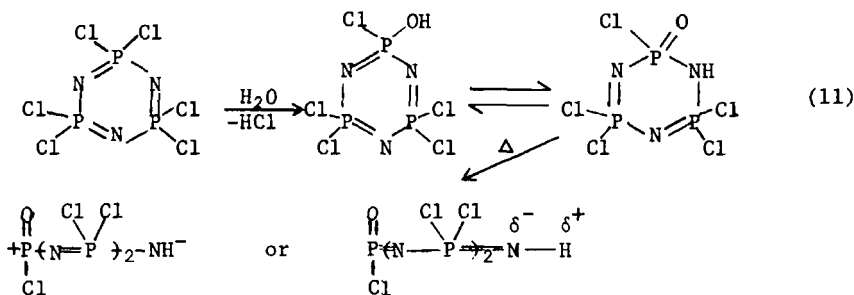
The dramatic increase in gel formation at about 70% conversion of trimer during melt polymerization [20] is indicative of a change in mechanism. At high conversions where viscosity is so

ization mixtures are kept at room temperature. However if the residual trimer is removed from the polymer, crosslinking reactions are indicated in that the solubility of the trimer decreases with time. Experiments suggest that the crosslink units are different from P-O-P type crosslinks which are due to hydrolysis [55]. Speculation is that ionization and crosslinking [Eq. (6)] are possible at room temperature.

The preceding discussion assumes that thermal ionization is an effective initiation mechanism for polymerization. There is some question whether polymerization would occur at 250°C using a totally pure trimer in an inert environment [29, 33]. Minute amounts of impurities acting as catalysts may initiate polymerization and dictate the course of polymerization [Fig. (1)]. Mechanism (b) in Eq. (3) may explain the catalysis by compounds which facilitate removal of chlorine from phosphorus; however the actual mechanism is probably more complex. Since Lewis acid catalysts are particularly effective in promoting polymerization of trimer [45-51], perhaps a different cationic mechanism should be considered for initiation. In cationic systems polymerization is commonly initiated by Bronsted acids (water, alcohols, mineral acids, etc); but when the Bronsted acids do not initiate sufficiently, a Lewis acid (e.g., halides of aluminum, iron, tin, titanium and boron) can serve as an effective cocatalyst [Eq. (10)]. Mechanism (d) is similar to (b) in Eq. (3) and would explain the generation of hydrogen chloride observed in many catalyzed polymerizations. In mechanism (e) the proton attaches itself to a nitrogen atom to form an intermediate structure which ring-opens producing a positive center for chain propagation. Considering that the nitrogen atom is more electronegative than phosphorus, mechanism (f) may occur but does not involve the generation of hydrogen chloride. Mechanism (g) is a possible intermediate route for mechanism (d). An intermediate similar to the one in mechanism (g) has been proposed to explain catalysis by the surfaces of glass polymerization tubes [32].



Catalysis by water also may involve an oxophosphazene intermediate [33]. Hydrolysis of the trimer by catalytic amounts of water (0.005-0.10 mol%) may produce an oxophosphazene unit which is thermally unstable and may cause the ring to open and generate active species for either anionic or cationic chain propagation [Eq. (11)].



COMMENTS

The production and development of technologically useful poly(organo)phosphazenes depend directly on optimizing the polydichlorophosphazene polymerization reaction. Promising developments have been made in the areas of high temperature,

melt and solution polymerization. Advances are being made in gaining a better understanding of the polymerization mechanism(s). However there are still major problem areas which must be surmounted for polyphosphazenes to be commercially viable. Polymerization run times are often too long and temperatures are too high for safe and efficient handling and cost effectiveness. Highly pure trimer must be used and conversions must be limited to prevent crosslink formation. The polymerization behavior from batch-to-batch of trimer is not reproducible and polymer chain structure cannot be controlled with certainty. And finally, there are problems in handling hydrolytically unstable polydichlorophosphazene and controlling or preventing changes in polymer chain structure that may occur during nucleophilic substitution [5]. More basic research is required, especially in developing catalysts and chain transfer agents for lowering polymerization temperatures, obtaining higher conversions, preventing crosslink and cyclic oligomer formation, and controlling polymer molecular weight, molecular weight distribution, and branching. Up to the present, efforts to expand polymer production have relied upon scaled-up laboratory polymerization conditions. Consideration should be given to innovations required for the pilot plant and full scale production of polydichlorophosphazene.

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