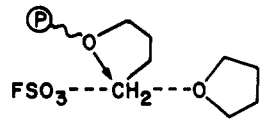
for $n = 2, 3, 4$. Ivin[30] has interpreted the stereospecificity of several polymerizations in terms of two propagating species **18** and **19**. **18** leads to cis product and **19** leads to trans product. The relative rates of dissociation for several

18 **19**

olefins were reported to be NBE > cyclopentene > COE ~ COD.

Finally, the higher rate of cationic polymerization of THF compared with other cyclic ethers has been attributed to the geometry of the transition state: the oxygen is in the proper position to stabilize the transient oxionic species **20**.[14]



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Conclusions

We have demonstrated that the rate of tungsten hexachloride/tetramethyltin-catalyzed olefin metathesis polymerization is independent of ring strain in the monomer but very dependent on the structure of the propagating carbene. The ease with which the closest double bond in the growing polymer chain can coordinate to the metal center determines the carbene reactivity. Relative reactivities of carbenes can be determined by measuring the change in rate of COD polymerization upon introduction of a second olefin.

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Plasma-Initiated Polymerization of Hexachlorocyclotriphosphazene

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ABSTRACT: The polymerization of $(NPCl_2)_3$ to $(NPCl_2)_n$ has been carried out via the recently developed technique of plasma-initiated polymerization. Samples were polymerized following plasma exposure using a radio-frequency generator and capacitive coupling. Plasma initiation leads to significant rates of polymerization at lower temperatures than those required for the thermal reaction, but temperature sensitivity is less extreme. Cross-linking is encountered only after total conversion at high temperatures. At lower temperatures, a limiting conversion is reached. Polymer yield goes through a maximum with plasma power and increases linearly with plasma duration. Though thermally obtained polymers have molecular weights in excess of 10^6, plasma initiation leads to much smaller molecular weights. Molecular weight, as measured by dilute solution viscometry, rises with polymerization time but is insensitive to polymerization temperature.

Introduction

The polyphosphazenes are an important family of polymers which have attracted much interest in the past 20 years. The reasons behind this interest include the unique nature of the inorganic –P=N– skeleton and the vast range of properties attainable through a wide variety of pendant groups.[1,2] A major problem in research on polyphosphazenes is the difficulty of their syntheses. Although halogenated cyclic triphosphazenes polymerize by ring-opening, the poly(dihalophosphazenes) that result are hydrolytically unstable[3,4] and hence of little practical use. On the other hand, poly(organophosphazenes) exhibit

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interesting properties for such diverse applications as low-temperature elastomers,[5-7] flame-resistant coatings and foams,[8,9] and biocompatible materials[10] but are inaccessible via ring-opening of the analogous organocyclic triphosphazenes.[4,11] These polymers must be synthesized by an indirect route, involving the polymerization of hexachlorocyclotriphosphazene ($(NPCl_2)_3$) (1) to poly(dichlorophosphazene) ($(NPCl_2)_n$) (2), followed by nucleophilic substitution of the pendant chlorine atoms with organic groups.[4,12]

The polymerization of 1 is important to the development of the polyphosphazenes. However, the reaction mechanism is only beginning to be understood.[4,11,13-17] It is known that polymerization takes place upon heating purified trimer (1) at 200 °C or above.[17] The rate of polymerization rises rapidly with temperature.[12,17,18] Unfortunately, polymerization is accompanied by a cross-linking reaction, which also accelerates at higher temperatures.[12] It is necessary, in fact, to perform 1 polymerizations at no higher than 250 °C in order to isolate soluble, un-cross-linked 2 in reasonable yield. Conversion (50–75%) to soluble polymer is possible only in the most carefully performed experiments.[12] At higher conversions, even polymerizations carried out at lower temperatures can yield cross-linked polymers.[12] In a recent publication, Sennett et al.[19] reported the kinetics and product characterization results of BCl_3-catalyzed reactions. Apparently, reproducible experiments are obtainable with certain catalysts, such as BCl_3.

The polymerization of 1 is extremely sensitive to the presence of impurities.[12,13,20,21] These affect both the rate of polymerization and the likelihood of cross-linking.[4] As a consequence, it is desirable to perform 1 polymerization in tightly controlled environments.[14] The difficulty of reproducing kinetic data suggests that the "thermal" polymerization may actually be catalyzed by impurities, even at concentrations below detectable levels.[20]

An additional problem with 1 polymerization is the slow rate at which it takes place. Higher rates are often seen in systems containing large amounts of impurities or intentionally introduced catalysts,[17] but such reactions have generally been accompanied by cross-linking.[12] Conditions leading to soluble polymers rarely give 50% conversion to polymer in less than 12 h, and slower rates are common. Renewed interest is being shown, however, in the search for non-cross-linking catalysts.[22-28] Because the effects of impurities at low levels are so acute, it is impossible to predict the rate of polymerization or the onset of gelation a priori. Thus, a polymerization must be monitored throughout its course and quenched before such time as the viscosity has increased sufficiently to cause the tube contents to cease flowing.[1] This is particularly unappealing from a practical standpoint.

Caution must be exercised since little control can be exerted over the properties of the 2 obtained.[1,15,29] Molecular weights are usually high ($>10^6$)[30] and often increase with conversion, but no method of controlling the molecular weight has been published. The molecular weight distribution is almost always broad and frequently bimodal or even multimodal.[29] This is believed to be a consequence of the cross-linking reaction, which at its outset may bond together only two or three chains into branched structures of higher molecular weight.[31]

In this paper, a new technique for initiating polymerization, called plasma-initiated polymerization, is applied to the problem of 2 synthesis. Plasma initiation was first reported, for methyl methacrylate polymerization, by Osada, Bell, and Shen[32] in 1978. In this technique, a radio-frequency glow discharge plasma is created in the vapor space adjacent to a condensed phase, resulting in traditional chain-growth polymerization after the plasma has been "quenched". In this way, plasma initiation differs from the more familiar "plasma polymerization", in which active species created in the glow discharge react to deposit a highly cross-linked polymer film on a substrate placed in or near the discharge.[33]

The most complete, detailed study of a plasma-initiated polymerization reaction published to date is that of Paul et al.[34] on methyl methacrylate polymerization. In it, the effects of the plasma and postpolymerization conditions on the rate of polymerization and molecular weight of resulting polymers were investigated. Some work was also reported concerning the mechanism of this unique reaction. A preliminary study has been published by Osada et al.[35] concerning the application of plasma initiation to 1 polymerization. This short work demonstrated the possibility of preparing 2 at lower temperatures. This might be expected to lead to a decreased probability of cross-linking and better reaction control. It is the purpose of this work to investigate more thoroughly the effects of the plasma and postpolymerization conditions on the polymerization of 1 and the molecular weight of the 1 so obtained. In this way, it was hoped conditions might be found that will lead, even at lower temperatures, to fast rates and/or higher conversions with reduced (or no) cross-linking and an increased degree of predictability and molecular weight control.

Experimental Section

Materials. 1 was obtained from Inabata and Co. in the form of a commercial product trade-named Phosnic 390. Two lots were acquired: MA-37, containing 4% cyclic tetramer, and KIB-21, containing 9% tetramer. All manipulations of Phosnic 390, purified 1, or 2 were performed under dried nitrogen. Tetramer and traces of volatile impurities were removed by a single vacuum sublimation at 50 °C. Sublimations were carried out on 120-g batches by using a detailed procedure described elsewhere.[36] Care was taken to contact the Phosnic 390 and purified 1 only with glass or porcelain implements. Purified 1 from either lot of Phosnic 390 was found to contain only a trace of cyclic tetramer (by ^{31}P NMR). Sublimed 1 was either used immediately or stored in a sealed dark glass jar in a desiccator.

Reagent grade toluene (Mallinckrodt AR) was dried by distillation from sodium–benzophenone ketyl. Phosphoric acid (85%) (Mallinckrodt AR), reagent grade acetone (Mallinckrodt AR), deuteriated chloroform ($CDCl_3$, 99.8 atom % D, Aldrich Gold Label), and chlorotrimethylsilane (Aldrich) were used as received.

Glassware Preparation. All glassware was carefully washed with Alconox, rinsed copiously with distilled water, allowed to stand filled with hot chromic acid–sulfuric acid "cleaning solution" for 30 min, rinsed several more times, and oven-dried at least 60 min at 200 °C. Reaction tubes were prepared even more rigorously. Only new Pyrex glass was used in their fabrication. The tubes were rinsed thoroughly with distilled water between steps; they were washed in Alconox, hot chromic acid–sulfuric acid (2 h), and hot aqueous 2% NaOH/1% ethylenediaminetetraacetic acid (EDTA) (2 h). They were then boiled in distilled water (2 h) and oven-dried at 250 °C for at least 8 h. This treatment was found to be sufficient to obtain reproducible results with the sensitive thermal (uncatalyzed) polymerization reaction.[36]

Polymerization Sample Preparation. Polymerization was carried out in 25-mm-i.d. Pyrex tubes sealed at one end. Each tube was pumped out on a vacuum manifold to 0.001 Torr and then heated in excess of 250 °C for 10 min while pumping. The tube was removed from the manifold (sealed by a stopcock attachment), and 20 g of purified 1 was introduced under dry nitrogen. The filled tube was reevacuated and pumped for 30 min. Then the tube was subjected to melt–freeze–degas cycling until the manifold pressure gauge showed no pressure change upon opening the stopcock to degas (typically, three cycles were required). The tube contents were then pumped a final 30 min,

and the tube was melt-sealed. The contents of each sealed tube were melted at not more than 140 °C, and the tube was then rolled horizontally while the trimer cooled and recrystallized. This redistributed the 1 crystals from a solid mass at one end of the tube to a relatively uniform coating over the entire interior tube surface. The merits of this uniform coating will be discussed below.

As plasma product molecules and especially reactive fragments impact a surface, the nature of that surface has a great effect on the reactions they undergo. If the surface is glass, recombinations such as those involved in standard plasma polymerization are likely to take place, resulting in cross-linked, insoluble film. If the surface is a trimer crystal surface, the reactions are more likely to be bimolecular chemical reactions forming new phosphazene structures. In addition, where the walls are coated with trimer, the impact path for product molecules and active species is countercurrent to the diffusion path for "fresh" replacement trimer vapor. This further enhances the likelihood of the formation of new phosphazene molecules, with large enough molecular weights to cause precipitation as liquids, before film formation by active fragment impacts can occur.

Thus the redistribution of trimer to the walls of the reaction tube also serves the purpose of maximizing contact between the plasma and the trimer and minimizing the contact between the plasma and glass. This promotes the formation of plasma "oil" and retards the formation of plasma film. In addition, minimization of the contact between the plasma and the glass reduces the risk of etching away, into the vapor phase, the sorts of glass surface impurities suspected of causing difficulty in reproducible $(NPCl_2)_3$ polymerization.

Plasma-Generating Equipment. The 13.56-MHz radio-frequency source was a Tracerlab radio-frequency generator, Model RFG-600 [Laboratory for Electronics (LFE), Inc.]. Power was measured by a through-line wattmeter, Model 43 (Bird Electronic Corp.). The matching network used was an LFE Tracerlab plasma activator, Model PAI-600. The power was capacitively coupled to the plasma, using two parallel plate copper electrodes mounted on a Teflon base at a plate spacing of 3.5 cm. The electrode dimensions were 15 cm (extension from the base) by 10 cm. The sealed reaction tube was centered in all three dimensions between the electrodes. An air blower was suspended about 5 cm above the tube and was used to maintain the tube temperature near ambient by blowing room air along the length of the tube. A Tesla coil was used to initiate the glow discharge after turning on the generator. The area around the discharge tube was enclosed in a Faraday screen.

Plasma Initiation and Postpolymerization. Glow discharges were sustained for various predetermined lengths of time. Plasma duration was measured from the moment the glow discharge was initiated (not the instant power was turned on) to the moment the glow was extinguished, or quenched. Exactly 60 s after quencing, the tube was inserted in the polymerization oven. Polymerizations were carried out in an oven capable of maintaining a constant temperature to ±1 °C. Each tube was inserted into a wire cage designed to contain fragments in case of breakage. "Time zero" was defined as the moment of insertion, although it is recognized that the tube contents require some time to reach the oven temperature. Measurements and calculations both indicate that this heat-up time is negligible in all but the shortest duration experiments. In any event, removal from the oven, rather than resolidification, was taken as the end point of reaction time, and this has a compensating effect. Upon removal from the oven, tubes were set aside and analyzed when convenient. Long-term storage at room temperature in the sealed tube was found to have no effect on thermally produced or plasma-initiated polymers.

Yield Determination. Plasma-initiated **2** tends to be less rubbery than the thermally produced polymer, often having a sticky or even an oily consistency. This makes separation by solution techniques difficult. For this reason, all yield determinations were done by vacuum sublimation at 60 °C. Polymers were protected from atmospheric moisture at all times by handling only under nitrogen. Yields were determined gravimetrically from the weights of recovered polymer and trimer. Where any reason existed to suspect the presence of cross-linked polymer, a toluene solution of the trimer-free polymer was prepared and filtered to isolate the gel.

IR and ^{31}P NMR Spectroscopy. Infrared spectra of both thermally produced and plasma-initiated polymers were obtained by using 5–10-μm films cast under dry nitrogen from toluene solution onto KBr disks. A Perkin-Elmer 597 instrument was used. ^{31}P NMR spectra of trimer, thermal polymers, and plasma-initiated polymers were obtained by using a 180-MHz NMR spectrometer. H_3PO_4 (85%) was used as an external reference, and chemical shifts are reported in parts per million relative to H_3PO_4. The traces of trimer found in the polymer samples were also used as internal references. Approximately 200 scans were necessary to obtain high-quality spectra.

Dilute Solution Viscometry. Dilute viscometry was used to determine the viscosity-average molecular weight, M_v, of **2**. The viscometer was of the standard Ubbelohde type. Since **2** is prone to hydrolysis, precautions were taken to exclude water. The polymer was dissolved in toluene containing 0.1% chlorotrimethylsilane as a water scavenger and polymer stabilizer.[29] Nominal 1 g/dL solutions were filtered and then introduced into the viscometer by using a syringe. The gas space in the viscometer was purged continuously with dry nitrogen saturated with toluene. The efflux time from the viscometer was measured for the initial charge of polymer solution. The charge was then diluted and the efflux time remeasured. In this way, efflux times were obtained at five concentration levels for each polymer sample. Sets of efflux times were converted to values of the intrinsic viscosity.[37] Huggins/Kramer plots were then constructed and used to determine the intrinsic viscosity, $[\eta]$. Viscosity-average molecular weights, M_v, were then calculated by using the Mark–Houwink equation

$$[\eta] = KM_v^a \tag{1}$$

where K and a were 3.42×10^{-6} and 0.902, respectively. Values of K and a were obtained from the data of Knoesel et al.[38] and Hagnauer et al.[30,39,40] Since the Mark–Houwink constants were taken from literature values, there was no independent calibration to verify the accuracy of molecular weights deduced from the above equation. However, the molecular weights thus calculated can be used as qualitative indicators of the relative size or product species from thermal and plasma-initiated procedures as will be shown later.

Results and Discussion

Appearance of Plasma-Initiated 2. When **1** is polymerized thermally at 250 °C, the contents of the reaction tube are gradually transformed from a low-viscosity clear colorless liquid to a solid plug of clear colorless rubber. The picture is different for the plasma-initiated polymerization of **1**. The reaction mixtures rarely get very viscous and never gel for the conditions used in this study. In fact, at all but the highest conversions, the reaction contents are quite fluid at polymerization temperatures.

^{31}P NMR and IR Spectra of Thermal and Plasma-Initiated 2. The first concern upon discovery of the fluid nature of plasma-initiated reaction mixtures was whether high polymer was indeed being formed at all or whether conversion to some other product was taking place. This question is easily answered by ^{31}P NMR and IR spectroscopy. Members of the $NPCl_2$ series show distinct ^{31}P chemical shifts. For the cyclic trimer, values averaging about +19.7 ppm have been reported.[41–49] The chemical shift for cyclic tetramer is reported at about −6.9 ppm[41,43,45–51] and that of the high polymer at about −18.7 ppm.[4,42,50,52] Higher cyclics have chemical shifts very near that of the high polymer, but are distinguishable up to octamer or nonamer if a spectrometer capable of 0.1 ppm resolution is available.[43,45,46,49] Short-chain linear species are known and may have a variety of terminal groups. Thus they exhibit at least one more peak, in addition to the −18.7 ppm chain $-N{=}PCl_2-$ peak, and often exhibit broadening or splitting of the latter due to the proximity of penultimate chain units to the terminal groups. From a quantitative standpoint, ^{31}P NMR is sensitive to about

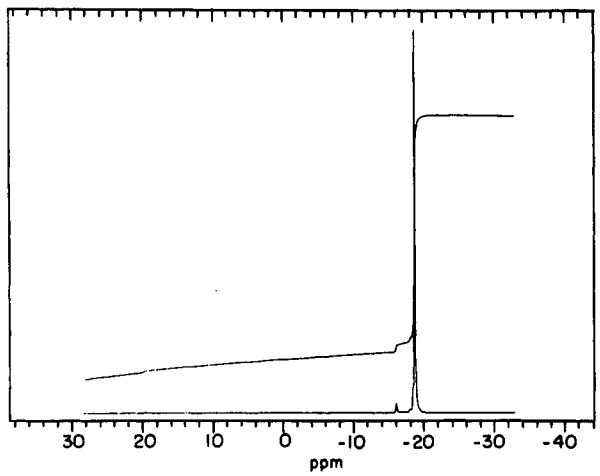

Figure 1. ^{31}P NMR spectrum of thermally initiated poly(dichlorophosphazene).

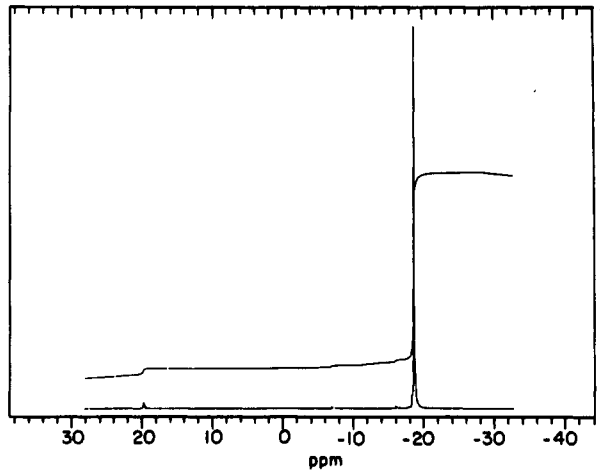

Figure 2. ^{31}P NMR spectrum of plasma-initiated poly(dichlorophosphazene).

5% concentration, so ends present at a level of 1 out of 40 repeat units or below are not detectable. The absence of peak broadening or splitting thus indicates that the species produced are at least 40 repeat units long.

Figure 1 shows a typical ^{31}P NMR spectrum of thermally polymerized 2. This sample was made at 250 °C, in 4 h of polymerization time, and the unreacted trimer was removed by a 60 °C vacuum sublimation. Hence, any higher cyclics formed during the polymerization should be evident in the polymer spectrum. The spectrum shows a large, sharp singlet at −18.7 ppm, indicative of the high polymer, and several much smaller peaks, at +19.7 ppm (trimer), −16.1 ppm, and −17.9 ppm (higher cyclics). There is also a shoulder on the downfield (less negative) side of the principal peak, which is probably due to higher cyclics. It should be noted that formation of higher cyclics in this polymerization is slight, accounting for only 6% of the product phosphorus (by peak area ratio, including the shoulder among the cyclics).

Figure 2 shows the spectrum obtained from a typical plasma-initiated reaction of 1 and demonstrates that the product is, indeed, a polymer. This sample was produced via plasma exposure at 100 W for 10 min, followed by postpolymerization at 180 °C for 24 h. The conversion to polymer was in excess of 10%, while thermal polymerization at this temperature yields, at best, only minute traces of high polymer. Thus the product formed is due only to the plasma exposure. A large, sharp singlet is again observed at −18.7 ppm. Several much smaller peaks appear

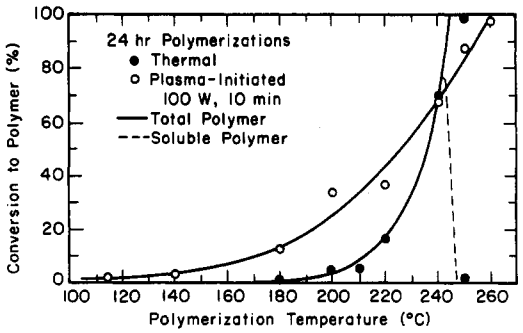

Figure 3. Effect of polymerization temperature on the conversion to polymer for plasma-initiated and thermally initiated polymerization.

at +19.7 ppm (trimer), −7.0 ppm (tetramer), and −16.0 and −17.9 ppm (higher cyclics). A small shoulder also appears on the principal peak in this spectrum. When it is counted once again with the higher cyclics, the plasma-initiated polymerization also yields approximately 6% of product phosphorus in the form of higher cyclics. A final point of interest is that the polymer peak is actually less broad for the plasma-initiated polymer. This may be due to chain branching in the thermal polymer, the existence of which has been the subject of considerable debate in the literature.[29-31,53-57]

The infrared spectra of the same two polymers were identical in appearance and match that published by Manley and Williams[58] very closely. The only difference is the lack of a peak at 2910–2930 cm^{-1}, which Manley and Williams attributed to hydrolysis sites. This serves as further evidence, then, of the polymeric nature of the plasma-initiated reaction product.

Effect of Postpolymerization Temperature. The sensitivity of the thermal polymerization reaction of 1 to polymerization temperature is well-known and has been discussed above. In Figure 3, the effect of postplasma reaction temperature on the plasma-initiated polymerization is compared to the temperature effect for the thermal reaction. The figure shows plots of conversion to polymer as a function of polymerization temperature. All polymerizations presented here were carried out for 24 h of polymerization time.

The filled circles and the solid best-fit curve drawn through them show the results of thermal polymerization. The results obtained in this study are consistent with those presented in the literature.[4,12,13,18] No polymerization is seen to occur below a temperature of about 200 °C. Above 210 °C, the rate accelerates sharply, as demonstrated by the rapid increase in conversion at 24 h. At 240 °C, a conversion near 70% was obtained with essentially no insoluble, cross-linked polymer. Above 240 °C, conversion in 24 h is complete, and the product at 250 °C or above is entirely cross-linked and insoluble. The dotted curve represents schematically that, between 240 and 250 °C, the polymer obtained after 24 h changes very abruptly from totally soluble to totally cross-linked. Evidence from experiments at 250 °C with variable polymerization times indicates that once cross-linking begins in such a purified system as the one used here it is exceedingly rapid. Allcock suggests[4] that the cross-linking which inevitably takes place at high conversions may not be hydrolytic, but may involve attack by growing chain ends on the P–Cl bonds of chain phosphorus, made more likely by the depletion of available cyclic trimer. This would adequately explain sudden cross-linking at high conversion. The important point is that great care and precision must be exercised in a thermal polymerization if maximum conversion to soluble

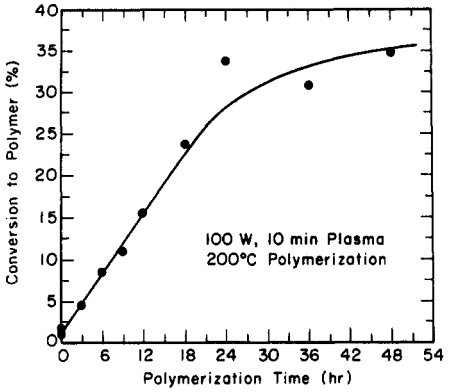

Figure 4. Effect of polymerization time on the conversion to polymer for plasma-initiated polymerization.

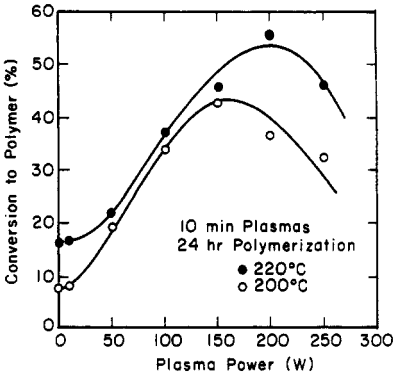

Figure 5. Effect of plasma power on the conversion to polymer for plasma-initiated polymerization.

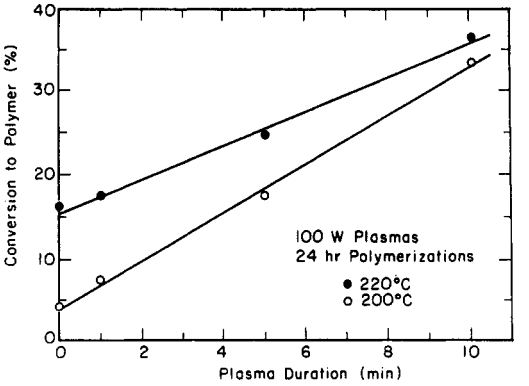

Figure 6. Effect of plasma duration on the conversion to polymer for plasma-initiated polymerization.

polymer in a reasonable time is desired.

The situation is considerably different for the plasma-initiated reaction. In Figure 3, the open circles and the best-fit curve drawn through them represent the results of this reaction. Polymerization commences at a significantly lower temperature, and the rate rises much more slowly with temperature. In fact, at temperatures above 240 °C, the plasma-initiated yield is actually lower than that for thermal polymerization. Furthermore, conversions in excess of 95% are possible without producing insoluble products. Experiments run at 250 °C for longer postpolymerization times indicate that cross-linking does eventually occur in the plasma-initiated reaction but not until several hours after conversion is complete. A plausible explanation for this involves the relatively low viscosity of plasma-initiated reaction mixtures. Assuming Allcock's explanation of cross-linking at high conversions,[4,12] one expects less cross-linking in a mixture of lower viscosity because of greater molecular mobility. Encounters between growing chain ends and trimer molecules would be more frequent, and the chain ends would thus be less prone to attack the less preferred chain phosphorus sites. Even when no trimer at all remained, the attack of live ends on other chain molecules would result only in the formation of larger branched polymers, up to a certain point.

The practical implication of these results is to make available additional degrees of freedom in choosing conditions. First, nearly 100% conversion to soluble polymer can be obtained, and some flexibility remains in choosing the time at which to terminate the reaction without risk of cross-linking. Previously, the only initiator species demonstrated in the literature to lead to such high conversions without cross-linking were BCl_3 and BCl_3·$(C_6H_5O)_3P{=}O$,[22] although sulfur may also be effective.[23] Second, polymerization can be carried out at reasonable rates at much lower temperatures, which may be of benefit in designing an energy-efficient polymerization process. Again, only BCl_3 and its triphenyl phosphate adduct have shown activity at 180 °C or below.[22,24,26] Finally, precise temperature control is much less important for the plasma-initiated reaction, since the rate changes considerably less abruptly with temperature than it does in the temperature range of interest (230–250 °C) for the thermal reaction. The BCl_3-initiated polymerization rate appears to be more sensitive to temperature.[22]

Effect of Polymerization Time. Figure 4 shows a plot of conversion to soluble **2** as a function of time for the plasma-initiated polymerization, using a 100-W, 10-min plasma exposure and 200 °C postpolymerization temperature. At this temperature, the rate of thermal polymerization is exceedingly small, so there should be little "interference" from the thermal reaction in these experiments. The most interesting feature of this plot is that the conversion seems to reach a plateau, remaining essentially unchanged at a little under 35% for polymerization times well in excess of 24 h. It was mentioned above that at 250 °C, the plasma-initiated reaction continues to total conversion and eventually yields cross-linked polymers. The results presented here indicate that at lower temperatures, more specifically, at temperatures at which thermal polymerization can play little role, polymerization stops well short of the high conversions associated with the formation of nonhydrolytic cross-links. This provides yet another degree of freedom. It is possible, at the cost of accepting a low yield (a cost generally accepted anyway when thermal **1** polymerizations are performed), to completely avoid any risk of cross-linking. This makes control of polymerization temperature and reaction time even less critical than in the case of plasma-initiated polymerization at higher temperature. It also implies that changes in the concentrations of noncatalytic impurities, such as the cyclic tetramer, would be much less important, since their effect on the rate of polymerization could in no way result in cross-linking due to misjudging the necessary change in allotted polymerization time. This would allow one to cope more easily with changes in the sources of supply or purification process of the **1** starting material.

Effect of Plasma Conditions. Figures 5 and 6 present data concerning the effects of the conditions of the glow discharge on the plasma-initiated polymerization reaction. The scope of this study did not permit a thorough examination of all variables pertinent to glow discharge chemistry. However, two of the most important variables were studied, the discharge power and the plasma duration.

Figure 5 shows the effect of plasma power on conversion to polymer when a plasma exposure time of 10 min and a postpolymerization time of 24 h are used. Data for

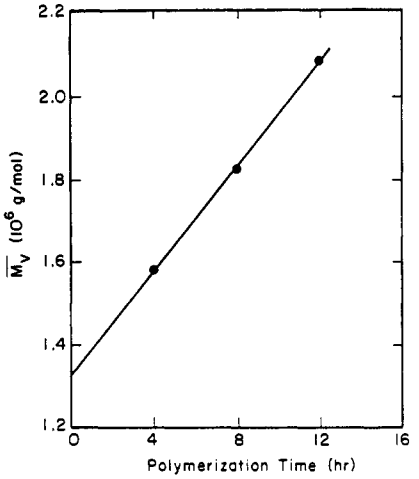

Figure 7. Molecular weight of thermally initiated poly(dichlorophosphazene).

polymerization at 200 and 220 °C are given.

For both temperatures, the conversion to polymer goes through a maximum when plotted against plasma power. The increase in monomer conversion with increasing power observed at low powers an be attributed to the formation of an increasing amount of initiator. A maximum in conversion is reached at the point when the power is great enough to degrade initiator produced during the initial period of exposure of the monomer to the plasma. Paul et al.[34] reported the same effect of power for the plasma-initiated polymerization of methyl methacrylate.

Figure 6 illustrates two plots of conversion to polymer as a function of plasma duration (or glow discharge exposure time) for experiments utilizing a discharge power of 100 W and a polymerization time of 24 h. For polymerization at 200 and 220 °C, a linear increase in conversion with increased plasma duration is seen. The explanation is fairly straightforward. If one assumes that the polymerization-active products of the plasma condense out of the vapor phase, increasing the time of exposure will do nothing to further alter their structure. On the other hand, as they condense out, more trimer molecules will evaporate into the gas phase, and these will be converted as well. The result is that more oil, of roughly the same composition, is produced in a longer exposure time. Therefore, a linear increase in polymer yield would be expected, as a consequence of the linear increase in initiator production. Again, a similar effect was seen by Paul et al.[34] for the plasma-initiated polymerization of methyl methacrylate.

Molecular Weight Analysis. Compromises must be made in evaluating the molecular weight of **2**. Since the polymer is so hydrolytically unstable (cross-linking eventually occurs in solution even in the driest solvents),[12] it is difficult to characterize by conventional techniques. Traditionally, molecular weight determinations have been carried out after performing a nucleophilic substitution reaction on the polymer to yield a hydrolytically stable poly(organophosphazene). However, as pointed out by several authors,[29,21,40,59] there is no guarantee that the properties of substituted polyphosphazenes will accurately reflect the properties of their precursor poly(dichlorophosphazenes). If the amount of residual water varies even a little among several experiments, the amount of cross-linking induced in the polymers will vary, and this will have the effect of scrambling the order of their molecular weights. There is also some risk of the opposite problem: variable amounts of chain cleavage due to insufficient control of the temperature and duration of the substitution reaction.

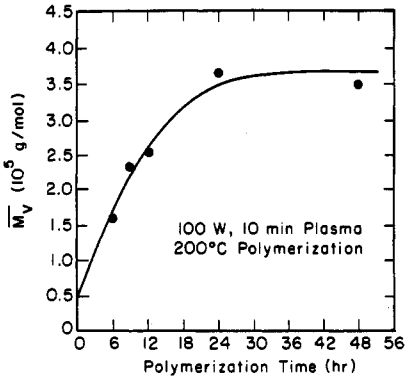

Figure 8. Effect of polymerization time on the molecular weight of plasma-initiated poly(dichlorophosphazene).

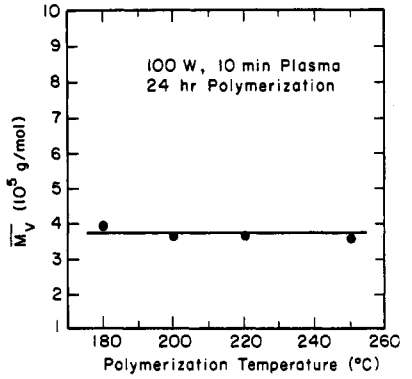

Figure 9. Effect of polymerization temperature on the molecular weight of plasma-initiated poly(dichlorophosphazene).

For these reasons it is desirable to analyze the unsubstituted polymers directly. Several publications have recently suggested that through very careful handling and rigorous exclusion of moisture this can be done.[15,29,30,39,40,60] Specifically, dilute solution characterization of **2** has been reported by Hagnauer et al.[15,30,39,40] and by Adams et al.[29]

Figure 7 shows some results obtained for **2** made by thermal polymerization. The molecular weights are all greater than 10^6, and there is an increase in molecular weight with polymerization time (or, equivalently, with conversion, since conversion also increased linearly with polymerization time).[36] This is consistent with results published by Hagnauer.[15] Other authors have also suggested an increase in molecular weight with conversion.

Figures 8 and 9 show molecular weight results for the plasma-initiated polymerization of **1**. The most outstanding feature of these data is that the molecular weights of all plasma-initiated polymers examined were much lower than even the lowest value obtained for thermal polymerization, yet all values were in the high-polymer range ($>10^5$). This is the final evidence that the product of plasma-initiated polymerization of **1** is indeed high polymeric **2**. Several other recent studies have also reported **2** molecular weights in the $(1–5) \times 10^5$ range, using a variety of initiators[28,61] and direct synthesis from $Cl_2P(O)N=PCl_3$.[62] The synthesis of $[NP(Me)(Ph)]_n$ from $Me_3SiN=P(Me)(Ph)(OCH_2CF_3)$ also results in molecular weights in this range.[63] BCl_3-initiated polymerization usually yields still lower molecular weights,[24,26] but there is some evidence that molecular weight might be raised by adjusting catalyst concentration.[22]

Figure 8 is a plot of the viscosity-average molecular weight of plasma-initiated **2** as a function of polymerization time, at constant plasma conditions of 100-W discharge power and 10-min exposure time and a constant post-polymerization time of 24 h. It can be seen from this graph

that the molecular weight is invariant, at a value of just under 4×10^5, with polymerization temperature. This is a remarkable result, because it implies that, until the supply of trimer is exhausted and growing chain ends begin attacking other chains, plasma-initiated polymers obtained at temperatures capable of supporting thermal polymerization are no different from those obtained at lower temperatures. This suggests that even as the polymerization is being initiated by species created in the plasma the processes involved in thermal polymerization are being suppressed, or at least in some way counteracted.

Mechanistic Speculations. In this final section, we offer some informed speculations regarding the reaction mechanism. These ideas, while not entirely proven by the data at hand, at least provide an explanation consistent with the phenomena observed.

It has been assumed, without proof to this point, that the species responsible for initiating postpolymerization in $(NPCl_2)_3$ are contained in the oily product of the plasma. There is some supporting evidence for this assumption. Three classes of product are obtained from plasma exposure of $(NPCl_2)_3$. These are the oil, the traces of insoluble film, and the small-molecule gases that ultimately result in the self-extinction of the plasma due to increased pressure. The first argument in favor of "active" oil is by analogy to the plasma-initiated polymerization of methyl methacrylate. Paul et al.[34] examined the structure of the oily plasma product of methyl methacrylate and elucidated the mechanism by which it initiates polymerization. The second argument in favor of "active" oil rests on observations of the $(NPCl_2)_3$ polymerization, specifically on the differences between the experiments performed by Osada et al.[32,35] and those reported here. Osada's experiments utilized different procedures in which the reaction tube was evacuated and pumped out continuously during the time of plasma exposure. Therefore, the gaseous products of the plasma were continually removed from the reaction tube. The fact that Osada et al. obtained postpolymerization similar to that reported here indicates that the active species is not among the gaseous products. The possibility of the film containing the active species can also be discounted, on the basis of visual observations. If the film initiates chain growth onto its own surface, the polymerization would proceed heterogeneously and most likely yield a cross-linked insoluble product. If the film initiates polymerization by decomposing into active soluble species, there would be a net loss of film during the polymerization process. Neither of these effects is observed. The polymerization is completely homogeneous, and soluble polymers are isolated at all conditions except near-total conversion at high temperature. The traces of film formed in the plasma are always recoverable after the polymerization is completed and, in fact, are sometimes slightly more voluminous than before postpolymerization. This indicates that there may be some minor chain addition to the insoluble film, but it is insignificant compared to the homogeneous polymerization in the melt. Thus, initiation by gaseous products or insoluble film is highly unlikely, and the initiator can be reasonably assumed to be contained in the oil by process of elimination, as well as by analogy to methyl methacrylate polymerization.

If one assumes that a substance in the oily product dissociates into $N_3P_3Cl_5^+$ and Cl_3PN^- fragments and the formation of the ions is the controlling step, propagation may proceed even at lower temperatures, just as in the mechanism proposed by Allcock for thermal polymerization.[5] In plasma initiation, with no Cl^- counterion (which would immediately recombine at low temperatures) present, polymerization is free to occur. However, a growing chain would inevitably be expected to encounter one of the acyclic phosphazenyl anions. Recombination might then be expected to be favored and rapid, because the high polymer is not known to dissociate into chain ion pairs at any temperature. Such recombination would serve as a termination reaction. Since the thermal reaction is believed to be terminated only by impurities (or not at all), this helps to account for the observed low molecular weights of plasma-initiated $(NPCl_2)_n$.

An objection might be raised at this point that the proposed growing polymer molecule very closely resembles the plasma oil molecule whose instability was held to be the cause of initiation—an acyclic phosphazene chain joined to a phosphazene ring. One possible explanation would be to propose that plasma oil molecules are more stable when their acyclic substituents are very long or unbranched. This is entirely speculative since, as mentioned above, no thermal decomposition data on these compounds is available. However, the idea of decreased stability for compounds with branch sites near the ring is attractive from a steric point of view. If initiation is rate controlling, the $N_3P_3Cl_5$ cation would very quickly grow a long, linear polymer chain. If such a substituent were less likely to dissociate from the ring, the polymer molecule would be stable once terminated by the addition of a phosphazenyl anion.

Phosphazenyl side group ionization also helps explain why a limiting conversion is reached in plasma-initiated polymerization, provided the reaction is performed at temperatures incapable of supporting thermal polymerization. Basically, the initiator is consumed in the reaction, with each half of a plasma oil molecule providing one end of the finished polymer molecule. The effect of postpolymerization temperature is also explained by this mechanism. If the plasma oil molecules vary in their ionizability with substituent size and shape, the same collection of molecules would be expected to provide increasing amounts of cations at increasing temperatures, hence both the rate and the limiting conversion would rise.

The most difficult aspect of the plasma-initiated polymerization of $(NPCl_2)_3$ to explain is the high-temperature behavior. Recall that at temperatures over 240 °C the conversion to polymer in 24 h is actually lower than that obtained thermally, and so is the molecular weight. At first glance, this gives the appearance of inhibition of the thermal reaction, but this is not necessarily the case. One can argue that the acceleration of the thermal polymerization rate at high temperatures may be due, at least in part, to the high viscosity of the reacting medium. This could result in a decrease in the likelihood of encounters between the growing chain end and its chloride counterion, resulting in increased propagation. If there is a termination reaction involving trace impurities, this would also be inhibited at high viscosity. Plasma initiation may counter this simply by depressing the viscosity of the reaction mixture as a consequence of the lower molecular weights obtained. At high temperatures, the greatest number of plasma oil molecules would be expected to dissociate. Thus, there would always be plenty of phosphazenyl anions available for termination reactions, and the solution viscosity would remain low. This in turn would prevent the viscosity-related high-temperature acceleration seen thermally. Conversions approaching 100% would be possible while still at low viscosity, and this is in fact what is observed. Ultimately, with all trimer exhausted, any remaining initiator would be expected, upon dissociation, to attack chain sites. The cyclic cation could conceivably

abstract a chloride ion to form a $(NPCl_2)_3$ molecule, and the phosphazenyl anion could add to a site such as the one just created. When all the initiator was consumed as well, thermal ionization of chain chlorine would lead to molecular weight increase and eventually cross-linking.

Conclusion

The plasma-initiated polymerization of hexachlorocyclotriphosphazene to poly(dichlorophosphazene) has been shown to exhibit a number of advantages over the thermal polymerization reaction. The polymers obtained are of considerably lower molecular weight, yet are still well within the range normally attributed to "polymers". The polymerization proceeds at temperatures significantly lower than those required for thermal polymerization. at higher temperatures, conversions of over 95% to soluble, un-cross-linked polymer are possible. The plasma-initiated polymerization rate is much less temperature sensitive than the thermal rate. At lower temperatures, cross-linking is averted altogether, but conversion is limited to a value well under 100%. This limiting value may be adjusted by altering the parameters of the glow discharge, such as power and duration.

Molecular weight may be controllable, but further research is necessary to establish this point. Clearly, molecular weight rises with polymerization time. At high postpolymerization temperatures, reaction mixture viscosity continues to rise after 100% conversion has been reached. This may reasonably be assumed to be due to the linking of the relatively low molecular weight molecules into larger, probably branched, structures. No characterization work was done on such polymers, and some is needed before firm conclusions can be reached. It is possible, though, that this effect can be manipulated to yield polymers of any arbitrary molecular weight.

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Registry No. **2** (SRU), 26085-02-9; **2** (homopolymer), 25231-98-5.

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