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A STUDY OF SOLUTION POLYMERIZATION OF POLYPHOSPHAZENES

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Several alkoxy/aryloxy substituted phosphazene polymers $[P(OR)_2{=}N]_n$, where R=CH_3, C_6H_5, $C_6H_5CH_3$, CH_2CF_3, C_6H_4-C_6H_5, C_6H_5-Cl, C_6H_5-Br, C_8H_{10} were prepared by the reaction of polydichlorophosphazene with their corresponding sodium salts. The polydichlorophosphazene was obtained by the solution polymerization of hexachlorocyclotriphosphazene in 1,2,4-trichlorobenzene. Sulfamic acid and ammonium sulfamate were used as catalysts Apparently sulfamic acid functions as a catalyst through its acid group in some decomposed form. Toluenesulfonic acid and sulfobenzoic acid were new calalysts developed for solution polymerization. The polymerization favors a cationic mechanism. Promoters were found to speed up the polymerization reaction and reduce branching. Effect of different parameters including dilution, catalyst concentration, and promoter concentration on the properties of the final polymer were investigated. The changes in molecular weight and molecular weight distribution of the polymer as a function of polymerization reaction time was noted. The nucleophilic reaction was studied and the effect of time pressure, and temperature on the properties of the final polymer were investigated. Ring opening on fully substituted cyclotriphosphazenes at elevated pressures and temperatures were unsuccessful. The polymers were characterized by differential scanning calorimetry, gel permeation chromatography, and infrared spectroscopy.

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A STUDY OF SOLUTION POLYMERIZATION OF POLYPHOSPHAZENES

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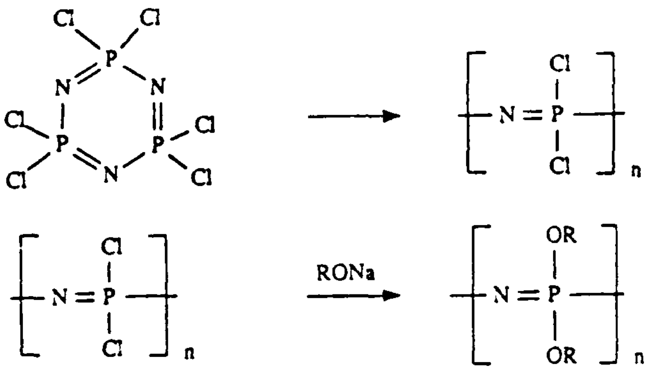
ABSTRACT:

Several alkoxy/aryloxy substituted phosphazene polymers $[P(OR)_2{=}N]_n$, where $R{=}CH_3$, C_6H_5, $C_6H_5CH_3$, CH_2CF_3, C_6H_4-C_6H_5, C_6H_5-Cl, C_6H_5-Br, C_8H_{10} were prepared by the reaction of polydichlorophosphazene with their corresponding sodium salts. The polydichlorophosphazene was obtained by the solution polymerization of hexachlorocyclotriphosphazene in 1,2,4-trichlorobenzene. Sulfamic acid and ammonium sulfamate were used as catalysts Apparently sulfamic acid functions as a catalyst through its acid group in some decomposed form. Toluenesulfonic acid and sulfobenzoic acid were new calalysts developed for solution polymerization. The polymerization favors a cationic mechanism. Promoters were found to speed up the polymerization reaction and reduce branching. Effect of different parameters including dilution, catalyst concentration, and promoter concentration on the properties of the final polymer were investigated. The changes in molecular weight and molecular weight distribution of the polymer as a function of polymerization reaction time was noted. The nucleophilic reaction was studied and the effect of time, pressure, and temperature on the properties of the final polymer were investigated. Ring opening on fully substituted cyclotriphosphazenes at elevated pressures and temperatures were unsuccessful. The polymers were characterized by differential scanning calorimetry, gel permeation chromatography, and infrared spectroscopy.

INTRODUCTION:

Inorganic polymers with a backbone of alternating phosphorus and nitrogen atoms, known as polyphosphazenes have attracted growing attention in recent years. They comprise a relatively new class of polymers that show promise for further development. Many such polymers with a variety of substituents at the phosphorus have been prepared and they often exhibit useful properties like fire retardancy, low temperature flexibility, resistance to chemical attack, and biocompatibility amongst others.(1-3)

The most commonly used synthetic route to linear polyphosphazene is a two step process developed by Allcock in the mid-1960's.(4) It involves ring opening polymerization of cyclic trimer, hexachlorocyclotriphosphazene, to produce linear high molecular weight polydichlorophosphazene and subsequent replacement of the chlorine groups with the nucleophilic substituents. This synthetic route is different than conventional polymer synthesis in that a variety of polymers can be prepared from one polymer source namely, polydichlorophosphazene.



Cyclic phosphazene is polymerized to linear polydichlorophosphazene by either solution polymerization or melt polymerization. Melt polymerization of hexachlorocyclotriphosphazene has been most widely studied. Thermal polymerization proceeds at a faster rate and at lower temperature with trimer than with higher oligomers,(5,6) however the time involved in melt polymerization is more than an order of magnitude longer than is required for solution polymerization.(7) The reaction is usually carried out in evacuated sealed tubes and at temperatures of about 230°-300°C. Heating is continued until the reaction mixture ceases to flow. If polymerization is continued after this stage, the polydichlorophosphazene may crosslink and become unsuitable for further substitution. Crosslinking is unpredictable and is generally enhanced by the presence of impurities. In solution polymerization, the reaction temperature required is lower the viscosity of the reaction mixture is relatively low, and the chain structure can be better controlled to produce high molecular weight polymer using shorter reaction times.(8)

The solution and melt polymerization of hexachlorocyclotriphosphazene each gave poly(organo)phosphazenes in which the organic side group is bonded to the phosphorus atom through oxygen or nitrogen links, thereby providing pathways for decomposition or depolymerization upon heating well above 200°C.(9) Recently, Neilson prepared polyphosphazenes with organic side groups attached directly to the phosphorus atom by a condensation polymerization of n-silylphosphinimines.(10,11) By designing the appropriate precursor, it is possible to synthesize polyphosphazenes with different side groups directly attached to the main chain. This method produces linear polymer with molecular weight in the range of 50,000 to 2,000,000 and with relatively narrow molecular weight distribution.

The mechanism of the conventional polymerization reaction is not known with certainty. Attempts to study the polymerization in detail have not been completely successful due to hydrolytic instability of polydichlorophosphazene and also due to some degree of irreproducibility.(12,13) Second and first order kinetics have been reported for uncatalyzed and and catalyzed melt polymerization respectively.(14,15) Studying the polymerization reaction in situ is difficult to do for both solution and melt polymerization because of the high reaction temperatures involved and the sensitivity of the reaction products to moisture. However, Hagnauer and coworkers recently used Raman spectroscopy and laser light scattering equipment to investigate solution and melt polymerizations.(16,17) The results of these experiments indicate that the cationic mechanism of chain propagation is predominant in these polymerizations. Conductance and dielectric data also supports the cationic mechanism. However the exact nature of the active center for chain growth is still unknown.

Polydichlorophosphazene has no commercial use due to the facile hydrolysis of the chlorine substituents in the presence of atmospheric moisture. Hence the chlorine atoms must be replaced by the organic groups to obtain a useful polymer. This is accomplished usually by reacting polydichlorophosphazene with alkoxy or aryloxy sodium salt in a suitable solvent. The properties of the resulting poly(organo)phosphazene are determined by the type of alkoxy or aryloxy substituents coupled to the P-N backbone of the polymer.

We have synthesized polyphosphazenes with many different substituents varying from small groups including OCH_3 to bulky groups such as OC_6H_4-C_6H_5. The polydichlorophosphazene was prepared by solution polymerization of hexachlorocyclotriphosphazene which was then reacted with a corresponding sodium alkyloxide/aryloxide to produce the desired poly(organo)phosphazene. The solution polymerization was carried out in 1,2,4-trichlorobenzene using catalysts that include sulfamic acid, toluenesulfonic acid, and ammonium sulfamate and a promoter $CaSO_4 \bullet 2H_2O$. The polymerization that was promoted by $CaSO_4 \bullet 2H_2O$ in presence of sulfamic acid in optimum proportion is fast and yields high molecular weight polymer with fairly narrow molecular weight distribution. In order to understand the mechanism of the reaction, we have studied the effect of different parameters on the properties of the final polymer. Changes in the molecular weight and dispersity of the polyphosphazene as a function of reaction time was monitored to study the mechanism of the reaction. Attempts were made to ascertain the nature of the active catalyst.

EXPERIMENTAL SECTION:

Material: The hexachlorcyclotriphosphazene was obtained from Dr. T. Nishakawa of Shin Nisho Kaku

Corporation, Japan. It was 99(+)% trimer with the remaining being tetramer. The trimer was dried in vacuum oven to remove any traces of moisture and stored in dry box to avoid contact with moisture. 1,2,4-trichlorobenzene and all other solvents were obtained from Aldrich Chemicals and were used as received. All solvents were stored over molecular sieves to keep them in a dry state.

Sulfamic acid, toluenesulfonic acid, ammonium sulfamate, and $CaSO_4 \bullet 2H_2O$ were purchased from Aldrich Chemicals and were used as supplied after they were dried over silica gel, where they were stored. Dried nitrogen was bubbled through the reaction mixture to maintain an inert atmosphere in the reaction flask.

Equipment and Technique: A three neck round bottom flask with a condenser arrangement for reflux was used for polymerization. The mixture was stirred constantly using a magnetic stirrer and heated to keep the temperature at 210°C in an inert atmosphere. A similar arrangement was used for the synthesis of sodium alkyloxide/aryloxide and the substitution reaction of polydichlorophosphazene to poly(organo)phosphazene.

CHARACTERIZATION:

DSC Analysis: Thermal characterization of the dried polymer was made with a Perkin-Elmer differential scanning calorimeter (DSC-II). The Tg, T(1), and Tm transitions were determined whenever applicable. The sample was cooled to least 20°C below their Tg and then heated at a scanning rate of 10°C/min Heating was stopped before decomposition occurred and the sample was again cooled below its Tg at a rate of 10°C/min. This procedure was repeated twice to observe any change in T(1) transition on sample history.

GPC Analysis: The determination of molecular weight and molecular weight distribution of the polyphosphazene samples was determined using a Waters 150C HPLC/GPC. Five microStyragel columns (500, 10^3, 10^4, 10^5, 10^6 A) were used for the analysis. The operating temperature was 35°C with a flowrate of 1.0 ml/min of tetrahydrofuran solution. The detector was a refractometer (optical deflection type utilizing fiber optics). The data acquisition and calculations were performed with a Waters 730 Data Module. The polymer samples were dissolved at 0.05 wt% in HPLC grade tetrahydrofuran containing 0.05 wt% 2,6-di-tert-butyl-4-methylphenol as a stabilizer. The solution was filtered through 0.5 micron stainless steel filters just before injection. The GPC was calibrated with 9 monodispersed polystyrene samples ranging from 1,800 to 1,800,000 molecular weight. The samples were purchased from Pressure Chemicals and Waters Corporation.

POLYMERIZATION OF HEXACHLOROCYCLOPHOSPHAZENE:

The trimer (24 gms) with 1,2,4-trichlorobenzene (20 ml) was placed in a 250 ml three neck round bottom flask attached to a condenser. The catalyst, sulfamic acid (50.8 mg) and the promoter, $CaSO_4 \bullet 2H_2O$ (45 mg) were also added to the flask. The reaction mixture was stirred and constantly heated to maintain its temperature at 210°C. Dry nitrogen was bubbled through the reaction mixture. The reaction mixture became viscous as the reaction progressed and the reaction was stopped at a stage when any further heating would result in crosslinking. The yield was approximately 35%. It took an hour for the reaction mixture to become viscous in the presence of the promoter and about three hours in the absence of the promoter. The polymer was precipitated by pouring into 400 ml of heptane. The unreacted trimer dissolved in heptane and separated from the polymer. Polydichlorophosphazene was then dissolved in 150 ml of tetrahydrofuran. Crosslinked polymer, if present, does not dissolve in this solvent and may be removed by filtration. The precipitation and filtration is performed in dry box to avoid contact with moisture.

Synthesis of Sodium Alkyloxide/Aryloxide: Sodium hydride (11 gms, 97%) and 50 ml of tetrahydrofuran was placed in a 500 ml three neck round bottom flask attached to a condenser arrangement. Appropriate molar quantities of ROH was dissolved in 100 ml of tetrahydrofuran. 10% excess of ROH was used to ensure that all sodium hydride reacted, as unreacted sodium will react with the polydichlorophosphazene and crosslink the polymer. The solution of ROH was then added dropwise to the sodium hydride suspended in tetrahydrofuran to produce the corresponding sodium alkyloxide/aryloxide. The reaction was very exothermic and started refluxing from the beginning of the addition. To ensure complete substitution, the reactants were allowed to react further at room temperature overnight. During this period, a nitrogen atmosphere was maintained to exclude moisture from the reaction. The polydichlorophosphazene dissolved in tetrahydrofuran was then slowly added to sodium alkyloxide/aryloxide to produce the appropriate poly(organo)phosphazene. The time and temperature needed for complete substitution varied depending upon the strength of the nucleophile.

When the reaction was stopped*, the reaction mixture was cooled to room temperature and neutralized with glacial acetic acid. The polymer was isolated by precipitating the reaction mixture in either methanol or water and purified by dissolving in tetrahydrofuran and followed by precipitation again after removing insoluble impurities. Finally, the samples were dried in vacuum oven, to remove residual solvent.

RING OPENING REACTIONS:

It is well known that the cyclic trimer $(NPCl_2)_3$ ring opens under thermal stress to yield polydichlorophosphazene, but that fully substituted rings do not polymerize under the same conditions. It would be highly advantageous from the point of view of synthesis to be able to accomplish a one step polymerization using elevated temperatures and pressures.

Soulen and Silverman(18) have reported a series of experiments in which $[NPCl_2]_3$ was polymerized at high pressure and temperatures. Pressures between 10 and 20 kbar were used with temperatures up to 1200°C. They found that increased pressure favored the formation of high polymer. However depolymerization of polydichlorophosphazene occurred at 1050°C and above 70 Kbar pressure. At 10 Kbar pressure, depolymerization occurred at 900°C.

Numerous attempts have been made to thermally and catalytically polymerize organo-substituted cyclophosphazenes. Hexaphenoxycylotriphosphazene does not polymerize when heated to 350°C at atmospheric pressure.(19) The fluorolkoxycyclotriphosphazenes, $[NP(OCH_2CF_3)_2]_3$, $[NP(OCH_2C_2F_5)_2]_3$,

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*i.e., whenever the system became highly viscous (before gelling)

$[NP(OCH_2C_3F_7)_2]_3$ were found to be stable for long periods of time at 250°C-300°C and atmospheric pressure. These compounds were unaffected after 24 hours in contact with benzoyl peroxide in boiling benzene. The above trifluoroalkoxycyclotriphosphazenes were also unaffected when heated at 300°C for 24 hours in the presence of traces of aluminum chloride.(20)

Several experiments in our investigation were conducted with the phenoxy substituted trimer, $[NP(OC_6H_5)_2]_3$, to determine if this phosphazene trimer would ring open to yield the fully substituted polymer whenever it is heated under pressure. Both melt and solution polymerization in tetrahydrofuran were conducted independently at 250°C and 1400 psig in a high pressure reactor. In each case, the polymerization was unsuccessful. The time of reaction used was varied from 20 min to 24 hours. The ring opening polymerization was also attempted using the trifluoroethoxy substituted trimer $[NP(OCH_2CF_3)_2]_3$, but again it proved to be unsuccessful. The infrared spectra of the products showed that P-O-C bonds in the starting trimer were missing, thus indicating that side groups were no longer present on the trimer.

Another type of high pressure reactor (P=90,000 psig) was also utilized for polymerization. A solution of bis(2-methoxy ethyl)ether with the phenoxy and trifluoroethoxy trimers respectively were independently charged into the reactor. The products were examined after the reactants were held at room temperature and 90,000 psig for 48 hours. Again, infrared spectra and gel permeation chromatograph indicated that the original material was recovered unchanged. These two experiments were also conducted in presence of sulfamic acid and ammonium sulfamate respectively as catalysts. Again no polymerization occurred at room temperature. We were unable to conduct experiments at elevated temperatures since the high pressure reactor was not designed for such experiments.

STABILITY STUDIES OF POLYPHOSPHAZENES AT HIGH PRESSURE AND TEMPERATURE:

Whenever a 1% solution of poly[bis(phenoxy)phosphazene] homopolymer in tetrahydrofuran was placed in the high temperature reactor and was heated at 225°C and 1400 psig, it depolymerized. Samples were removed from the reactor at 3 hrs, 6 hrs, 12 hrs, and 24 hrs and the molecular weight of each sample was determined using gel permeation chromatography. Figure 1 shows that the molecular weight decreases with prolonged heating. The original material had a Mw of 813,700, and after 24 hours, the Mw was 145,000. This data clearly shows that the polymer is unstable under this temperature and pressure. Therefore polymerization will not occur at this temperature and pressure since a "decomposition product" of lower molecular weight than the starting polymer is favored under these conditions.

RESULTS AND DISCUSSION:

Effect of Dilution: A series of different polymerization reactions were carried out by changing the amount of 1,2,4-trichlorobenzene in the reaction mixture and keeping the other parameters constant. Temperature was lowered to stop the reaction and to avoid gelation when the reaction mixture became very viscous. The precipitation and the substitution reaction was carried out in an identical manner in each case. The reaction time for the solution polymerization was found to be very dependent on the

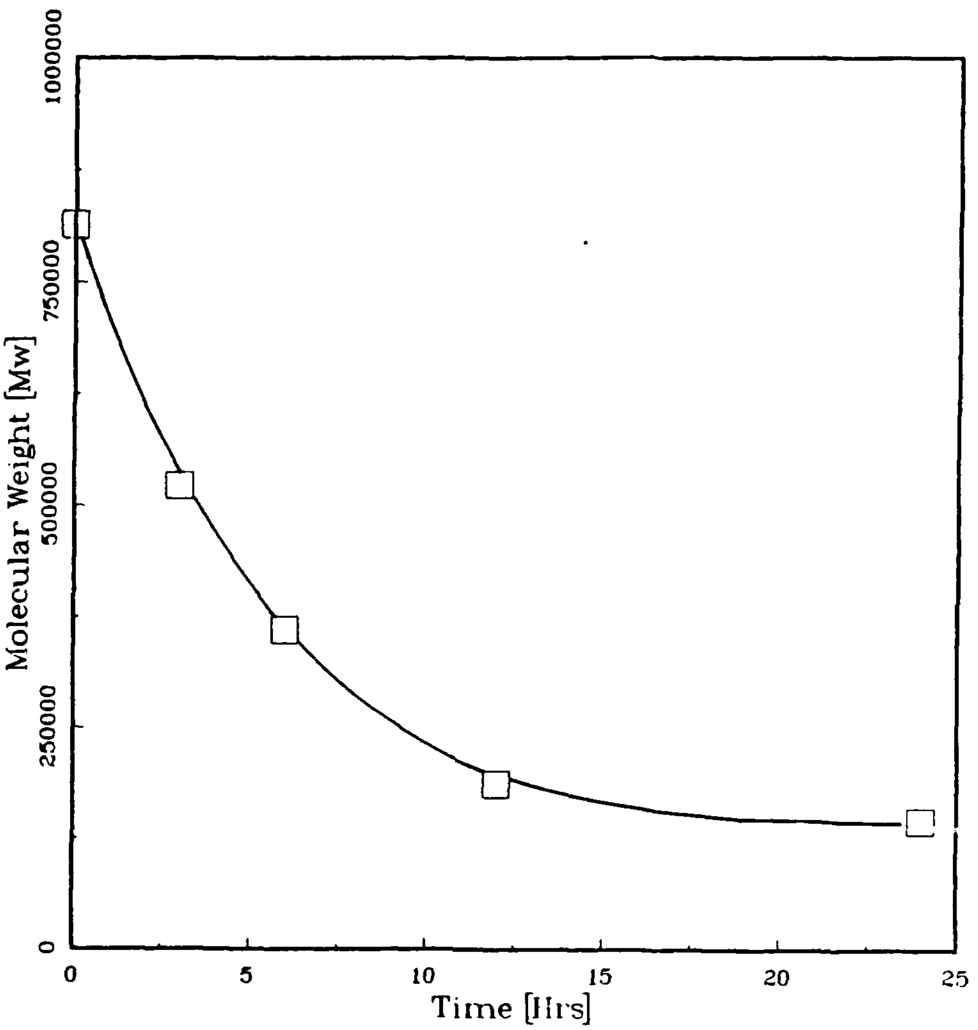

Figure 1: Effect of Reaction Time on the Molecular Weight of Poly[bis(phenoxy)phosphazene] heated at 225°C and 1400 psig.

amount of solvent in the reaction mixture. The time needed for different dilutions is given in Table 1. As shown in Figure 2, a plot of dilution against reaction time is a straight line indicating a direct proportionality. The reaction rate decreases as the amount of solvent is increased. This behavior could be associated with the decrease in catalyst concentration (gm of catalyst/ml of solvent). But the molecular weight, molecular weight distribution and the thermal properties of each of the polymers obtained from these reactions are similar, suggesting a similar reaction mechanism. Changing the amount of solvent alters the rate of reaction but not the mechanism of the reaction. However, the reaction time is increased when the trimer concentration is decreased.

Effect of Catalyst Concentration: A series of reactions was performed when only the sulfamic acid catalyst concentration (gm of catalyst/gm of trimer) was altered. The reaction time is greatly influenced by the catalyst concentration. The reaction times for specific catalyst concentrations are summarized in Table 2. As the catalyst concentration is increased, the reaction time decreases proportionately as shown in Figure 3. The plot asymptotically decreases and finally becomes parallel to the x-axis indicating the minimum time needed for the polymerization reaction irrespective of the catalyst concentration.

NATURE OF ACTIVE CATALYST:

Sulfamic acid is thermally stable up to its melting point of 205°C. Thermal decomposition starts at 209°C. Since the reaction temperature employed in this work is higher than 209°C, the catalyst slowly decomposes during the polymerization. Sulfamic acid is insoluble in trichlorobenzene. The reaction mixture is heterogeneous and the decomposition of the catalyst is visible during the reaction, since blackening occurs. The catalytic activity may be due to the decomposed catalyst and not due to the pure sulfamic acid as claimed.(8) No appreciable polymerization takes place whenever sulfamic acid is in pure form, but polymerization occurs when the catalyst is converted to its decomposed state.

The plot in Figure 3 shows that although increasing the catalyst concentration decreases the reaction time, it is not possible to reduce the polymerization time below one hour. This plot shows an initial time period where no appreciable reaction takes place. The reaction time can be divided into an initial inactive period or 'induction time' and an active 'reaction period'. The catalyst concentration affects the actual reaction period and not the induction period.

To verify that the catalytic activity and induction period depended upon decomposed sulfamic acid, solution polymerization was conducted using predecomposed sulfamic acid instead of pure sulfamic acid. Whenever predecomposed sulfamic acid was used, the reaction was completed approximately an hour earlier than when pure sulfamic acid was used. The polymer obtained in each case was identical. The difference in reaction time corresponds to the period required for converting the catalyst into the active degraded form. This period is the induction period of the solution polymerization reaction.

Sulfamic acid has two functional groups, an acid and an amine respectively. We have tried to identify the catalytically active group by testing different compounds which contain only one of the two groups, as catalyst. Toluenesulfonic acid which contains only the acid group acted as a catalyst for the solution polymerization. The molecular weight and the molecular weight distribution of the polymer obtained

Table 1: Reaction Time for Polymerization for Different Dilutions.

No.	Trimer gm	Solvent ml	Catalyst mg	Reaction Time hr
1	24.0	15.0	50.8	2.75
2	24.0	20.0	50.8	3.10
3	24.0	30.5	50.8	4.33
4	24.0	40.0	50.8	5.75
5	24.0	50.0	50.8	7.25

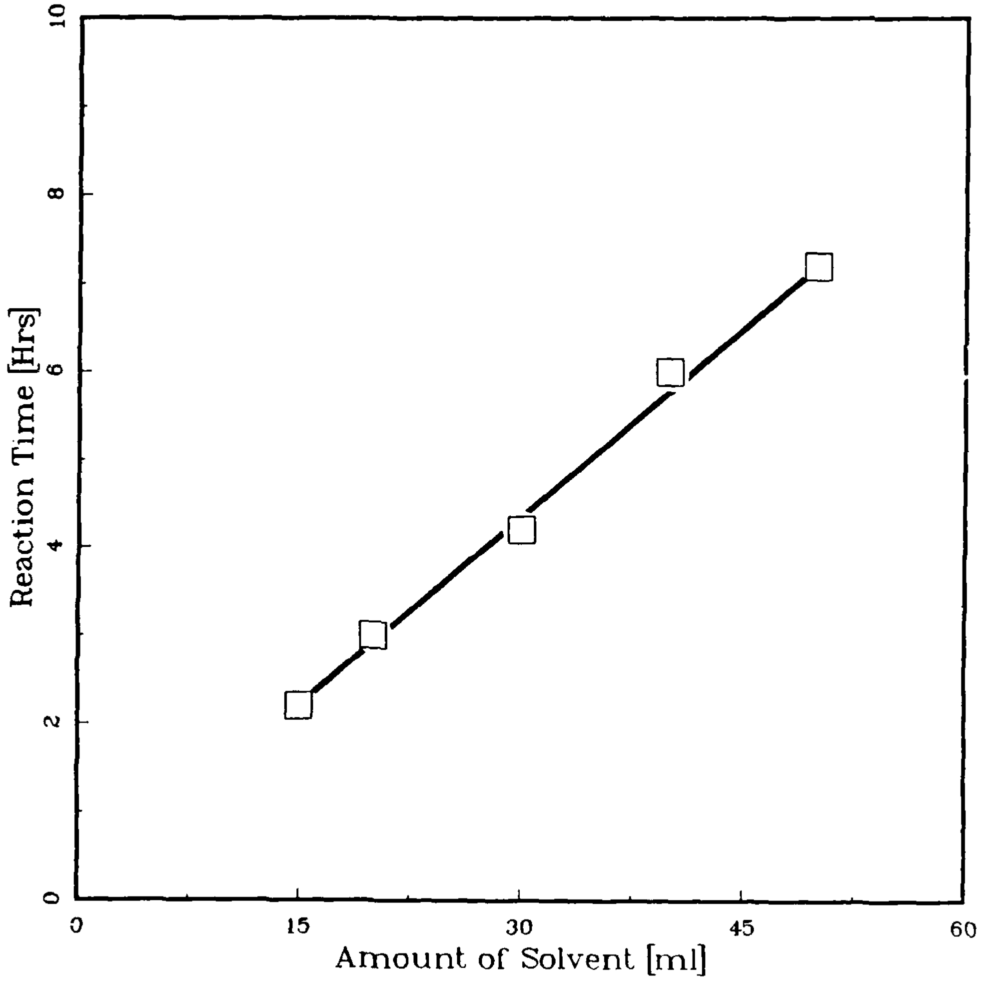

Figure 2: Relationship Between Reaction Time and Dilution.

Table 2: Reaction Time for Polymerization for Different Catalyst Concentrations.

No.	Trimer gm	Solvent ml	Catalyst mg	Reaction Time hr
1	24.0	20.0	12.7	9.5
2	24.0	20.0	25.4	5.10
3	24.0	20.0	50.8	3.10
4	24.0	20.0	76.2	4.50
5	24.0	20.0	101.6	1.75
6	24.0	20.0	127.0	1.75

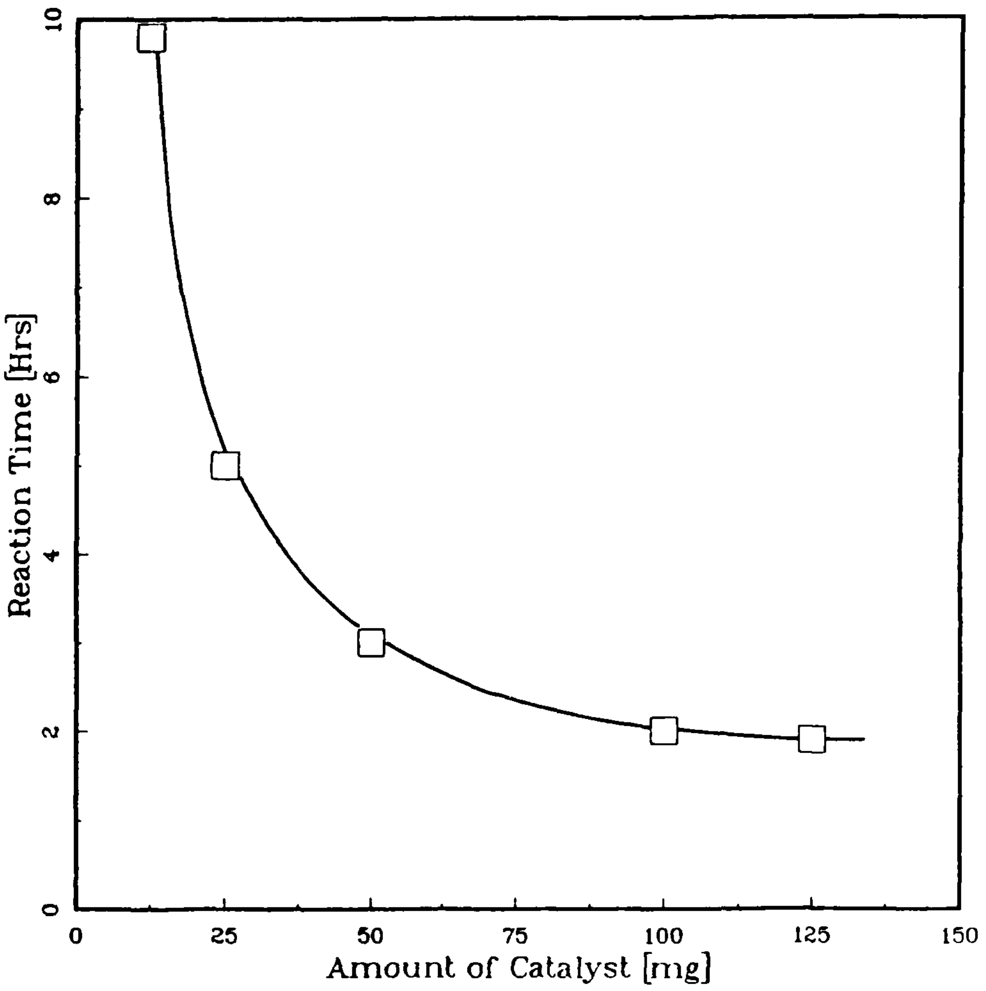

Figure 3: Plot of Total Reaction Time vs. Catalyst Concentration.

using toluenesulfonic acid was identical to that of polymer obtained using only sulfamic acid. The mechanism of reaction in each case is likely to be same. Sulfobenzoic acid was also found to give identical results. This clearly shows that the catalytic activity of sulfamic acid is due to the acid group and not due to the amine group. The main advantage of using toluenesulfonic acid is that it exists in the liquid state at the reaction conditions and is completely miscible with the reaction mixture. The reaction mixture is homogeneous and the catalyst is distributed uniformly.

MECHANISM OF POLYMERIZATION:

Although many investigators now agree that the mechanism is chain growth and not step growth, the exact nature of the growing chain end is not yet clear. Claims have been made for both cationic(21) and free radical(15) polymerization but the answer may vary depending on the catalyst and/or the temperature employed. The solution polymerization process was studied recently in situ by Hagnauer and coworkers(16) by using laser light scattering and Raman spectroscopy. Hagnauer concluded that the mechanism was cationic. The sulfamic acid catalyzed solution polymerization has not been studied previously. We monitored the change in the molecular weight and the molecular weight distribution as a function of the solution polymerization. Due to the hydrolytic instability of the polydichlorophosphazene and the high temperatures involved, we did not withdraw reaction samples from the polymerization reaction for fear of contamination. So distinctly different reactions were performed every time. The polymerization time was different in each reaction but the proportion of trimer, catalyst, and solvent was the same in each case. The molecular weight of the samples obtained in this experiments are given in Table 3. The molecular weight was found to be high throughout the entire reaction period. Taking into consideration the presence of an induction period, it is clear that high molecular weight chains must have been obtained in the very beginning of the reaction. So the increase in the viscosity of the reaction mixture is due to an increase in the yield of the polymer and not due to an increase in molecular weight.

PROMOTERS:

It has been reported in literature that small amounts of water has a beneficial effect on the reaction system, influencing the yield and the molecular weight of the resulting polymer(21,22). Thermal polymerization of hexachlorocyclotriphosphazene in the presence of small quantities of water forms essentially linear polydichlorophosphazene. Water has been reported to act as a good catalyst in melt polymerization(23,24). It has been proposed that water is not the actual catalyst, but that it reacts with the trimer to form HCl which actually catalyzes the reaction. The catalytic effect of HCl has been confirmed by the introduction of anhydrous HCl into the reaction system, under conditions when neither the hydrolysis of P-Cl bonds nor the formation of polydichlorophosphazene in the absence of HCl was observed(23). Note however that the reaction of P-Cl bonds with water gives rise to P-OH bonds which may form P-O-P linkages between two chains. When water is used as catalyst, its concentration is critical. A slight excess over that necessary for catalytic activity may cause the hydrolysis of the chlorine on the main chain and this may produce crosslinking.

Whenever water is tested as a catalyst, monitoring the water concentration is a crucial step. Concentration of water can be easily monitored through the dehydration of salt hydrates employed

Table 3: Molecular Weight and Polydispersity of Poly[bis(phenoxy)phosphazene] for Different Reaction Times.

No.	Reaction Time (hr)	Mn	Mw	Mw/Mn*
1	3.1	.76E5	1.7E6	23.5
2	2.0	3.7E5	2.8E6	7.7
3	1.25	.87E5	1.3E6	14.8
4	0.80	.56E5	4.8E5	8.6

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*Estimated by GPC

successfully in melt polymerization. Various salt hydrates used for this purpose have been reported in literature$^{(24)}$. Although any salt hydrate can serve the purpose, the selection of the metal is also important. The metal ion can influence the polymerization to a significant extent by coordinating to the phosphorus units via the skeletal nitrogen atoms. The bond created between the metal ion and the backbone can cause the chain to break. Often ring or chain cleavage products are formed as a result of this type of interaction. Hence the choice of metal ion should be such that the bonding between the metal ion and the backbone is minimum. Since the extent of reaction of Cu^{2+}, Ni^{2+}, Co^{2+} or Mg^{2+} with the skeletal nitrogen is greater than it is between Ca^{2+} and the phosphazene chain, the polymer molecular weight obtained by using these salt hydrates is expected to be lower than it is when $CaSO_4•2H_2O$ is used. This has been proven in the melt polymerization$^{(24)}$ so that $CaSO_4•2H_2O$ is preferred to other salt hydrates in these experiments.

Solution polymerization of the trimer catalyzed with $CaSO_4•2H_2O$ only, did not yield any polymer. The trimer was heated for about 8 hours with $CaSO_4•2H_2O$ in presence of 1,2,4-trichlorobenzene. It may be concluded that water did not act as a catalyst in solution polymerization even though water has been found to be a very effective promoter when used in conjunction with sulfamic acid. However, $CaSO_4•2H_2O$ helps to speed up the reaction considerably when sulfamic acid is present. Using sulfamic acid independently, it takes about three hours to give a 40% polymer yield. In the presence of $CaSO_4•2H_2O$ along with sulfamic acid, the reaction takes about an hour (time reduced by 60%). More importantly is the change in the molecular weight distribution of the polymer. Polymer obtained using the sulfamic acid and $CaSO_4•2H_2O$ has a significantly narrower molecular weight distribution and less branching.

To study the mechanism of water, we carried out reactions at different promoter concentrations and measured the changes in some relevant properties of the final polymer. Table 4 provides the molecular weight and molecular weight distribution of PBPP samples obtained by changing the promoter concentration, but keeping the catalyst concentration constant. From Table 4, it is seen that the reaction time does not vary greatly with the concentration of promoter. It can be concluded that the reaction rate is dependent primarily on the catalyst concentration and not on the promoter concentration. It was observed that the molecular weight decreased and the molecular weight distribution became broader as the concentration of the promoter was increased. The higher the concentration of water in the system, the higher the concentration of hydrogen chloride, so chain termination will be favored. These conclusions are in accordance with the results obtained in melt polymerization.$^{(24)}$ Similarly as the amount of water is increased, more P-Cl bonds are hydrolyzed, and thus promotes branching.

The promoter helps to speed up the reaction but could not be further exploited since it caused excessive polymer branching. It has been pointed that water functions by reacting with the trimer and producing HCl. The only way to avoid branching but still take advantage of the promoter, is by introducing anhydrous HCl into the reaction system. It is easier to introduce anhydrous HCl into the solution polymerization than into melt polymerization. This step should prevent the formation of P=O linkages that are believed to be the main cause of branching.

In summary, the absence of water results in long reaction times and broad molecular weight distribution due to excessive branching. An optimum quantity of water helps to increase molecular weight and to

Table 4: Molecular Weight and Polydispersity of Poly[bis(β-napthoxy)phosphazene] at Different Promoter Concentrations.

Promoter mg	Reaction Time (min)	Mn	Mw	Mw/Mn*
45.0	55	1.79E5	2.2E6	12.5
180.0	45	.36E5	1.0E6	27.3

---

[*] Estimated by GPC

narrow molecular weight distribution. This is due to the generation and role of HCl in the reaction. The reaction mechanism is still cationic, but the chain ends[**] are different now. Exceeding the optimum quantity of water results in the generation of excess HCl which promotes termination and branching, thereby reducing molecular weight and increasing polydispersity.

As discussed already, the solution polymerization catalyzed by sulfamic acid without promoter has a induction period of the order of an hour. With promoter, the reaction mixture is viscous from the beginning of the reaction and the reaction time is reduced substantially. However the promoter cannot eliminate the induction period completely. To establish the presence of the induction period, we performed solution polymerization in the presence of both catalyst and promoter and stopped the polymerization at very short times by precipitating the reaction mixture in heptane. No polymer was obtained whenever the reaction was stopped after 5 minutes, whereas small quantities of polymer were obtained after a 10 minute reaction. The yield was appreciable for a reaction time of 20 minutes and the reaction was judged to be completed in about an hour. It is clear from this work that the induction period, though reduced substantially, still exists. The molecular weight and molecular weight distribution of the samples from these reactions are given in Table 5. It is obvious from these results, that high molecular weight chains are being formed in the early stages of the reaction, in support the chain propagation mechanism.

Clearly, the promoter helps the reaction in two ways. It quickly transforms the catalyst, sulfamic acid into an active form, since the induction period is reduced from about an hour to approximately five minutes. In addition, it also speeds up the polymerization reaction. The useful polymerization reaction time is reduced from two hours to about 50 minutes. The yield of polymer that is obtained in presence or absence of promoter is almost the same. The promoter helps to produce high molecular weight, narrow molecular weight distribution and faster reaction without sacrificing yield.

CHAIN ENDS:

Since the exact nature of the active catalyst is not known, the nature of chain ends still remains moot. The reaction catalyzed by anhydrous HCl is claimed to produce a chain with a terminal =NH groups rather than $-NH_2$ groups which are obtained when water is used to produce HCl.(23) In the absence of water and HCl, PCl_3 is another possibility.(12) However the polymer chain ends formed in solution polymerization, in presence of a catalyst like sulfamic acid have not been studied until now. The catalyst itself may be present as a chain end but not in its pure state. If this is so, the concentration of chain ends and hence the molecular weight should depend upon the catalyst concentration.

We carried out the solution polymerization with different catalyst concentrations and at fixed promoter concentration. The promoter was added in order to produce narrower molecular weight distribution, faster reaction and less branching. The results are shown in Table 6. It is observed that as the catalyst concentration is increased, the molecular weight decreases correspondingly. It may be anticipated that the greater the catalyst concentration, the larger the number of chain ends. Although the actual nature of

---

[**] still not clearly identified

Table 5: Molecular Weight, Polydispersity, and Yield for Poly[bis(phenoxy)phosphazene] at Short Reaction Times.

No.	Reaction Time (min)	Mn	Mw	Mw/Mn*	Yield
1	5	..	...	...	no yield
2	10	2.3E5	.8E6	3.47	~2%
3	20	1.5E6	3.9E6	3.04	~15%

---

*Estimated by GPC

chain ends is not known with certainty, the catalyst is playing a major role in forming these chain ends. It follows that by decreasing the catalyst concentration, higher molecular weight polymer was obtained. The real nature of the chain ends still remains unsolved at present.

NUCLEOPHILIC SUBSTITUTION REACTION:

Most of the studies regarding the synthesis of polyphosphazenes have concentrated on the polymerization reaction of hexachlorocyclotriphosphazene to polydichlorophosphazene. The changes in the molecular weight and molecular weight distribution are related to different conditions for solution or melt polymerization. However the nucleophilic substitution reaction has not been studied in detail until recently(25). The morphology and structure of the resulting polymer depend greatly on the temperature and the time for which the nucleophilic substitution reaction is carried out. The time needed for complete substitution depends upon the strength of the nucleophile. Particularly for PBFP, the thermal and structural properties of the polymer were found to be highly dependent on the duration of the reaction between the polydichlorophosphazene and sodium trifluoroethoxide.

Sodium trifluoroethoxide being a very strong nucleophile, replaces the chlorine from the polydichlorophosphazene readily. The temperature of the reaction mixture increases on addition of polydichlorophosphazene to the sodium trifluoroethoxide solution. The effect of reaction time and temperature on the properties of substituted polymer was studied in detail only for PBFP since the effect is likely to be more pronounced in this polymer. After the polydichlorophosphazene was added to the sodium trifluoroethoxide, aliquots of the reaction mixture were withdrawn at intervals of 1, 6, and 12 hours at room temperature. The reaction was then heated to reflux. Another sample was withdrawn after 24 hours and the rest of the reaction was precipitated after 48 hours from the beginning of the reaction. The polymers isolated at room temperature were white and fibrous whereas those products obtained after longer heating were brown, sticky, and gummy. The results are summarized in Table 7. This procedure was repeated several times. The IR spectra of the sample, so produced matched the spectra of reference materials. All samples were stable to atmospheric moisture so that residual chlorine was presumed to be absent or negligible.

The T(1) transition temperature of the samples was found to decrease as the reaction time was increased. T(1) temperature vs. the reaction time is shown in Figure 4. Samples isolated after a long heating period did not show a T(1) transition. The polymers produced were either highly branched or otherwise degraded during the reaction. Since the substitution reaction occurs in presence of an excess of nucleophile (to ensure complete substitution), there an opportunity for the excess nucleophile to attack the substituted trifluoroethoxide moieties, and so introduce altered side groups. The greater the percentage of altered side groups, the larger the difference between polymer properties from those reported in the literature

Heating is not necessary for the substitution reaction of PBFP, which is fast and is completed within an hour. Keeping the polymer in contact with the excess nucleophile for longer times apparently causes secondary reactions, and hence changes the physical properties of the polymer. It was found that the reaction of sodium phenoxide and polydichlorophosphazene is far from complete at room temperature.

Table 6: Molecular Weight and Polydispersity of Poly[bis(trifluoroethoxy)phosphazene] for Different Catalyst Concentrations.

No.	Catalyst mg	Promoter mg	Mn	Mw	Mw/Mn*
1	50.8	45	1.7E5	2.2E6	12.5
2	203.2	45	1.3E5	1.6E6	12.3
3	762.0	45	.81E5	.96E5	1.17

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*Estimated by GPC

Table 7: T(1) Transition of Poly[bis(trifluoroethoxy)phosphazene] Samples Obtained at Different Conditions of Substitution Reactions.

No.	Reaction Time (Hr)	Condition	T(1), K.	Appearance
1	1.0	R.T.	349	White, Powdery
2	6.0	R.T.	339	White, Powdery
3	12.0	R.T.	335	White, Powdery
4	24	70^{o}C.	No T(1)	Brown, Gummy
5	48	70^{o}C	No T(1)	Brown, Gummy

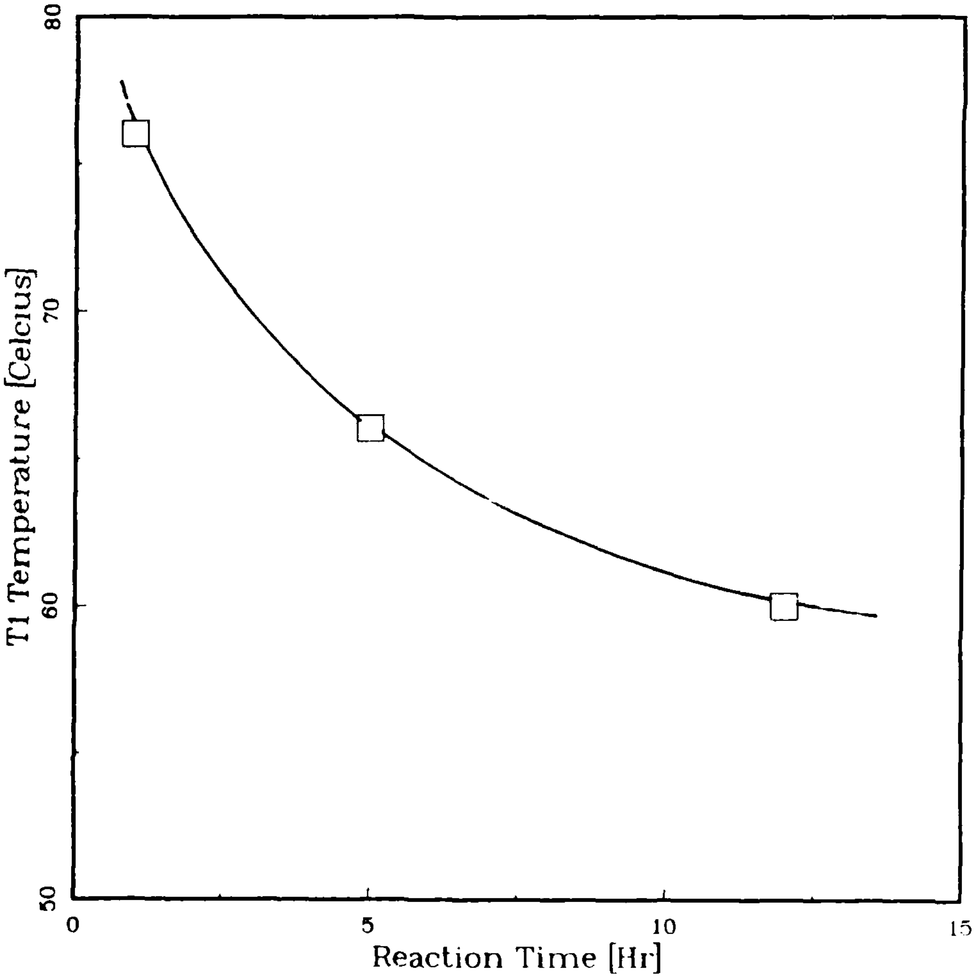

Figure 4: Plot of T(1) vs. Substitution Reaction Time.

The reaction is not fast and the temperature rise is not appreciable when the polydichlorophosphazene is added to the sodium phenoxide solution. Heating is necessary to ensure as complete substitution as possible. PBPP samples obtained without heating to force the substitution reaction were not stable to moisture in the atmosphere.

$[-P(Cl)_2=N-]_n$ reacts similarly towards sodium phenoxide and/or the sodium p-cresoloxide. When a mixture of two aryloxides is used, the composition of the mixed substituted polymer is solely determined by the stoichiometric ratio of the aryloxides. But whenever a mixture of sodium phenoxide and sodium trifluoroethoxide is used, the sodium trifluoroethoxide is consumed completely and some sodium phenoxide will even remain unreacted if sodium trifluoroethoxide is sufficient to complete the substitution.(24) This observation emphasizes the need for adjusting the reaction conditions and duration of the reaction, depending on the strength of the nucleophile. It is reported that at 70°C and 15 minutes from the start of the reaction, the content of the residual chlorine in the linear phosphazene is reduced to about .057% (wt), which corresponds to 99.8% degree of substitution and the chlorine content practically does not change on further heating for as long as 20 hours.(24)

CONCLUSION:

The solution polymerization of hexachlorocyclotriphosphazene to polydichlorophosphazene catalyzed by sulfamic acid was investigated. The substitution reaction of polydichlorophosphazene to poly(organo)phosphazene was also studied in an attempt to obtain information about the mechanism of the reaction, the nature of active catalyst and possible chain ends.

The effect of solvent concentration and catalyst concentration on the reaction rate was established. The catalytic activity is due to a decomposition product of sulfamic acid no the pure acid. The exact nature of the catalyst still not clear at this time. Solution polymerization reaction has an induction period of an hour. This is the time needed for the catalyst to become converted into its active form. The catalytic activity is associated with the acid group of the sulfamic acid, not the amine group. Molecular weights of the polydichlorophosphazenes are high from the beginning of the polymerization, indicating that a chain propagation mechanism, but the exact nature of the active center for kinetic chain growth is still not clear. In contrast with melt polymerization, water did not act as a catalyst when used with sulfamic acid in solution polymerization, but it had an appreciable an effect on the reaction rate and on the polymer properties. Water present or released in controlled amounts functions as an effective promoter and provides high molecular weight polymer with relatively narrow molecular weight distributions. Exceeding the optimum promoter concentrations results in branching and smaller chain length. Water reduced the induction period to about five minutes, but did not eliminate it. Although the exact nature of the chain ends is not certain, we observed that the decompostion product of sulfamic acid plays an important role in forming the chain ends. This was evident from the fact that polymers synthesized with high catalyst concentration were of low molecular weight. The time and temperature needed for substitution in the nucleophilic substitution reaction depend upon the strength of the nucleophile. The physical properties of the polymer can be adversely altered through prolonged heating.

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