be compared to the poly(1,6-heptadiyne)[3] and poly(dipropargyl sulfide)[5] at 107 and 160 °C, respectively.

The electrical conductivity of poly(DPPGe) at 25 °C is 2.9×10^{-11} S cm^{-1}.

Fairly good thermal, oxidative stability and solubility of the present polymer are notable characteristics. We are now attempting to increase electrical conductivity by various doping methods.

Acknowledgment. We thank the Korea Science and Engineering Foundation for support of this work.

Registry No. DMPGe, 123639-65-6; DMPGe (homopolymer), 123639-66-7; DPPGe, 6262-84-6; DPPGe (homopolymer), 29317-06-4; $(n\text{-Bu})_4Sn$, 1461-25-2; $EtAlCl_2$, 563-43-9; $PdCl_2$, 7647-10-1; $MoCl_5$, 10241-05-1; WCl_6, 13283-01-7; propargyl bromide, 106-96-7; dichlorodimethylgermanium, 1529-48-2.

References and Notes

(1) Butler, G. B. *Acc. Chem. Res.* **1982**, *15*, 370.
(2) Stille, J. K.; Frey, D. A. *J. Am. Chem. Soc.* **1961**, *83*, 1697.
(3) Gibson, H. W.; Bailey, F. C.; Epstein, A. J.; Rommelamann, H.; Kaplan, S.; Harbour, J.; Yang, X. Q.; Tanner, D. B.; Pochan, J. M. *J. Am. Chem. Soc.* **1983**, *105*, 4417.
(4) Masuda, T.; Hasegawa, K.; Higashimura, T. *Macromolecules* **1974**, *7*, 728.
(5) Gal, Y. S.; Choi, S. K. *J. Polym. Sci., Polym. Lett.* **1988**, *26*, 115.
(6) Gal, Y. S.; Choi, S. K. *Polymer (Korea)* **1987**, *11*, 563.
(7) Kim, Y. H.; Gal, Y. S.; Kim, U. Y.; Choi, S. K. *Macromolecules* **1988**, *21*, 1995.
(8) Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier: New York, 1971.
(9) Gal, Y. S.; Cho, H. N.; Choi, S. K. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 2021.
(10) Masuda, T.; Higashimura, T. *Adv. Polym. Sci.* **1986**, *81*, 121.

A Study of Solution Polymerization of Polyphosphazenes

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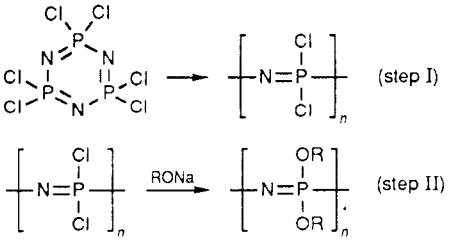
ABSTRACT: Several alkoxy/aryloxy-substituted phosphazene polymers $[P(OR)_2{=}N]_n$ (R = CH_3, C_6H_5, $C_6H_4CH_3$, CH_2CF_3, $C_6H_4C_6H_5$, C_6H_4Cl, C_6H_4Br, C_8H_{10}) were prepared by the reaction of poly(dichlorophosphazene) with their corresponding sodium salts. The poly(dichlorophosphazene) 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 catalysts developed for solution polymerization. The polymerization favors a cationic mechanism. Promoters were found to speed up to polymerization reaction. Effects 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 were noted. The nucleophilic reaction was studied, and the effect of reaction time and temperature on the properties of the final polymer was investigated. Ring opening on fully substituted cyclotriphosphazenes at elevated pressures and temperatures was unsuccessful. The polymers were characterized by differential scanning calorimetry, gel permeation chromatography, infrared spectroscopy, and ^{31}P solution nuclear magnetic resonance 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 including fire retardancy, low-temperature flexibility, resistance to chemical attack, and biocompatibility among others.[1-3]

The most commonly used synthetic route to linear polyphosphazene is a two-step process developed by Allcock in the mid-1960s.[4] It involves ring-opening polymerization of cyclic trimer, hexachlorocyclotriphosphazene, to produce linear high molecular weight poly(dichlorophosphazene) (step I) and subsequent replacement of the chlorine groups with the nucleophilic substituents (step II).

Scheme I



This synthetic route is different than conventional polymer synthesis in that a variety of polymers can be prepared from one polymer source, namely, poly(dichlorophosphazene).

Cyclic phosphazene trimer is polymerized to linear poly(dichlorophosphazene)[5,6] (step I) by either solution polymerization[7] or melt polymerization.[8,9] The melt poly-

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merization reaction is usually carried out for approximately 70 h in evacuated sealed tubes and at temperatures of about 230–300 °C until the reaction mixture ceases to flow. The reaction temperature is lower in solution polymerization than it is in melt polymerization, and the molecular weight can be better controlled by using shorter reaction times.[8] Recently, Neilson prepared polyphosphazenes with organic side groups attached directly to the phosphorus atom by a condensation polymerization of *N*-silylphosphinimines,[10,11] producing linear polymer in the molecular weight range of 50 000 to 2 000 000 with relatively narrow molecular weight distribution.

The mechanism of the conventional polymerization reaction (step I) is not known with certainty. Attempts to study the polymerization in detail have not been completely successful due to the hydrolytic instability of poly(dichlorophosphazene) and also due to some degree of polymer product irreproducibility.[12,13] Second- and first-order kinetics have been reported for uncatalyzed and catalyzed melt polymerizations, respectively.[14,15] The polymerization reaction is difficult to study in situ because of the high reaction temperatures and the sensitivity of the reaction products to moisture. However, Hagnauer and co-workers recently used Raman spectroscopy and laser light scattering equipment to investigate solution and melt polymerizations,[16,17] which indicate that the cationic mechanism of chain propagation is predominant in these polymerizations. More recently, mechanistic studies of polyphosphazenes have been made by using BCl_3 as a catalyst, but relatively low molecular weights were reported.[18] Still, the exact nature of the active center for chain growth is still unknown.

Poly(dichlorophosphazene) has no known commercial use due to the facile hydrolysis of the chlorine substituents in the presence of atmospheric moisture. The chlorine atoms may be replaced by the organic groups to provide useful polymers (step II). The properties of the resulting poly(organophosphazene) are determined by the type of alkoxy or aryloxy substituents coupled to the P–N backbone of the polymer.

Polyphosphazenes with many different substituents varying from small groups such as OCH_3 to bulky groups like $OC_6H_4C_6H_5$ have been synthesized by using solution polymerization of hexachlorocyclotriphoshazene which was converted to poly(dichlorophosphazene) and then reacted with a corresponding sodium alkyloxide/aryloxide to produce the desired poly(organophosphazene). The solution polymerization was carried out in 1,2,4-trichlorobenzene by using catalysts that include sulfamic acid, toluenesulfonic acid, and ammonium sulfamate and a promoter $CaSO_4 \cdot 2H_2O$. The reaction is fast and yields high molecular weight polymer with fairly narrow molecular weight distribution. Changes in the molecular weight and polydispersity of the polyphosphazene have been measured as a function of reaction time. An attempt was made to ascertain the nature of the active catalyst.

Experimental Section

Materials. The hexachlorocyclotriphosphazene was kindly provided by Dr. T. Nishakawa of Shin Nisho Kako Corporation, Japan. It was 99(+)% trimer, the remainder being tetramer. The trimer was dried in a vacuum oven to remove any traces of moisture and stored in a drybox 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 $CaSO_4 \cdot 2H_2O$ were purchased from Aldrich Chemicals and were used as supplied after they were dried over silia 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 by 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 poly(dichlorophosphazene) to poly(organophosphazene).

Characterization. DSC Analysis. Thermal characterization of the dried polymer was made with a Perkin-Elmer differential scanning calorimeter (DSC-II). The T_g, $T(1)$, and T_m transitions were determined whenever applicable. The sample was cooled to at least 20 °C below its T_g 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 T_g 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 by using a Waters 150-C ALC/GPC. Five microStyragel columns (500, 10^3, 10^4, 10^5, 10^6 Å) were used for the analysis. The operating temperature was 35 °C with a flow rate 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. {In the case of poly[bis(trifluoroethoxy)phosphazene] a 0.3 wt % solution permitted GPC characterization even though the refractive difference is small between polymer and solvent.} An addition of 0.1 wt % of $(n\text{-Bu})_4NBr$ was added to the mobile phase as an ionic species. The solution was filtered through 0.5-μm stainless-steel filters just before injection. The GPC was calibrated with nine monodisperse polystyrene samples ranging from 1800 to 1 800 000 molecular weight. The samples were purchased from Pressure Chemicals and Waters Corp.

Solution ^{31}P Nuclear Magnetic Resonance (NMR) Analysis. The ^{31}P solution NMR spectra were obtained with a Brüker AM500 NMR spectrometer operated at 202 MHz to determine the state of branching in all polymer samples. Spectrophotometric grade *N*,*N*-dimethylformamide was used as the solvent for the polyphosphazene samples. Phosphoric acid was used as the reference standard (0 ppm). A small amount of D_2O was used as a lock solvent.

Polymerization of Hexachlorocyclophosphazene. The trimer (24 g) 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, $CaSO_4 \cdot 2H_2O$ (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. As the reaction progressed, the reaction mixture became viscous and it was stopped before cross-linking occurred. The yield was approximately 35% under these conditions. It took an hour for the reaction mixture to become viscous in the presence of the promoter and about 3 h in the absence of the promoter. (This same procedure has been recommended by researchers in melt polymerization; for example, see ref 19.) The polymer was precipitated by pouring into 400 mL of heptane. The unreacted trimer dissolved in heptane and separated from the polymer. Poly(dichlorophosphazene) was then dissolved in 150 mL of tetrahydrofuran. Cross-linked polymer, if present, does not dissolve in this solvent and may be removed by filtration. The precipitation and filtration are performed in a drybox to avoid contact with moisture.

Synthesis of Sodium Alkyloxide/Aryloxide. Sodium hydride (11 g, 97%) and 50 mL of tetrahydrofuran were placed in a 500-mL three-neck round-bottom flask attached to a condenser arrangement. The appropriate molar quantity of ROH was dissolved in 100 mL of tetrahydrofuran. Excess of ROH (10%) was used to ensure that all sodium hydride reacted, to avoid cross-linking of the polymer. The poly(dichlorophospha-

zene) dissolved in tetrahydrofuran was slowly added to sodium alkyloxide/aryloxide to produce the appropriate poly(organophosphazene). The time and temperature needed for complete substitution varied depending upon the strength of the nucleophile.

After 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 then purified by dissolving it in tetrahydrofuran and repeated precipitation after insoluble impurities were removed. Finally, the samples were dried in a 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 poly(dichlorophosphazene) 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.

Soulen and Silverman[20] 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 poly(dichlorophosphazene) occurred at 1050 °C and above 70 kbar of pressure. At 10 kbar of pressure, depolymerization occurred at 900 °C.

Numerous attempts have been made to thermally and catalytically polymerize organo-substituted cyclophosphazenes. Hexaphenoxycyclotriphosphazene does not polymerize when heated to 350 °C at atmospheric pressure.[21] The (fluoroalkoxy)cyclotriphosphazenes $[NP(OCH_2CF_3)_2]_3$, $[NP(OCH_2C_2F_5)_2]_3$, and $[NP(OCH_2C_3F_7)_2]_3$ were found to be stable for long periods of time at 250–300 °C and atmospheric pressure. These compounds were unaffected after 24 h in contact with benzoyl peroxide in boiling benzene. The above (trifluoroalkoxy)cyclotriphosphazenes were also unaffected when heated at 300 °C for 24 h in the presence of traces of aluminum chloride.[22]

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 when 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 reaction time was varied from 20 min to 24 h. The ring-opening polymerization was also attempted by using the trifluoroethoxy-substituted trimer $[NP(OCH_2CF_3)_2]_3$, but again it proved to be unsuccessful. Afterward, the infrared spectra of the products showed that P–O–C bonds in the starting trimer were missing, 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-methoxyethyl) ether with the phenoxy and trifluoroethoxy trimers were independently charged into the reactor. The products were examined after the reactants were held at room temperature and 90 000 psig for 48 h. Again, infrared spectrometry and gel permeation chromatography 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. Experiments were not conducted 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(diphenoxyphosphazene) homopolymer in tetrahydrofuran was placed in the high-temperature reactor and heated at 225 °C and 1400 psig, it depolymerized. Samples were removed from the reactor at 3, 6, 12, and 24 h, and the molecular weight of each sample was determined by using gel permeation chromatography. Figure 1 shows that the molecular weight decreases with prolonged heating. The original material had a M_w of 813 700, and after 24 h, the M_w was 145 000. Thus, the polymer/solvent mixture is unstable at this temperature and pressure since the polyphosphazene depolymerizes. (The reviewer has suggested that THF may induce instability in polyphosphazenes.)

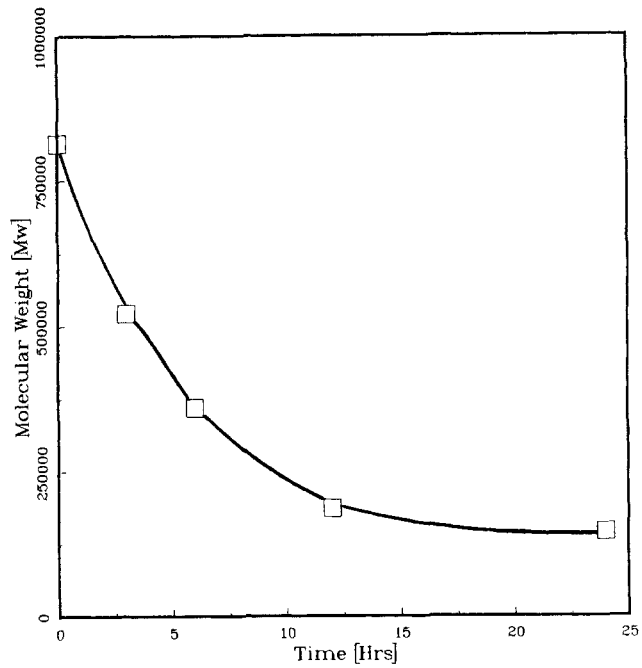

Figure 1. Effect of reaction time on the molecular weight of poly(diphenoxyphosphazene) heated at 225 °C and 1400 psig.

Table I
Reaction Time for Polymerization for Different Dilutions

no.	trimer, g	solv, mL	cat., mg	reactn time, h
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

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 whenever the reaction mixture became very viscous. The precipitation and 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 amount of solvent in the reaction mixture. The time needed for different dilutions is given in Table I. A plot of dilution against reaction time is linear as shown in Figure 2, so that the apparent reaction rate decreases as the amount of solvent is increased. This behavior can be associated with the decrease in catalyst concentration (g 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 each time. However, the reaction time increases whenever the trimer and catalyst concentration is decreased (see Figures 2 and 3).

Effect of Catalyst Concentration. Several reactions were performed where only the sulfamic acid catalyst concentration (g of catalyst/g of trimer) was altered (see Table II). Figure 3 shows that the reaction time decreases proportionately as the catalyst concentration increases and finally becomes parallel to the x axis indi-

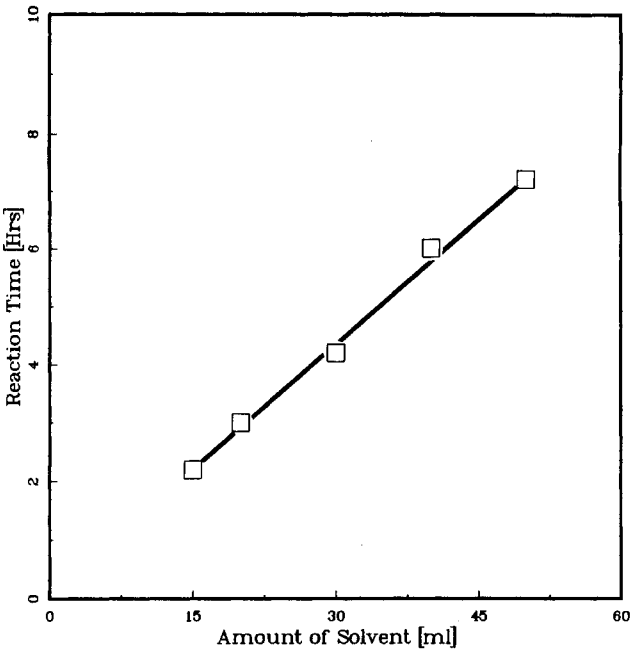

Figure 2. Relationship between reaction time and dilution.

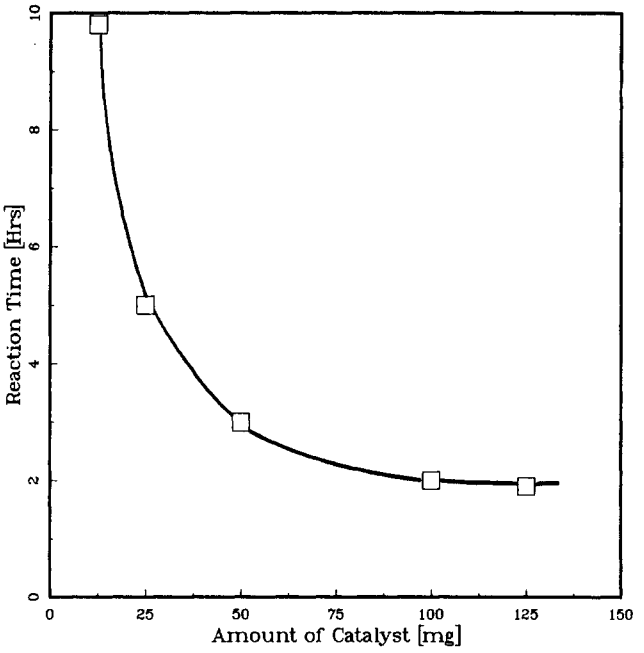

Figure 3. Plot of total reaction time vs catalyst concentration.

Table II
Reaction Time for Polymerization for Different Catalyst Concentrations

no.	trimer, g	solv, mL	cat., mg	reactn time, h
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

cating that a minimum time needed for the onset of the polymerization reaction per se, 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. Since sulfamic acid is insoluble in trichlorobenzene, the reaction mixture is heterogeneous. Decomposition of the catalyst is visible during the reaction, since blackening often 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 the sulfamic acid is pure, but polymerization occurs whenever the catalyst is decomposed.

Figure 3 indicates that although increasing the catalyst concentration decreases the reaction time, it is not possible to reduce the polymerization time below 1 h. This plot shows an initial time period where no appreciable reaction takes place. Therefore 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.

Solution polymerizations were conducted by using predecomposed sulfamic acid instead of pure sulfamic acid to verify that the catalytic activity and induction period depended upon the evolution of decomposed sulfamic acid. Whenever predecomposed sulfamic acid was used, the reaction was complete 1 h approximately 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. Identification of the catalytically active group was performed by testing different compounds that contained only one of the two groups. Toluenesulfonic acid, which contains only the acid group, acted as a catalyst for the solution polymerization. (Unlike sulfamic acid no degradation was observed.) The molecular weight and the molecular weight distribution of the polymer obtained by using toluenesulfonic acid were identical with that of the polymer obtained by using only sulfamic acid. Sulfobenzoic acid was also found to give identical results. (Unlike sulfamic acid no degradation was observed.) This clearly shows that the catalytic activity of sulfamic acid is due to the acid group and not due to the amine group. An 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 unlike sulfamic acid per se.

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[23] 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 co-workers[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. The change in the molecular weight and the molecular weight distribution as a function of the time of reaction was measured. Reaction samples were not withdrawn from the polymerization reaction for fear of contamination due to the hydrolytic instability of the poly(dichlorophosphazene) and the high temperature of reaction. Distinctly different reactions were performed every time. The polymerization

Table III
Molecular Weight and Polydispersity of Poly(diphenoxyphosphazene) for Different Reaction Times

no.	reactn time, h	$10^{-5}M_n$	M_w	M_w/M_n[a]
1	3.1	0.76	1.7×10^6	23.5
2	2.0	3.7	2.8×10^6	7.7
3	1.25	0.87	1.3×10^6	14.8
4	0.80	0.56	4.8×10^5	8.6

[a] Estimated by GPC.

time was changed in each reaction, but the proportion of trimer, catalyst, and solvent was unaltered. Table III provides the molecular weight of the samples obtained, and it was found to be high throughout the entire reaction period. It is clear that high molecular weight chains must have been present at the beginning of the reaction after the induction period. 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 have a beneficial effect on the reaction system, influencing the yield and the molecular weight of the resulting polymer.[23,24] Thermal polymerization of hexachlorocyclotriphosphazene in the presence of small quantities of water forms essentially linear poly(dichlorophosphazene). Water has been reported to act as a good catalyst in melt polymerization.[25,26] 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 poly(dichlorophosphazene) in the absence of HCl was observed.[25] Note that the reaction of P–Cl bonds with water gives rise to P–OH bonds that may form P–O–P linkages between two chains. When water is used as a catalyst, its concentration is found to be 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 cross-linking. Monitoring the water concentration is a crucial step. It is controlled through the dehydration of salt hydrates[26] which has been employed successfully in melt polymerization. The nature of the metal ion can influence the polymerization to a significant extent by coordinating to the phosphorus units via the skeletal nitrogen atoms. "Bonding" between the metal ion and the backbone can cause the chain to break. The degree of "bonding" 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. This has been proven in the melt polymerization[26] where $CaSO_4 \cdot 2H_2O$ is preferred to other salt hydrates. It is reported that the polymer molecular weight obtained by using the above salt hydrates is lower than when $CaSO_4 \cdot 2H_2O$ is employed.[26]

Solution polymerization of the trimer catalyzed with $CaSO_4 \cdot 2H_2O$ alone does not yield polymer. Trimer heated with $CaSO_4 \cdot 2H_2O$ in presence of 1,2,4-trichlorobenzene for about 8 h did not induce polymerization even though water has been found to be a very effective promoter when it is used with sulfamic acid. With only sulfamic acid, the reaction time to obtain a 40% yield of polymer is 3 h. When $CaSO_4 \cdot 2H_2O$ is present with sulfamic acid, the reaction takes about an hour and the polymer has a significantly narrower molecular weight distribution.

Reactions at different promoter concentrations were performed and the changes in some relevant properties of the final polymer were measured. Results are shown in Table IV for poly[bis(β-naphthoxy)phosphazene] samples obtained by changing the promoter concentration at constant catalyst concentration. The reaction time does not vary greatly with the concentration of promoter and is dependent primarily on the catalyst concentration. The molecular weight is found to decrease, and the molecular weight distribution broadens as the concentration of the promoter was increased beyond an optimal level.

Table IV
Molecular Weight and Polydispersity of Poly[bis(β-naphthoxy)phosphazene] at Different Promoter Concentrations

promoter, mg	reactn time, min	$10^{-5}M_n$	$10^{-6}M_w$	M_w/M_n[a]
45.0	55	1.79	2.2	12.5
180.0	45	0.36	1.0	27.3

[a] Estimated by GPC. Branching due to excess water from promoter was confirmed by ^{31}P NMR.

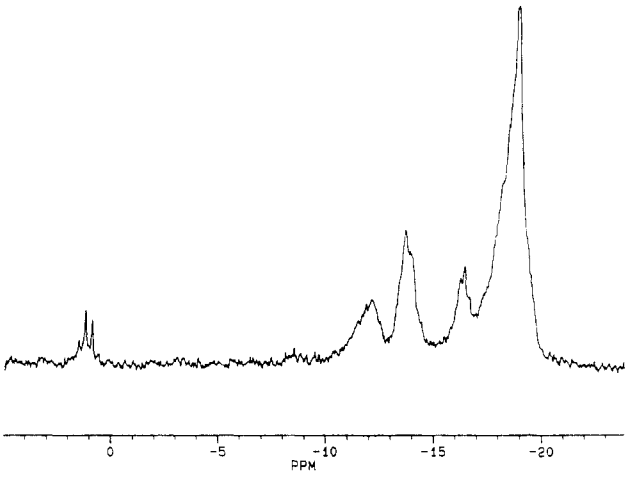

Figure 4. ^{31}P NMR spectrum of poly(diphenoxyphosphazene) showing branching is present.

It therefore follows that the promoter, $CaSO_4 \cdot 2H_2O$ with sulfamic acid, helps to speed up the reaction but cannot be used in large excess since it causes excessive branching and cross-linking attributed to excess water, liberated from the breakdown of $CaSO_4 \cdot 2H_2O$. Branching has been assessed on our polyphosphazenes when large quantites of promoter (180 mg/24 g of trimer) were added. This was proven by ^{31}P solution NMR as an analytical procedure that was used for all samples. Figure 4 is an example of a ^{31}P NMR spectra for poly(diphenoxyphosphazene) which is branched. Multiple ^{31}P resonances indicate the polymer is not linear.

In summary, longer reaction times are required whenever water is absent. Under these conditions polymers with broader molecular weight distribution are obtained. However, an optimum quantity of water helps to increase molecular weight and to narrow the molecular weight distribution. This is due to the generation and role of HCl in the reaction. The reaction mechanism may still be cationic, but now the chain ends (still not clearly identified here or in the literature) are different. Exceeding the optimum quantity of water results in the generation of excess HCl which promotes initiation, thereby reducing molecular weight and increasing polydispersity as shown in Table IV.

The solution polymerization catalyzed by sulfamic acid without promoter has an induction period of 1 h. The reaction mixture is viscous from the beginning of the reaction whenever promoter is present and the reaction time is reduced substantially, but the induction period is not

Table V
Molecular Weight, Polydispersity, and Yield for Poly(diphenoxyphosphazene) at Short Reaction Times

no.	reactn time, min	M_n	$10^{-6}M_w$	M_w/M_n[a]	yield, %
1	5	...	...	...	no yield
2	10	2.3×10^5	0.8	3.47	~2%
3	20	1.5×10^6	3.9	3.04	~15%

[a] Estimated byy GPC. Polymer was determined to be linear by ^{31}P solution NMR.

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

no.	cat., mg	promoter, mg	$10^{-5}M_n$	M_w	M_w/M_n[a]
1	50.8	45	1.7	2.2×10^6	12.5
2	203.2	45	1.3	1.6×10^6	12.3
3	762.0	45	0.81	0.96×10^5	1.17

[a] Estimated by GPC.

eliminated. Solution polymerizations in the presence of both catalyst and promoter were stopped at various times by precipitating the reaction mixture in heptane. No polymer was recovered (however, this does not rule out trace amounts) after 5 min had elapsed, whereas small quantities (~2% yield) of polymer were isolated after a 10-minute reaction (see Table V). The yield was ~15% for a reaction time of 20 min, and the reaction was judged to be completed in 1 h. The molecular weight and molecular weight distribution of the samples from these reactions are given in Table V. From these results it is apparent that high molecular weight chains are being formed in the early stages of the reaction. This supports a chain propagation mechanism.

Chain Ends. Since the exact nature of the active catalyst in solution polymerization is not known, the structure of chain ends still remains moot. The reaction catalyzed by anhydrous HCl is claimed to produce a chain with a terminal =NH group rather than a $-NH_2$ group which is obtained when water is used to produce HCl.[25] In the absence of water and HCl, PCl_3, is another possibility.[12] The polymer chain ends formed in solution polymerization, in presence of a catalyst like sulfamic acid, have not been studied until now. The catalyst may be present as a chain end. Therefore the concentration of chain ends and hence the molecular weight should depend upon the catalyst concentration.

Solution polymerizations were performed with different catalyst concentrations and at a fixed promoter concentration. The promoter was added in order to produce narrower molecular weight distribution and faster reaction times. The results are shown in Table VI. Note 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 structure of chain ends is unknown, the catalyst seems to play a major role in forming chain ends.

Nucleophilic Substitution Reaction. Most of the studies regarding the synthesis of polyphosphazenes have concentrated on the polymerization reaction of hexachlorocyclotriphosphazene to poly(dichlorophosphazene). Molecular weight and molecular weight distribution depend upon the conditions used for solution or melt polymerization. The nucleophilic substitution reaction has not been studied in detail until recently.[27] The morphology and structure of the resulting polymer depend greatly upon the temperature of reaction and the substituents.

Table VII
$T(1)$ Transition of Poly[bis(trifluoroethoxy)phosphazene] Samples Obtained at Different Conditions on Substitution Reactions[a]

no.	reactn time, h	conditn[b]	$T(1)$, K	appearance
1	1.0	RT	349	white, powdery
2	6.0	RT	339	white, powdery
3	12.0	RT	335	white, powdery
4	24	70 °C	no $T(1)$	brown, gummy
5	48	70 °C	no $T(1)$	brown, gummy

[a] Numbers 4 and 5 were found to be branched from ^{31}P solution NMR. [b] RT = room temperature.

The time needed for "complete" substitution depends upon the strength of the nucleophile. The thermal and structural properties of poly[bis(trifluoroethoxy)phosphazene], PBFP, were found to be highly dependent on the reaction time between the poly(dichlorophosphazene) and sodium trifluoroethoxide.

Sodium trifluoroethoxide is a strong nucleophile, and the reaction with polydichlorophosphazene is exothermic. An experiment in which poly(dichlorophosphazene) was added to the sodium trifluoroethoxide was performed. Aliquots of the reaction mixture were withdrawn at intervals of 1, 6, and 12 h at room temperature. The reaction was then heated to reflux. Another sample was withdrawn after 24 h, and the rest of the reaction was precipitated after 48 h. The polymers isolated at room temperature were white and fibrous whereas those products obtained after longer heating periods were brown, sticky, and gummy. The results are summarized in Table VII. This procedure was repeated several times. The IR spectra of the samples matched the spectra of the reference materials. ^{31}P NMR indicated the absence of branching except for numbers 4 and 5 listed in Table VII (obtained after a reaction time of 24 and 48 h). Figure 5 shows an example of a ^{31}P NMR spectra for linear PBFP. The single resonance at -6.9 ppm indicates a linear polymer.

The $T(1)$ transition temperature of these samples (Figure 6) was found to decrease as the reaction time was prolonged. Samples isolated after 24 h did not show a $T(1)$ transition, since the polymers were highly branched or degraded as ^{31}P NMR indicated. Since the substitution reaction occurs in presence of an excess of nucleophile (to ensure complete substitution), the excess nucleophile may attack the substituted trifluoroethoxide moieties, introducing side groups. The greater the percentage of such side groups, the larger the depression of $T(1)$.

It was found that the reaction of sodium phenoxide and poly(dichlorophosphazene) is much slower and is far from complete at room temperature compared to highly reactive sodium trifluoroxide. Furthermore, the temperature rise is not appreciable since the reaction occurs slowly. Heating is necessary to ensure complete substitution for this and other substituted aryloxides. When a mixture of two aryloxides is used, the composition of the mixed substituted polymer is determined by the stoichiometric ratio of the aryloxides and their relative reaction rates. However when a mixture of sodium phenoxide and sodium trifluoroethoxide is used, the sodium trifluoroethoxide is consumed completely so that some sodium phenoxide will remain unreacted if sodium trifluoroethoxide is sufficient to complete the substitution.[26] This observation emphasizes the need for adjusting the reaction conditions depending on the strength of the nucleophile. (This has been established by using OCH_3, OC_6H_5, $OC_6H_4CH_3$, OCH_2CF_3, $OC_6H_4C_6H_5$, OC_6H_4Cl, OC_6H_4Br, and OC_8H_{10} which has not been detailed in this paper in the

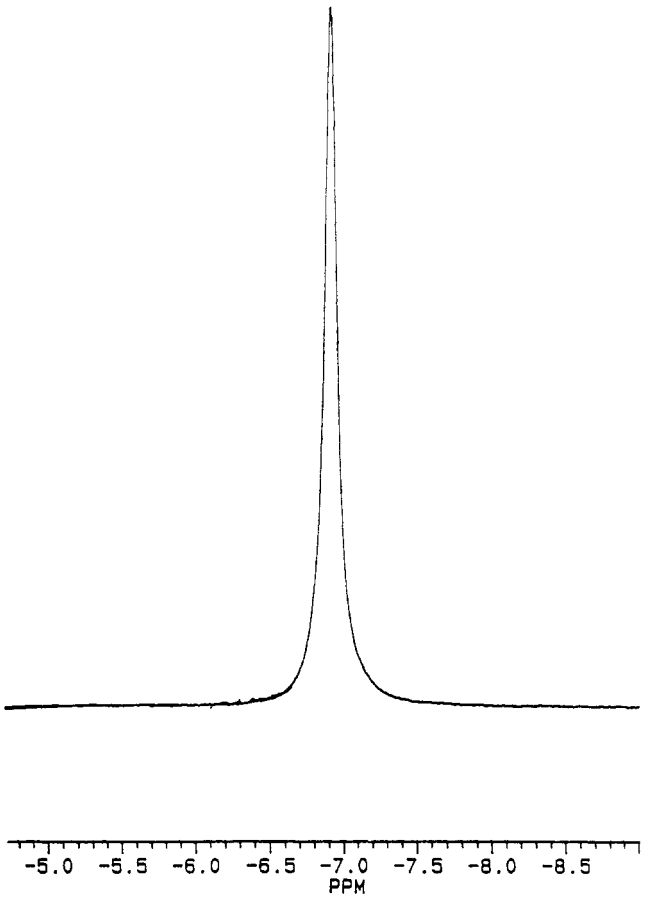

Figure 5. ^{31}P NMR spectrum of poly(diphenoxyphosphazene). The single resonance indicates linear polymer was synthesized.

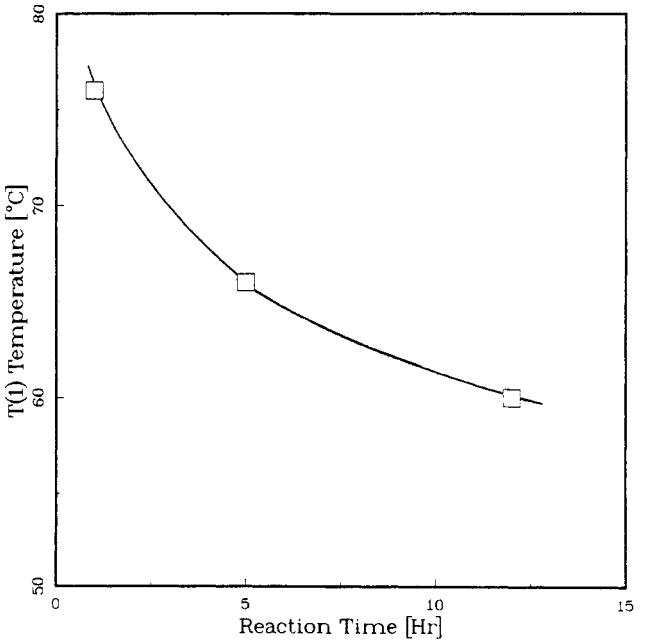

Figure 6. Plot of $T(1)$ vs substitution reaction time.

interest of brevity and because of the similarity of the synthesis procedure used.) It is reported that at 70 °C and 15 min from the start of the reaction, the content of the residual chlorine in the linear phosphazene is reduced to about 0.057% (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 h.[26]

Conclusion

The solution polymerization of hexachlorocyclotriphosphazene to poly(dichlorophosphazene) catalyzed by sulfamic acid was investigated. The substitution reaction of poly(dichlorophosphazene) to poly(organophosphazene) 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 attributed to a decomposition product of sulfamic acid, not the pure acid. The exact nature of the catalyst is still not clear at this time. The solution polymerization reaction has an induction period of an hour which is the time needed for the catalyst to become converted into its active form. The catalytic activity is associated with the acid group of the sulfamic acid, not the amine group. Molecular weights of the poly(dichlorophosphazenes) are high from the beginning of the polymerization, indicating a chain propagation mechanism, but the exact nature of the active center for kinetic chain growth is unknown. In contrast with melt polymerization, water did not act as a catalyst when used with sulfamic acid in solution polymerization, but it had an appreciable effect on the reaction rate and on the polymer properties. Water present or released in controlled amounts from inorganic hydrates acts as an effective promoter and provides linear high molecular weight polymer with relatively narrow molecular weight distributions. Water reduced the induction period to about 5 min but did not eliminate it. Although the exact structure of the polymer chain ends is not known, the decomposition product of sulfamic acid must play an important role in forming the chain ends. This was evident from the fact that polymers synthesized with high catalyst concentration were of low molecular weight. The time and temperature needed for substitution in the nucleophilic reaction depended upon the strength of the nucleophile. The physical properties of the polymer can be altered adversely through branching if prolonged heating is employed.

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Registry No. $CaSO_4 \cdot 2H_2O$, 10101-41-4; hexachlorocycloniphosphazene (homopolymer), 25231-98-5; dichlorophosphazene (SRU), 26085-02-9; hexachlorocyclotriphosphazene, 940-71-6; sulfamic acid, 5329-14-6; toluenesulfonic acid, 104-15-4; sulfobenzoic acid, 30553-06-1.

References and Notes

(1) Singler, R. E.; Hagnauer, G. L.; Schneider, N. S. *Polym. News* **1986**, *5*, 9.
(2) Quinn, E. J.; Dieck, R. L. *J. Fire Flammability* **1976**, *7*, 5.
(3) Allcock, H. R.; Fuller, T. J.; Matsumura, K.; Austin, P. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1980**, *21*, 111.
(4) Murray, C. *Chem. Eng. News* **1975**, June 16, 70–71.
(5) Konecny, J. O.; Douglas, C. M.; Gray, M. Y. *J. Polym. Sci.* **1959**, *36*, 195.
(6) Jacques, J. K.; Mole, M. L.; Paddock, N. L. *J. Chem. Soc.* **1965**, 2112.
(7) Sinclair, D. P. U.S. Patent 4,242,316, 1980.

(8) Allcock, H. R.; Kugel, R. L.; Valan, K. J., *Inorg. Chem.* **1966**, *5*, 1709.
(9) Allcock, H. R. *Inorg. Chem.* **1966**, *5*, 1709.
(10) Neilson, R. H.; Hani, R.; Neilson, P. W.; Meister, J. J.; Hagnauer, G. *Macromolecules* **1987**, *20*, 910.
(11) Neilson, R. H.; Neilson, P. W. *J. Macromol. Sci., Chem.* **1981**, *A16*, 425.
(12) Hagnaeur, G. L. *J. Macromol. Chem.* **1981**, *16*, 385.
(13) Singler, R. E.; Schneider, N. S.; Hagnauer, G. L. *Polym. Eng. Sci.* **1975**, *15*, 321.
(14) MacCallum, J. R.; Werninck, A. *J. Polym. Sci.* **1967**, *5*, 3061.
(15) Chakraborty, D.; Ghosh, B. N. *J. Polym. Sci.* **1962**, *62*, 130.
(16) Lee, D. C.; Ford, J. R.; Fytas, G.; Chu, B.; Hagnauer, G. L. *Macromolecules* **1986**, *19*, 1586.
(17) Chu, B.; Lee, D. C. *Macromolecules* **1986**, *19*, 1592.
(18) Sennett, M. S.; Hagnauer, G. L.; Singler, R. E.; Davies, G., *Macromolecules* **1986**, *19*, 959.
(19) Hagnauer, G. L.; Schneider, N. S. *J. Polym. Sci.* **1972**, *10*, 669.
(20) Soulen, J. R.; Silverman, M. S. *J. Polym. Sci.* **1963**, 823.
(21) Jacques, J. K.; Mole, M. L.; Paddock, N. L. *J. Chem. Soc.* **1965**, 2112.
(22) Mcbee, E. T.; Allcock, H. R.; Capute, R.; Kalmas, A.; Roberts, C. W. *U.S. Gov. Res. Rep.* **1959**, *Ad. 209-699*.
(23) Allcock, H. R.; Best, R. J. *Can. J. Chem.* **1964**, *42*, 447.
(24) Allcock, F. R.; Gardner, J. E.; Smeltz, K. M. *Macromolecules* **1975**, *8*, 36.
(25) Vinagrodava, S. V.; Tur, D. R. *J. Polym. Sci.* USSR (*Engl. Transl.*) **1982**, *24*, 2572.
(26) Ganapathippan, S.; Dhathathrayan, K. S.; Krishnamurthy, S. S. *Macromolecules* **1987**, *20*, 1501.
(27) Ferrar, W. T.; Marshall, A. S.; Whitefield, J. *Macromolecules* **1987**, *20*, 317.

Synthesis and Polymerization Studies of New Azaethylene Monomers Carrying Electron-Acceptor Groups on Nitrogen

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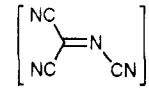
ABSTRACT: To explore the polymerizability of C=N monomers, the following compounds were synthesized: 2-phenylazaethylenecarbonitrile (benzylidenecyanamide; **1**), 2-*tert*-butylazaethylenecarbonitrile (pivalidenecyanamide; **2**), methyl 2-phenylazaethylenyl sulfone (*N*-(methylsulfonyl)benzylideneamine; **3**), ethyl 2-phenylazaethylenecarboxylate (*N*-carbethoxybenzylideneamine; **4**), and ethyl 2-*tert*-butylazaethylenecarboxylate (*N*-carbethoxypivalideneamine; **5**). Their electrophilic character was appraised using hydrolysis rates and NMR data. Monomer **1** homopolymerized in high yield under both anionic and free-radical conditions to yield a low molecular weight polymer (DP = 8). Monomer **2** polymerized poorly anionically and free radically. Monomer **4** oligomerized in low yield with weak bases. Compounds **3** and **5** did not polymerize. Low polymerizability of these compounds is ascribed to the required bulky substituent on carbon, and only the most electrophilic imine with a small cyano substituent on nitrogen and a phenyl substituent on carbon is able to oligomerize effectively.

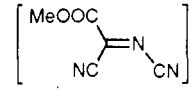
Introduction

Polymerizations involving C=C bonds are widely known. The same can be said of C=O bonds. In contrast, polymerizations involving C=N bonds are conspicuous by their rarity. With acid or base catalysis, common azaethylenes (imines) are known to cyclotrimerize, which, in analogy to the behavior of aldehydes, implies a tendency to polymerize. Moreover, azaethylenes with only one substituent on nitrogen prepared by flash vacuum pyrolysis are highly unstable and spontaneously polymerize.[1-4] Our studies of substituted 1- and 2-aza-1,3-butadienes showed that their C=N groups could indeed be polymerized. The best results were obtained for 1-phenyl-1-aza-1,3-butadiene and *N*-carbethoxy-3-methyl-1-aza-1,3-butadiene under anionic conditions,[5-7] but free radical reactions were also possible.

As to azaethylenes, we have already synthesized two imines with three electron-accepting substituents, tricyanoazaethylene and methyl 1,2-dicyanoazaethylene-2-carboxylate. These are so reactive that they can only be obtained in solution.[8,9] Attempted isolation gives oligomers. Mixing these monomers in solution with an electron-rich olefin such as *p*-methoxystyrene leads spontaneously to alternating copolymers.

In order to obtain azaethylene monomers, which can be isolated and purified and whose polymerization behavior can then be studied under controlled conditions, we have now synthesized electrophilic imines with one electron-accepting group on nitrogen in order to confer anionic





polymerizability and one substituent on carbon to provide thermal stability. The polymerization behavior of these imines was studied, mainly with anionic initiators.

Results

Monomer Synthesis. Because it is known that the unsubstituted CH_2=NX compounds are too reactive,[3] we selected the following electron-deficient imines with one β-substituent for study.

The easy tautomerization of electron-deficient imines with α-hydrogen-bearing alkyl groups to enamines[10] prevents use of methyl, ethyl, etc., alkyl groups and restricts us to aromatic and tertiary alkyl substituents.

Of our selected monomers, only **1** and **3** have been previously described in the literature. 2-Phenylazaethyl-

0024-9297/90/2223-0021$02.50/0