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Reaction of Poly(difluorophosphazene) with Phenyllithium

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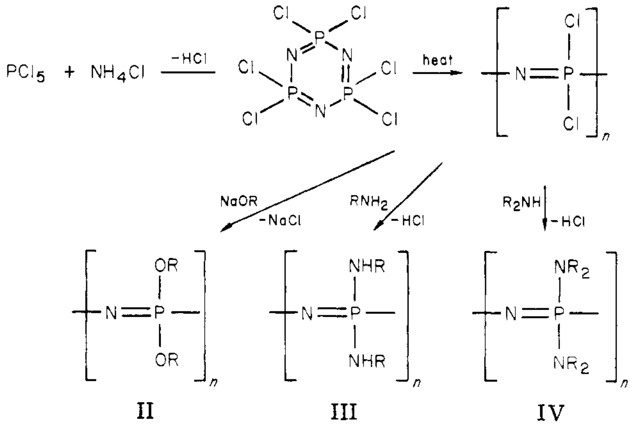
ABSTRACT: The reaction of poly(difluorophosphazene), $(NPF_2)_n$, with phenyllithium, followed by treatment with sodium trifluoroethoxide, has yielded a new class of high polymeric organophosphazenes of formula $[NP(C_6H_5)_x(OCH_2CF_3)_y]$, where x and y are 0.38 and 1.62, 0.64 and 1.36, 0.98 and 1.02, or 1.24 and 0.76, respectively. The macromolecules are the first examples of high molecular weight phosphazene polymers that contain a substantial number of organic groups bound directly to the skeleton through carbon–phosphorus bonds. The new polymers are nonelastomeric, film-forming materials with molecular weights (GPC average) above 1×10^6 and with glass transition temperatures at +7, +25, +45, and +60 °C, respectively. The structural characterization was by means of ^{31}P and ^{1}H NMR spectroscopy and by microanalysis. The replacement of fluorine in $(NPF_2)_n$ by phenyl is accompanied by a skeletal cleavage reaction. However, chain cleavage is significant only after 70% or more of the fluorine atoms have been replaced by phenyl. Although fully phenylated polymers of formula $[NP(C_6H_5)_2]_n$ were prepared, the molecular weights were low (GPC average mol wt = 50 000–80 000), with a glass transition temperature of +70 °C. The mechanisms of substitution and chain cleavage are discussed, and comparisons with the behavior of $(NPCl_2)_n$ are made. Thermolysis studies suggest that the phenyl side groups enhance the thermal stability of the polymers compared to the behavior of $[NP(OCH_2CF_3)_2]_n$.

The synthesis and study of macromolecules that contain inorganic elements in the backbone constitute an important challenge for the future development of polymer chemistry. It is well-known that a large and diverse range of new polymers can be synthesized by the reactions of poly(dichlorophosphazene) (I) with nucleophiles such as alkoxides, aryloxides, or amines[1–6] (Scheme I). The unusual feature of this synthetic route is the use of a highly reactive polymeric intermediate (I) as a substrate for side group replacement reactions. Polymers of types II–IV are, in general, hydrolytically stable and show unusual structural, physical, and chemical properties.

However, polymers of structures II–IV possess a number of limitations that can be attributed to the linkage of the organic group, R, to phosphorus through an oxygen or nitrogen atom. Specifically, these linkage atoms appear to play a role in the destabilization of the polymers at high temperatures (over 300 °C), especially in the presence of strong acids, or during ultraviolet irradiation.[7] Thus, the prospect existed that poly(organophosphazenes) which possess alkyl or aryl groups linked directly to the skeleton through carbon–phosphorus bonds might display a whole range of new and interesting properties.

An extension of the reactions shown in Scheme I to include the interactions of I with organometallic reagents provides one possible route for the preparation of such polymers. However, we have shown recently that I reacts with phenyllithium by a mechanism that involves concurrent halogen replacement by phenyl *and* skeletal chain cleavage.[8] Thus, the higher the phenyl group content of the reaction product, the lower is the molecular weight. In that paper, we speculated that the chain-cleavage process was favored by a high electron density in the lone-pair orbital at skeletal nitrogen. This could favor coordination of the lithium cation to nitrogen and hence facilitate cleavage rather than lithium chloride elimination. Thus, in principle, any phenomenon that would reduce the

Scheme I



$n \simeq 15\,000$; R = alkyl or aryl

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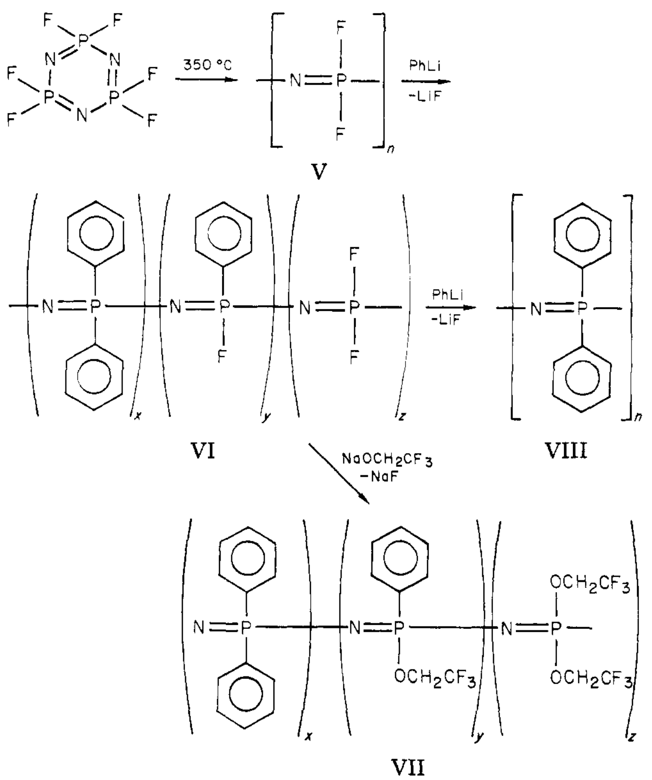
Scheme II



lone-pair electron density at nitrogen or would facilitate halogen ion removal should discriminate against chain cleavage and favor halogen replacement. The use of poly(difluorophosphazene), $(NPF_2)_n$ (V), as a reaction substrate might be expected to achieve these ends.

In an earlier publication,[9] we described the synthesis of a soluble form of poly(difluorophosphazene) (V) and explored its reactions with alkoxides, aryloxides, and amines. Here, we discuss the interaction of this polymer with phenyllithium.[10]

Results and Discussion

Overall Reaction Sequence. Scheme II illustrates the general reaction pathway used in this work. By variations in the reaction conditions (see Experimental Section), polymers of type VI could be prepared that contained 19%, 32%, 48%, 62%, and 100% phenyl substituent groups. Those polymers that contained residual fluorine atoms were then treated with sodium trifluoroethoxide to yield species of type VII. The composition of these polymers was deduced from ^{31}P NMR and ^{1}H NMR spectra and, when possible, from microanalysis data.

All of the polymers, except the fully phenylated $[NPPh_2]_n$ (VIII), showed molecular weights[11] above 1×10^6. The totally phenylated product (VIII) had a molecular weight near 50 000–80 000. The polymers of type VI were usually not isolated in the solid state because of the tendency for P–F bond hydrolysis to occur, particularly when few phenyl groups were attached to the chain. However, the polymers of structure VII were hydrolytically stable, nonelastomeric, film-forming materials in the solid state. The glass transition temperatures of VII varied with the ratio of phenyl to trifluoroethoxy groups. Specifically, the T_g values[12] (with the percentage of phenyl groups in parentheses) were −66 °C (0%), +7 °C (19%), +25 °C (32%), +45 °C (48%), and +60 °C (62%). Product VIII showed a "T_g" value of 70 °C, although its molecular weight was considerably lower than the other species. It seems clear that phenyl groups markedly affect the physical properties of polyphosphazenes, presumably by sterically restricting the torsional mobility of the skeletal bonds.

The following two sections deal with specific problems that were encountered with the synthesis method.

Effect of the Heterophase Reaction System. Poly(difluorophosphazene) (V) is not soluble in common organic solvents. Perfluorinated solvents, such as perfluorodecalin or perfluoro-2-butyltetrahydrofuran are required, often in the presence of a few percent of diethyl ether.[9] However, phenyllithium and sodium trifluoroethoxide are not soluble in the fluorinated solvents, but are soluble in tetrahydrofuran. Thus, the reactions described in this paper were carried out in a heterophase solvent system. This introduced a serious complication. Those polymers of structure VI that contain a low percentage of phenyl side groups are insoluble in *both* the fluorinated solvent phase and the THF. Thus, the partly phenylated polymer formed rapidly and then precipitated from solution, and subsequent reactions took place within this swelled but insoluble semisolid matrix. The overall effect of this phenomenon was to drastically reduce the reaction rate after the precipitation stage and, at the same time, require the use of roughly twice the amount of phenyllithium that would normally be needed to effect a certain degree of substitution. In fact, increases in the degree of substitution with higher phenyllithium concentrations may perhaps be attributed to increased substitution rates before precipitation occurs. However, treatment of these products with sodium trifluoroethoxide in THF brought about a rapid solution of the polymer as the residual fluorine atoms were replaced by trifluoroethoxy units. On the other hand, the treatment of V with an *excess* of phenyllithium in the heterophase system resulted in a transient precipitation of the partially subtituted polymer. As phenylation proceeded beyond the critical point ($\simeq$70% phenyl groups), the polymer dissolved in the THF phase and substitution continued at a detectable rate.

Restrictions to Total Fluorine Replacement. Steric effects play a significant role in the substitution chemistry of cyclic and high polymeric phosphazenes.[13] For example, the reactions of poly(dichlorophosphazene) (I) with bulky nucleophiles, such as diethylamine,[14] diphenylamine, amino–azo dyes,[15] or steroidoxy reagents,[16] lead to incomplete replacement of the chlorine by the organic species. Moreover, the presence of a bulky substituent group already attached to the ring or chain often retards the replacement of the residual halogen by less-bulky nucleophiles.

In these terms, the phenyl group is a bulky substituent, and the reactions of polymers of type VI with trifluoroethoxide ion are complicated by the low reactivity of the remaining fluorine atoms. For example, when 62% of the side groups in VI were phenyl groups, very large excess amounts of trifluoroethoxide ion and long reaction times (over 2 days) were required to effect a complete replacement of fluorine.

The shielding influence by the phenyl groups was responsible for a second unusual feature of polymers of type VI. Polyphosphazenes that contain phosphorus–halogen bonds are normally extremely sensitive to hydrolysis by traces of water—a reaction that leads to rapid cross-linking and chain cleavage. However, in VI, when less than 10% of the side groups were fluorine atoms, no hydrolysis of the P–F bonds could be detected (by ^{31}P NMR analysis) following exposure of the polymer to large amounts of water. Similar hydrolytic stability was observed for a polymer that possessed 62% phenyl, 30% trifluoroethoxy,

Table I
^{31}P NMR Integration Data for Products Formed by the Reaction of $(NPF_2)_n$ with an Excess of Phenyllithium

time, min	% PR_2	% PRF	% PR_2[a]	% fluorine	% phenyl
0	63	16	21	29	71
5	63	14	23	30	70
30	63	14	23	30	70
1080	86	0	14	7	93

[a] The NMR spectra provided evidence for the trace hydrolysis of some of the PF_2 units during the polymer purification process. The values in this column are corrected for this loss.

and 8% fluorine substituents. This polymer underwent no detectable chain cleavage during storage in the solid state for 1 year. However, if the fluorine atoms were present in amounts larger than 10%, evidence of hydrolysis and cross-linking was seen when the polymer was brought into contact with water.

A third influence by the phenyl groups is an effect on the rate of phenylation itself. ^{31}P NMR experiments were carried out to monitor the degree of phenylation of $(NPF_2)_n$ as a function of time in the presence of excess phenyllithium. The experiments were complicated by the initial precipitation of the partly phenylated products in the two-phase medium as described previously. Hence, the speed of the reaction could be followed only from the stage at which this partly phenylated polymer dissolved in the THF phase. The ^{31}P NMR spectra of species derived from 0, 5, and 30 min of exposure to phenyllithium of the THF-soluble form of VI are virtually identical and correspond to a composition of $[NP(C_6H_5)_{1.4}F_{0.6}]_n$ (Table I). Even after 1080 min in the homogeneous system, 7% of the substituent groups were fluorine atoms (as P(F)Ph units). The slowness of this phenylation process in the homogeneous system is remarkable when compared with the fact that 70% of the fluorine atoms were replaced by phenyl in less than 5 min at 25 °C in the heterogeneous reaction system.

These effects by the phenyl groups almost certainly represent shielding influences on the nearby P–F bonds. However, factors other than steric effects are also involved. This point will be amplified in a later section.

Chain Cleavage. One of the main reasons for the use of poly(difluorophosphazene) as a reaction substrate was the prospect that the electronegative fluorine atom might reduce the percentage of skeletal cleavage relative to phenylation. A plot of molecular weight[11] as a function of the degree of phenylation for seven polymers is shown in Figure 1. The molecular weight remained high until 70% of the fluorine atoms had been replaced by phenyl groups. Thereafter, the molecular weight declined dramatically from 1×10^6 to $\simeq 50000$. This latter value corresponds to only 250 repeating units per average chain. The use of a lower reaction temperature (-10 °C) did not reduce the degree of chain cleavage in the final stages of the reaction.

Thermal Behavior. A polyphosphazene which contained 62% phenyl substituent groups and 38% trifluoroethoxy groups (mol wt[11] $\simeq 1.2 \times 10^6$) was subjected to preliminary thermolysis experiments and was compared to the behavior of $[NP(OCH_2CF_3)_2]_n$ (mol wt $\simeq 2.0 \times 10^6$). Differential scanning calorimetry indicated a decomposition temperature of 385 °C for the phenylated derivative. The nonphenylated species showed a decomposition temperature of 315 °C. Differential scanning calorimetry results often overestimate thermal stability. Hence, the two polymers as films were also heated at 300 °C for 12 h in evacuated ampules. After this treatment, $[NP(OCH_2CF_3)_2]_n$ showed a complete loss of physical integrity to yield oils and pyrolyzed solids, with an average molecular weight decline to below 10000. The phenylated polymer retained its physical characteristics except for a slight darkening in color, but 80% of the material was now cross-linked. The molecular weight distribution of the uncross-linked portion had broadened to encompass lower molecular weight species, but the higher molecular weight components were still present. These results suggest that the introduction of phenyl groups into a fluoroalkoxyphosphazene high polymer does improve its resistance to thermolysis, perhaps by blocking an unzipping sequence. However, for the reasons discussed in a later section, a totally phenylated structure (VIII) would not be expected to show a high thermal stability.

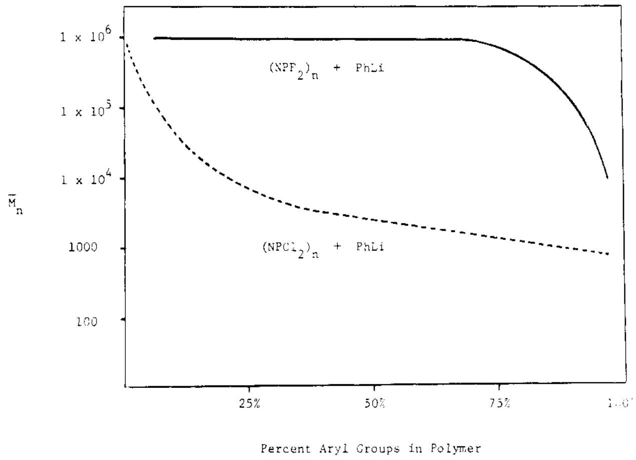
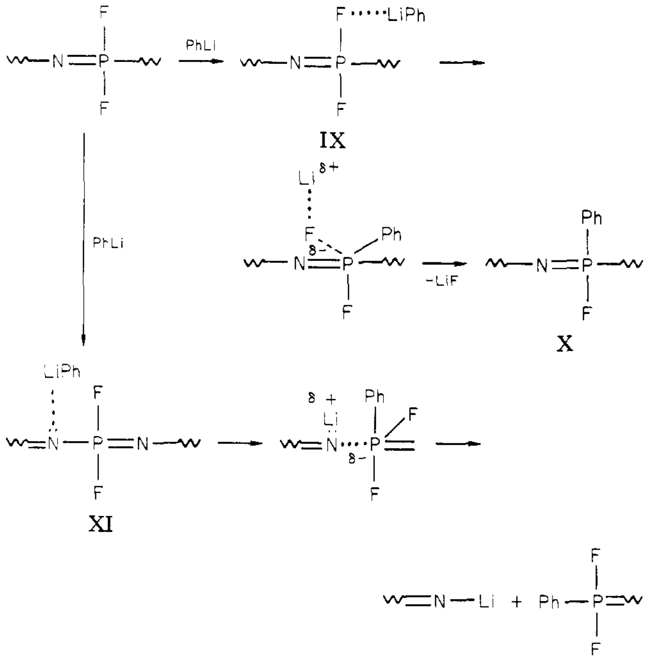


Figure 1. Comparisons of the variation in GPC average molecular weight for $[NP(C_6H_5)_x(OCH_2CF_3)_y]_n$ vs. the percentage of phenyl groups attached to the backbone. The broken curve represents the behavior of the system when $(NPCl_2)_n$ is used as a reaction substrate. The solid line illustrates the behavior with $(NPF_2)_n$.

Reaction Mechanism. (a) Substitution Pattern. Substitution in any cyclic or polymeric phosphazene can be by geminal or nongeminal replacement. ^{31}P NMR spectroscopy was used to assess the substitution patterns involved in the formation of VI and VII.

First, ^{31}P NMR spectra of VI showed unambiguously that polymers of composition $[NP(C_6H_5)_{1.4}F_{0.6}]_n$ contained 22% of all of the phosphorus atoms as PF_2, 15% as $P(C_6H_5)F$, and 63% as $P(C_6H_5)_2$ units. If a nongeminal replacement pattern were predominant, only $P(C_6H_5)_2$ and $P(C_6H_5)F$ units would be detectable.

Second, the ^{31}P NMR spectra of macromolecules of the type VII, with the composition $[NP(C_6H_5)_{0.38}(OCH_2CF_3)_{1.62}]_n$, $[NP(C_6H_5)_{0.64}(OCH_2CF_3)_{1.36}]_n$, $[NP(C_6H_5)_{0.98}(OCH_2CF_3)_{1.02}$, consisted of three bands at +3.10, -0.49, and -8.37 (±0.50) ppm, respectively, in THF solvent.[18] The more highly phenylated polymers gave a ^{31}P NMR spectra that showed considerable peak broadening, which prevented a complete assignment from being made. The -8.37 ppm resonance was assigned to phosphorus atoms that were linked to two trifluoroethoxy groups. This was inferred from the similarity of the chemical shift to that found in $[NP(OCH_2CF_3)_2]_n$ (-8.6 ppm). However, the assignments for the two downfield resonances required some assumptions to be made. Three facts suggested that the resonance at +3.10 ppm should be assigned to nongeminal $NP(C_6H_5)(OCH_2CF_3)$ residues and that the peak at -0.49 ppm resulted from the presence of geminal $NP(C_6H_5)_2$ structures. First, the low molecular weight polymer of structure VIII, discussed earlier, showed a negative ^{31}P NMR shift (-3.00 ppm), and a polymer of structure VII, Scheme III



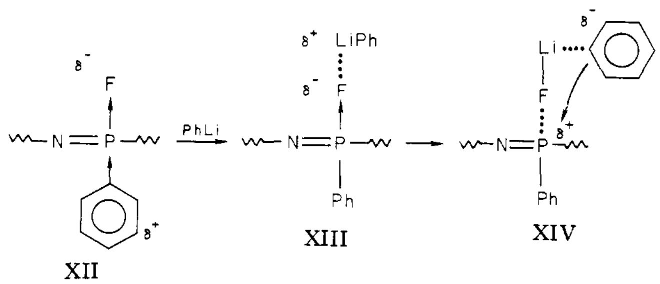
with 62% phenyl groups, showed a (broad) peak at −2.17 ppm. Hence, there appears to be some correlation between negative shift positions and the geminal diphenylphosphorus structure. Second, it is known from ^{31}P NMR studies of VI that the resonance for $P(C_6H_5)F$ units appears downfield (i.e., a more positive shift) from that of $P(C_6H_5)_2$ units, an effect attributed to the strong electron-withdrawing power of fluorine. Although the trifluoroethoxy group is not as electron-withdrawing as fluorine, it might be expected that the resonance for $P(C_6H_5)OCH_2CF_3$ should also appear downfield from $P(C_6H_5)_2$. Third, the ^{1}H NMR peak integrations can be explained satisfactorily only if the proposed ^{31}P NMR shift assignments are correct.

In these terms, the change in ratio of $P(C_6H_5)_2$:$P(C_6H_5)X$:PX_2 is compatible with a predominantly geminal phenylation pattern, at least in the early stages of the reaction. For example, at the point where 50% of the total substituent groups were phenyl, the NMR spectra could be explained only by the assumption that 38% of all of the phosphorus atoms were linked to two trifluoroethoxy groups. The result is incompatible with a nongeminal pathway or with a totally random disposition of the two substituent groups. Even at the 62% phenyl, 38% F, or CF_3CH_2O (X) stage, 33% of the phosphorus atoms in the polymer were shown by ^{31}P NMR analysis to be PX_2 units. However, in the more advanced stages of the phenylation reaction (93% phenylation), no PX_2 units could be detected, and this indicated that a nongeminal replacement pattern can occur in the final stages of the substitution.

(b) Underlying Principles. In this section, we propose explanations for the following experimental facts: (1) The fluorine replacement pattern by phenyl is predominantly geminal but with a nongeminal component in the final stages of the reaction. (2) The rate of reaction falls off markedly after $\simeq$70% of the fluorine atoms in V have been replaced by phenyl. (3) Chain cleavage becomes serious only in the final stages of the phenylation process.

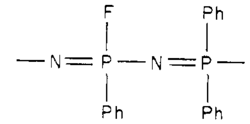
Although virtually no kinetic studies have been made of the reactions of organometallic reagents with cyclic or high polymeric halophosphazenes, it is reasonable to assume that these processes are nucleophilic substitution reactions in which halogen replacement involves an attack on phosphorus by a phenyl anion. The interactions of halophosphazenes with other nucleophiles, such as alkoxide ions or amines, follow an S_N2-type mechanism, sometimes with a substantial S_N1 component.[13] The S_N2 mechanism requires the transient formation of a pentacoordinate phosphorus atom, a process that appears possible in the present reaction also. Simplified initial steps for the interaction of $(NPF_2)_n$ with phenyllithium are suggested in the formation of IX and XI (Scheme III).

Scheme IV



Consider first the geminal nature of the initial phenylation reaction. Apparently, this is a feature common to a number of organometallic reactions, including the interactions of cyclic chloro-[19] and fluorophosphazenes[20] or $(NPCl_2)_n$[8] with organometallic reagents. It implies that the attack by a phenyl anion on a repeating unit, such as X, is favored over attack at an NPF_2 residue. This is surprising if substituent electronegativity (and the resultant electron deficiency at phosphorus) is the main activation force for substitution. Hence, it must be concluded that the electron supply from the phenyl to the geminal fluorine atom in a polarization process generates an enhanced negative charge on that fluorine atom (XII). Hence, because P–F bond cleavage is important in the approach to the transition state (XIII, XIV), geminal substitution is favored (Scheme IV). On the other hand, in the final stages of the phenylation reaction, it is likely that steric effects retard the attack by the phenyl anion on $P(C_6H_5)F$, relative to an attack on PF_2 units. One possible complication to this interpretation is the fact that the final (nongeminal replacement) stage takes place in a different solvent system (THF). Hence, solvent effects may also be involved. Careful mechanistic studies with small-molecule model systems may be needed before this question can be resolved.

The marked decrease in reactivity of the polymer following about 70% replacement of the fluorine by phenyl can be explained by the influence of steric hindrance effects on the mechanism shown in Scheme IV. Molecular models of structures that contain the repeating sequence shown in XV indicate that the attack on the $P(C_6H_5)F$ unit would be highly hindered by the flanking $P(C_6H_5)_2$ units.



XV

Finally, three explanations exist for the sudden onset of chain cleavage when attempts are made to increase the degree of phenylation beyond the stage represented by XV. First, the chain cleavage process takes place during the slow homogeneous substitution reaction in THF. Thus, it is conceivable that the chain cleavage sequence shown in Scheme III is favored by a solvent effect. Second, the more the composition of the polymer changes from XV toward VIII the more severe will be the intramolecular steric crowding. Space-filling molecular models of VIII are almost impossible to construct because of steric interference by the phenyl groups. Hence, these effects may lower the ceiling temperature of the polymer–oligomer system. Third, a simple mechanistic explanation can be derived from Scheme III. The two alternative pathways shown can lead to substitution (X) or to P–N bond cleavage. Cleavage of the P–N bond would be inhibited as long as strong electron withdrawal into the side groups reduced the electron density on nitrogen and strengthened the skeletal bonds. However, beyond a certain stage in the phenylation process, insufficient fluorine atoms will remain to maintain this effect, and chain cleavage will then occur.

Experimental Section

Equipment. ^{31}P NMR spectra were obtained in the Fourier transform mode at 40.0 MHz with a Jeol PS-100 FT spectrometer and were processed with the use of a Nicolet 1080 computer. Many of the ^{31}P NMR spectra were broad band ^{1}H decoupled. ^{1}H NMR and ^{13}C NMR spectra were obtained with the same spectrometer at 100 and 95 MHz, respectively. Approximate polymer molecular weights were determined with the use of a Waters Associates ALC/GPC 501 instrument fitted with a 120 cm × 1 cm, 10^6 styragel column. Glass transition temperatures (T_g) were measured with the use of a Chemical Instruments Corp. torsional braid analyzer kindly provided by N.A.S.A., Langley Field.

Materials. All experimental manipulations were performed under an atmosphere of dry nitrogen (Matheson). Tetrahydrofuran (THF) (Fisher) was freshly distilled under nitrogen from sodium benzophenone ketyl. Phenyllithium was prepared by the reaction of bromobenzene (Aldrich, dried over P_2O_5 and then distilled) with lithium metal (Foote mineral, purchased as a 50% dispersion in hexane). The commercial phenyllithium used in some experiments was used as received (Aldrich, 1.67 M solution in a mixed 70:30 benzene:ether solvent system). No differences in experimental results could be detected between freshly prepared phenyllithium and the material obtained commercially. Sodium trifluoroethoxide was prepared from sodium pellets (Matheson, Coleman, and Bell) and trifluoroethanol (Halocarbon Products) dried over 4 Å molecular sieves. Perfluorobutyltetrahydrofuran, PFBT (PCR), was used as received.

Synthesis of Poly(difluorophosphazene) (V). This polymer was prepared in 30–50% yield by the thermal polymerization of hexafluorocyclotriphosphazene, $(NPF_2)_3$, at 350 °C in sealed tubes by the method described previously.[9] The residual cyclic trimer was removed by vacuum sublimation.

Analyses. Elemental microanalysis was found to be an unreliable method for the estimation of the composition of these polymers. Those analyses reported were obtained by Galbraith Laboratories. A more reliable analytical technique was the use of ^{31}P NMR and ^{1}H NMR spectroscopy. The phenyl:trifluoroethoxy ratios determined by these two NMR methods generally agreed to within 5%. The agreement between the ratios determined by NMR techniques and the most reliable microanalyses was within 10%.

^{31}P NMR Study of the Phenylation Process. To each of four reaction vessels, which contained $(NPF_2)_n$ (0.50 g, 0.0060 mol) dissolved in PFBT (50 mL) and dry THF (100 mL), was added at 25 °C an equivalent amount of commercial phenyllithium (7.19 mL, 0.0012 mol). The reactions were deactivated at different times by the addition of isopropyl alcohol (distilled from dry Na_2SO_4). Zero reaction time was determined from the point at which the partially phenylated polymer (insoluble in both PFBT and THF phases) dissolved in the THF phase (this transformation usually required less than 5 min from the time at which the organometallic reagent was added to the heterophase reaction system). After the addition of isopropyl alcohol, the products were obtained by concentration of the reaction mixtures with a rotary evaporator, followed by filtration to remove the insoluble salts. ^{31}P NMR analyses of some of these reaction mixtures indicated the presence of phosphorus atoms that possessed one fluorine and one hydroxy pendent group (the peak was observed at −16.5 ppm). These units were identified further by ^{19}F NMR decoupling experiments which indicated a downfield shift for this resonance to −6.0 ppm (this shift suggests a coupling constant of 840 Hz) and by comparison with the ^{31}P NMR spectra of polymers of the general structure $[NP(C_6H_5)_x(F)_y(OH)_2]_n$ where $x \simeq 1.6$, $y \simeq 0.3$, and $z \simeq 0.1$. The values for the PF_2 integrations, described in Table I, were obtained by a summation of the ^{31}P integrated areas for PF_2 units and PFOH units.

Synthesis of $[NP(C_6H_5)_{0.38}(OCH_2CF_3)_{1.62}]_n$. A sample of $(NPF_2)_n$ (2.90 g, 0.035 mol) was dissolved in PFBT (200 mL), and dry THF (250 mL) was then added. A solution of commercial phenyllithium (13.0 mL, 0.022 mol) was then added dropwise to the reaction mixture during 5 min, while the reaction mixture was maintained at 25 °C by means of a water–ice bath. A polymeric solid precipitated almost immediately following the addition of the phenyllithium. This product did not dissolve in the THF phase during the subsequent stirring for 12 h. The mixture was then treated with trifluoroethanol (2 mL, 0.028 mol) to deactivate the phenyllithium, and a solution of sodium trifluoroethoxide, prepared from sodium (8.05 g, 0.35 mol) and an excess of trifluoroethanol (40.0 g, 0.40 mol) in THF (200 mL), was added. The mixture was then allowed to boil at reflux for 42 h. Isolation of the polymeric product was accomplished by concentration of the mixture on a rotary evaporator and by addition of the concentrate to aqueous dilute hydrochloric acid. The precipitated polymer was washed with water several times and reprecipitated twice from THF into water and twice from THF into hexane. The white product (35% yield)[21] had a GPC average molecular weight near 1.2×10^6. ^{31}P and ^{1}H NMR spectroscopy yielded spectra that were compatible with 19 ± 2% phenyl substitution. The T_g value was +7.0 °C.

Synthesis of $[NP(C_6H_5)_{0.64}(OCH_2CF_3)_{1.36}]_n$. The same procedure was followed as described above except that a larger amount of phenyllithium solution (25 mL, 0.042 mol) was used. Precipitation of the phenylfluorophosphazene polymer occurred when 20% of the phenyllithium had been added. Deactivation of the excess phenyllithium was accomplished with trifluoroethanol (3.0 mL, 0.042 mol). The reaction with sodium trifluoroethoxide took place over 48 h. Purification of the polymer was accomplished by three reprecipitations from THF into water and from THF into benzene to give a 40% yield of product. The GPC average molecular weight of this polymer was 1.1×10^6. The ^{31}P and ^{1}H NMR data suggested a 32 ± 2% degree of phenyl substitution. The T_g was +25 °C.

Synthesis of $[NP(C_6H_5)_{0.95}(OCH_2CF_3)_{1.05}]_n$. The same general procedure was employed as described above but with the use of $(NPF_2)_n$ (2.49 g, 0.03 mol) in PFBT (175 mL) and a filtered etheric phenyllithium solution (35 mL, 0.04 mol), prepared in the laboratory from bromobenzene (31.7 g, 0.20 mol) and finely divided lithium (4.0 g, 0.58 mol) in diethyl ether, to which had been added dry benzene (60 mL). The addition of the phenyllithium to the stirred fluorophosphazene solution at 0 °C took place during 1 h, and the mixture was then stored at 0 °C for 12 h. The sodium trifluoroethoxide solution was prepared from sodium (3.5 g, 0.15 mol) and trifluoroethanol (2.8 g, 0.28 mol) in THF (100 mL). The trifluoroethoxide substitution reaction was allowed to proceed for 8 h at 70 °C. The final yield was 17% (based on $(NPF_2)_n$). The product had a GPC average molecular weight of 1.5×10^6. Phenyl groups constituted 50 ± 2% of the total side groups (as determined by ^{31}P and ^{1}H NMR analysis). A microanalysis suggested 47.5% phenyl groups. The T_g was +45 °C. Anal. Calcd for the formula shown: C, 42.15; H, 3.13; F, 26.93; N, 6.30; P, 13.93. Found: C, 42.25; H, 3.11; F, 26.99; N, 6.67; P, 14.70.

Synthesis of $[NP(C_6H_5)_{1.24}(OCH_2CF_3)_{0.76}]_n$. The same general procedures were employed as those described above. Minor differences in procedure included an initial reaction between $(NPF_2)_n$ (4.6 g, 0.055 mol) in PFBT (175 mL) with diethyl ether (10 mL) in the presence of THF (1000 mL) and a filtered phenyllithium solution prepared from bromobenzene (26.2 g, 0.17 mol) and lithium (4.0 g, 0.57 mol) in diethyl ether (200 mL). The phenyllithium addition was carried out over a 6-min period. After a further 5 min of stirring, the mixture was treated with a solution of sodium trifluoroethoxide prepared from sodium (4.15 g, 0.18 mol) and trifluoroethanol (33.6 g, 0.34 mol) in THF (200 mL) and was boiled at reflux for 18 h. Final purification was effected by reprecipitation of the polymer twice from THF into water, once

Table II
^{31}P NMR Shift Values[18,a]

PF_2	$[NPF_2]_n$[b,c]	−23 ± 0.5	890 ± 20
PF_2	$[NP(C_6H_5)_x(F)_y]_n$[d]	−16 ± 0.5	952 ± 20
$P(C_6H_5)(F)$	$[NP(C_6H_5)_x(F)_y]_n$[d]	1.8 ± 0.5	927 ± 20
$P(C_6H_5)(F)$	$[NP(C_6H_5)_x(OCH_2CF_3)_y(F)_z]_n$[e]	7.0 ± 2.2	849 ± 44
$P(OH)(F)$	$[NP(C_6H_5)_x(OH)_y(F)_z]_n$[f]	−6.6 ± 2.0	960 ± 81
$P(OCH_2CF_3)(F)$	$[NP(C_6H_5)_x(OCH_2CF_3)_y(F)_z]_n$[g]	−13.8 ± 0.5	900 ± 20
$P(C_6H_5)_2$	$[NP(C_6H_5)_2]_n$	−2.36 ± 0.5	
$P(C_6H_5)_2$	$[NP(C_6H_5)_x(OCH_2CF_3)_y]_n$[h-j]	−1.26 ± 1.0	
$P(C_6H_5)(OCH_2CF_3)$	$[NP(C_6H_5)_x(OCH_2CF_3)_y]_n$[h-j]	3.19 ± 0.5	
$P(OCH_2CF_3)_2$	$[NP(OCH_2CF_3)_2]_n$	−8.5 ± 0.5	
$P(OCH_2CF_3)_2$	$[NP(C_6H_5)_x(OCH_2CF_3)_y]_n$[h-j]	−8.42 ± 0.5	

[a] The ^{31}P NMR shift value positions varied with the types and percentages of the different substituent groups and with the type of deuterated lock solvent employed. Peak broadening effects also limited the accuracy of the data to no better than a 0.5 ppm range at 20.2 Hz. [b] Peak broadening effects limited the accuracy of the data. [c] Recorded for a solution in PFBT. [d] $x \simeq 1.4; y \simeq 0.6$. [e] $x \simeq 1.4; y \simeq 0.54; z \simeq 0.06$. [f] $x \simeq 1.8; y \simeq 0.14; z \simeq 0.06$. [g] $x \simeq 1.4; y \simeq 0.54; z \simeq 0.06$. [h] $x = 0.38, 0.64, 0.98; y = 1.62, 1.36, 1.02$, respectively. [i] ^{13}C NMR data (acetone-d_6) for a compound where $x = 0.98$ and $y = 1.02$ indicated phosphorus–carbon coupling constants of 134 Hz for carbon-1, 11 Hz for carbon-2,6(ortho), and 9.5 Hz for carbon-3,5(meta). The carbon-4(para) coupling value was too small to measure. [j] ^{1}H NMR data for compounds where $x = 0.38, 0.64$, and 0.98 and $y = 1.62, 1.36$, and 1.02, respectively, consisted of two broad aromatic proton resonances with peak maxima at 7.75 and 7.25 ppm, together with a broad aliphatic resonance centered at 4.3 ppm.

from the THF into acetone, and once from THF into pentane. The GPC average molecular weight was 1 × 10^6. A ^{1}H NMR analysis suggested that the phenyl to trifluoroethoxy ratio was 66:34, a value that was compatible with the microanalysis data (62% phenyl groups). ^{31}P NMR analysis showed no peaks that could be attributed to $P(C_6H_5)(OCH_2CF_3)$ units, although these could have been obscured by the $P(C_6H_5)_2$ resonance. The T_g was +60 °C. Anal. Calcd for the formula shown: C, 49.88; H, 3.58; F, 20.07; N, 6.49; P, 14.35. Found: C, 50.20; H, 3.55; F, 19.60; N, 6.43; P, 14.30.

Synthesis of $[NP[C_6H_5]_{1.68}[OCH_2CF_3]_{0.32}]_n$ and $[NP(C_6H_5)_{1.8}(OCH_2CF_3)_{0.2}]_n$. Both polymers were prepared by modifications of the procedures described above, with the use of larger amounts of phenyllithium and different reaction times. Specifically, $(NPF_2)_n$ (2.9 g, 0.035 mol) in PFBT (200 mL) with THF (700 mL) was allowed to interact with a filtered phenyllithium solution prepared from bromobenzene (45.2 g, 0.28 mol) and lithium (4.3 g, 0.61 mol) in diethyl ether (200 mL). The addition of the phenyllithium took place during 5 min at 25 °C. Immediately after the addition was complete, a portion of the reaction mixture (300 mL) was removed under nitrogen, deactivated by the addition of trifluoroethanol (28 g, 0.28 mL), and treated with a solution prepared from sodium (10.0 g, 0.44 mol) and trifluoroethanol (50 g, 0.5 mol) in THF (200 mL). After 18 h at reflux, the product was isolated in the usual way and purified by precipitations from THF into water, acetone, and pentane. ^{31}P and ^{1}H NMR spectra indicated that the ratio of phenyl to trifluoroethoxy groups was 84:16. The GPC average molecular weight was near 250 000.

The remainder of the original reaction mixture was stirred with the phenyllithium for 14 h and treated in the same way with trifluoroethanol and sodium trifluoroethoxide for 18 h. After purification, it was found by ^{31}P and ^{1}H NMR analysis that the ratio of phenyl to trifluoroethoxy side groups was 90:10. The GPC average molecular weight was near 60 000.

Synthesis of $[NP(C_6H_5)_2]_n$. The procedure was essentially the same as those described previously, but with the following specific details. A filtered solution of phenyllithium, prepared from bromobenzene (34 g, 0.22 mol) and lithium (8.0 g, 1.14 mol) in diethyl ether (300 mL), was added during 5 min to a stirred solution of $(NPF_2)_n$ (3.90 g, 0.047 mol) in PFBT (200 mL) with THF (600 mL). The mixture was stirred at 25 °C for 20 h and deactivated by the addition of trifluoroethanol (22 g, 0.22 mol). No sodium trifluoroethoxide was added. Removal of most of the solvent and addition to aqueous dilute hydrochloric acid yielded a solid precipitate. After treatment with water and reprecipitations from THF into water, pentane, and acetone (17% yield),[21] ^{31}P NMR data of the product showed only one phosphorus environment. Chemical analysis indicated that no fluorine was present. The GPC average molecular weight was 5.8 × 10^4.

In another synthesis, the same polymer was prepared by the addition of commercial phenyllithium (100 mL, 0.186 mol) to a solution of $(NPF_2)_n$ (4.57 g, 0.055 mol) in PFBT (250 mL) in the absence of THF at 5 °C followed by a reaction at 25 °C for 18 h. The GPC average molecular weight was 5.0 × 10^4, and the T_g was +70 °C. Anal. Calcd for $C_{12}H_{10}NP$: C, 72.36; H, 5.85; N, 7.03; P, 15.59. Found: C, 71.27; H, 5.85; N, 6.31; P, 16.33.

$[NP(C_6H_5)_x(OCH_2CF_3)_y(F)_z]_n$. ^{31}P NMR Assignments and Hydrolytic Stability. A solution of commercial phenyllithium (43.1 mL, 0.072 mol) was added over 5 min to a solution of $(NPF_2)_n$ (3.0 g, 0.036 mol) in PFBT (200 mL) in the presence of THF (300 mL), and the mixture was then treated immediately with a solution prepared from sodium (3.31 g, 0.14 mol) and trifluoroethanol (17 g, 0.17 mol) in THF (200 mL). After 10 h of reaction at the reflux temperature, the polymer was isolated in the usual way (including the treatment with aqueous hydrochloric acid and water). The GPC average molecular weight was 1.1 × 10^6. This polymer as a thin film showed no changes in the ^{31}P NMR spectrum or the GPC average molecular weight after exposure to the atmosphere for 1 year, in spite of the presence of P–F bonds.

^{31}P NMR data obtained for this polymer indicated resonances at +15.9, −2.1, −8.1, and −25.0 ppm. ^{19}F decoupled ^{31}P NMR spectra of this same polymer indicated that the resonances at +15.9 and −25.0 ppm were actually portions of two doublet structures with their centers at +4.8 and −14.5, respectively. These resonance shifts following ^{19}F decoupling suggest the presence of P–F substituents with coupling values of 892 and 840 Hz, respectively. The resonance positions of the −2.1 and −8.1 ppm resonances remained unchanged on ^{19}F decoupling. Except for the two additional resonances at +15.9 and −25.0 ppm, the ^{19}F coupled spectrum of this compound was similar to that of the ^{31}P NMR spectrum of $[NP(C_6H_5)_{1.62}(OCH_2CF_3)_{0.38}]$, with the two doublet structures comprising 15% of the total phosphorus atoms.

The downfield doublet, centered at +4.8, was assigned to phosphorus atoms that possess both a phenyl and a fluorine substituent. This assignment was made by a comparison with the ^{31}P NMR spectra described earlier (see Table II). The upfield doublet was assigned to phosphorus atoms which possess both a fluorine and a trifluoroethoxy substituent. The alternative assignment of this resonance to a phosphorus linked to one hydroxy and one fluorine substituent is less appealing because all of the known examples of this unit gave spectra with a doublet centered at −6.6 ± 2 ppm.

The ^{31}P NMR results suggest that compounds of structure $[NP(C_6H_5)_x(OCH_2CF_3)_y(F)_z]_n$ (where $x \simeq 1.24, y \simeq 0.61, z \simeq 0.15$) undergo only a very slow hydrolysis. The hydrolytic stability is probably connected with the steric bulk of the phenyl substituents and the hydrophobicity of the phenyl and trifluoroethoxy groups.

Thermolysis Studies with $[NP(C_6H_5)_{1.24}(OCH_2CF_3)_{0.76}]_n$. A polymer with a ratio of phenyl to trifluoroethoxy groups of 62:38 was cast as a thin film from THF and was then heated for 24 h at 50 °C under vacuum to remove traces of solvent. A sample of poly[bis(trifluoroethoxy)phosphazene], $[NP(OCH_2CF_3)_2]_n$, was cast as a thin film from acetone and was dried in the same way. The GPC average molecular weights of these polymers were above 1 × 10^6.

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Differential scanning calorimetry analysis of these two polymers indicated decomposition temperatures of 385 and 305 °C, respectively.

In a second study, films of the mixed substituent polymer and the homopolymer were sealed in evacuated ampules and placed for 12 h in an oven maintained at 300 °C. After being cooled to 25 °C, the film prepared from the phenyl trifluoroethoxyphosphazene had darkened in color and was now only partially soluble in THF. The GPC average molecular weight of the soluble portion showed a broadening toward the low molecular weight region. However, a significant quantity of the material still had a molecular weight in excess of 1×10^6. By contrast, the film cast from poly[bis(trifluoroethoxy)phosphazene] had been converted to an insoluble solid and a soluble oil. The soluble species had a molecular weight of less than 1×10^4.

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References and Notes

(1) H. R. Allcock and R. L. Kugel, *J. Am. Chem. Soc.*, **87**, 4211 (1965).

(2) H. R. Allcock, R. L. Kugel, and K. J. Valan, *Inorg. Chem.*, **5**, 1709 (1966).

(3) H. R. Allcock and R. L. Kugel, *Inorg. Chem.*, **5**, 1716 (1966).

(4) H. R. Allcock, *Science*, **193**, 1214 (1976); *Angew. Chem., Int. Ed. Engl.*, **16**, 147 (1977).

(5) D. P. Tate, *J. Polym. Sci., Polym. Symp.*, **48**, 33 (1974).

(6) R. E. Singler, N. S. Schneider, and G. L. Hagnauer, *Polym. Eng. Sci.*, **15**, 321 (1975).

(7) J. P. O'Brien, W. T. Ferrar, and H. R. Allcock, *Macromolecules*, **12**, 108, (1979).

(8) H. R. Allcock and C. T.-W. Chu, *Macromolecules*, **12**, 551 (1979).

(9) H. R. Allcock, D. B. Patterson, and T. L. Evans, *Macromolecules*, **12**, 172 (1979).

(10) A brief communication on part of this work appeared earlier: H. R. Allcock, D. B. Patterson, and T. L. Evans, *J. Am. Chem. Soc.*, **99**, 6095 (1977).

(11) The molecular weights quoted are gel permeation chromatography average values relative to polystyrene standards in THF solution.

(12) T_g values were determined with the use of a modified Chemical Instruments Corp. torsional braid analyzer kindly provided by N.A.S.A., Langley Field.

(13) H. R. Allcock, "*Phosphorus-Nitrogen Compounds*", Academic Press, New York, 1972.

(14) H. R. Allcock, W. J. Cook, and D. P. Mack, *Inorg. Chem.*, **11**, 2584 (1972).

(15) H. R. Allcock, S. D. Wright, and K. M. Kosydar, *Macromolecules*, **11**, 357 (1978).

(16) H. R. Allcock, T. J. Fuller, and K. Matsumura, unpublished work, 1978.

(17) The side group ratios were determined by ^{31}P NMR analaysis.

(18) The ^{31}P chemical shift sign convention used in this paper is the one recently recommended by I.U.P.A.C.. Upfield shifts from H_3PO_4 are assigned negative values, and downfield shifts are given positive values. This convention is the opposite of the one used in papers from our laboratory published before 1978 and from most other laboratories in North America.

(19) R. A. Shaw and M. Biddlestone, *J. Chem. Soc.*, 1750 (1970).

(20) C. W. Allen and T. Moeller, *Inorg. Chem.*, **7**, 2178 (1965).

(21) These relatively low yields reflect mainly the losses incurred during reprecipitation purification of the polymer. They do *not* reflect the presence of unpolymerized trimer in the reaction mixture since this compound was removed by sublimation before the polymer was used for the substitution process. An examination of the products removed during the reprecipitation steps (before the 70% substituent stage) showed that these were high molecular weight species with the same composition as the polymer that was precipitated. This problem is a consequence of the large volumes of precipitant that must be employed and the anomalous precipitation behavior of these mixed substituent polymers.

Oligomerization Stereochemistry of Vinyl Monomers. 7. Diastereomeric Ion Pairs as Intermediates in the Stereoregular Anionic Oligomerization of 2-Vinylpyridines. A proposed Mechanism

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ABSTRACT: Oligomers of 2-vinylpyridine have been prepared by addition of 2-vinylpyridine to THF solutions of alkali salts of 2-ethylpyridine followed by termination with CH_3I. With Li and Na as counterions, these oligomers were highly (>95%) isotactic as determined with ^{1}H and ^{13}C NMR. With K and larger counterions, the formation of dimers is not stereoselective. Epimerization of these types of compounds yields statistically expected mixtures of stereoisomers. Thus stereoselection appears kinetically controlled. Dimerization of 4-vinylpyridine or addition of 4-vinylpyridine to lithio-2-ethylpyridine followed by methylation is not stereoselective. The results particularly with the Li and Na salts indicate that the stereochemistry of methylation and 2-vinylpyridine addition is identical. A mechanism is proposed taking the chirality of the ion pair itself into account. For the Li and Na salts of the living oligomers, the cation appears to be coordinated with the nitrogen lone pair of the penultimate 2-pyridine unit. In such a case, one of the two possible diastereomeric ion pairs is expected to be favored, and this is most likely the reason for the observed stereoselectivity. Electrophilic attack is apparently occurring in a "syn" fashion.

There has been an increased interest in recent years in the synthesis of oligomers of vinyl monomers such as styrene,[2] methyl acrylate,[3] vinyl chloride,[4] as well as dienes.[5] Such investigations have been mostly useful in the elucidation of polymer configuration and conformation. Recently the stereochemistry of vinyl oligomerization itself has been reported.[6-9] We now wish to give a more complete account of our investigations on the stereochemistry of anionic oligomerization of 2- and 4-vinylpyridines and to present a more detailed analysis of the results of this work.

In order to obtain a better understanding of the mechanism of stereoregular anionic polymerization of monomers such as alkyl methacrylates, acrylates, 2-vinylpyridines, and similar monomers, it seemed that a careful study of models such as **1** is indispensable. In anions of this type, only one asymmetric center is present, and a comparison of the stereochemistry of anions **1** and their higher molecular weight homologues should facilitate a resolution

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