Synthesis of polyphosphazenes from phosphoranimines and phosphine azides*

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A number of phosphoranimines were prepared via the Staudinger coupling of the suitably substituted phosphite with trimethylsilyl azide. These compounds were polymerized under various conditions using fluoride initiators and then characterized by ^{1}H and ^{31}P nuclear magnetic resonance, size exclusion chromatography *versus* polystyrene standards, and differential scanning calorimetry. The condensation by-products of the polymerization were analysed by gas chromatography–mass spectrometry. Mechanistic details of these polymerizations are also discussed. N-Blocked phosphoranimines were prepared and used as chain terminators to control the molecular weights of these polymers. Several random copolymers were produced by the simultaneous polymerization of two phosphoranimines, and the first reported block copolymers were synthesized by the homopolymerization of one monomer followed by the subsequent addition of a second. The synthesis of the first soluble aryl-substituted polyphosphazenes via the phosphine azide route is also discussed.

(Keywords: polyphosphazenes; Staudinger reaction; phosphoranimines)

INTRODUCTION

Polyphosphazenes have found applications as flame retardant materials with excellent vibration dampening, high temperature stability and solvent resistance[1]. They have also been used as advanced low temperature elastomers and have potential applications in the biomedical field. Polyphosphazenes are prepared commercially by the ring-opening polymerization of hexachlorocyclotriphosphazene[2] and the subsequent nucleophilic displacement of labile chlorine atoms by various alkoxy, aryloxy, alkyl, aryl, amino or thio groups. In this way, a wide variety of polymers with different properties have been prepared[2,3]. Poly(dichlorophosphazene) can also be prepared by the condensation of $Cl_2P(O)=N-PCl_3$ at high temperatures[4]. The resulting polymer, identical to that prepared by the ring-opening process, is hydrolytically unstable and must be modified by substitution of the chlorine atoms by alkoxy or aryloxy groups. Modification is usually performed with alkali metal alkoxides and aryloxides. Polymer stability is affected by the degree of substitution which may not be complete for very high molecular weight products. Substitution may also be accompanied by side reactions which affect thermal properties such as the mesophase transition and melting point of the resulting polymers.

Another approach to stable polyphosphazenes is based on the condensation of various phosphoranimines with labile *N*-silyl groups[5]. The thermal process requires temperatures around 200°C and a few days' reaction time to produce polymers with molecular weights, M_n, in the range[6] of 25 000–75 000. The polycondensation does not follow the classical step-growth mechanism because high polymer is formed at low conversion, as observed in a chain growth process. Chain growth processes must occur with some kind of active species which have reactivities much higher than the monomer. This observation turned our attention to the possibility of using catalysts or initiators in the polymerization of phosphoranimines. The challenge was to control molecular weights, end-group functionalities and to prepare various types of copolymers, including the first reported polyphosphazene block copolymers.

Another possible method for preparing polyphosphazenes with organic groups attached to the phosphorus atoms is based on the thermal condensation of phosphine azides. This method was first described 30 years ago and led to intractable poly(diphenylphosphazene)[7,8]. We were able to improve this method by using two different aryl groups at phosphorus to synthesize the first soluble poly(diarylphosphazene)s.

RESULTS AND DISCUSSION

Polymerization of P-*tris*(2,2,2-*trifluoroethoxy*)-N-*trimethylsilylphosphoranimine* (*1*)

Phosphoranimine (**1**) is prepared in >90% yield by the Staudinger reaction of trimethylsilyl azide with tris(2,2,2-trifluoroethyl)phosphite. Thermal polycondensation requires a few days at temperatures around 200°C to produce a polymer[9] with $M_n \approx 10\,000$.

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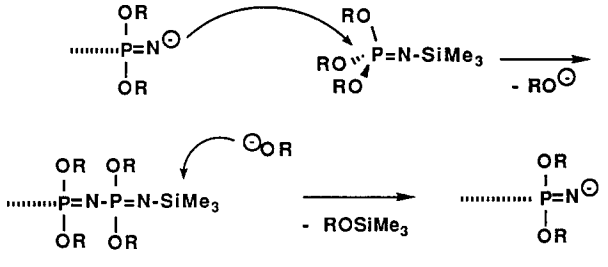
$$(RO)_3P + N_3SiMe_3 \xrightarrow[-N_2]{} Me_3SiN{=}P(OR)_3$$

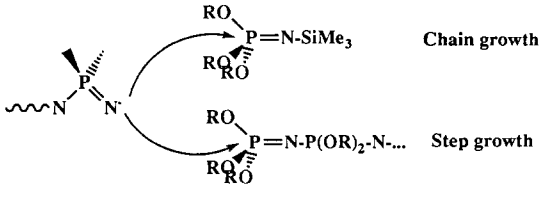
$$\xrightarrow[-ROSiMe_3]{\Delta} \cdots{-}N{=}P(OR)_2{-}\cdots$$

High polymer is formed at low conversions indicating a chain growth mechanism. The active species must be generated during the thermal process and must be of higher reactivity than analogous groups in the monomer. Si–N bonds are weak, and it is possible to exchange silyl groups between phosphoranimines and silyl halides[10]. Thus, compounds with a high affinity towards silicon were used as initiators and catalysts. Tetrabutylammonium fluoride was originally employed and rapid formation of volatile trimethylsilyl fluoride followed by fast polymerization at temperatures in the range of 100–120°C was observed[11,12]. It has been proposed that polymerization proceeds with the polymeric 'phosphazene anions' which attack monomer at the phosphorus atom followed by the displacement of the alkoxy leaving group. The anion then abstracts the silyl group from the chain end, regenerating the polymeric anion species. It is possible that this is a one-step rather than a two-step process.



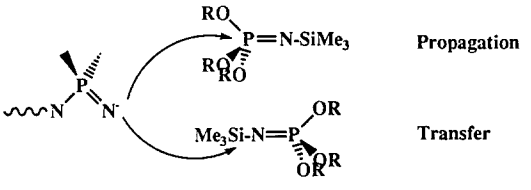
Attempts to directly observe phosphazene anions have not been successful, probably owing to rapid silyl exchange between the end group and phosphoranimine. The silyl group, also known as a 'bulky proton', is very labile. It is also possible that anionic polymerization may resemble a group transfer polymerization of acrylates initiated by silyl ketene acetals and catalysed by bifluoride anions. In the latter process, pentacoordinated silicon intermediates have been proposed. Kinetic studies of the polymerization of phosphoranimine (**1**) show first order in monomer and variable order in the catalyst (0.2 to 1), depending on the system. Low order may suggest that the catalyst is not involved in the rate-limiting step but interacts with a complex of polymeric *N*-silyl group and phosphoranimine[13]. Very strongly negative entropies of activation ($\Delta S\ddagger = -190\ J\ mol^{-1}\ K^{-1}$) support a transition state in which few components are involved.

Molecular weights in the polymerization of **1** rapidly reach a level of $M_n \approx 20000$ and then slowly increase[14]. This indicates that two mechanisms participate in the building of polymer chains: the first follows a chain growth process which is limited by transfer reactions, and the second follows a step growth process and involves condensation of the chains formed in the first step.



This dual mechanism suggests that polymeric *N*-silyl groups are much more reactive than those on the monomer. On the other hand, the growing chain ends (anions or activated *N*-silyl groups) react more rapidly with phosphorus atoms on the monomer than on the end of the polymer. This may be due to the intrinsically higher reactivity of the monomer phosphorus atom or to the higher concentration of monomer relative to end groups.

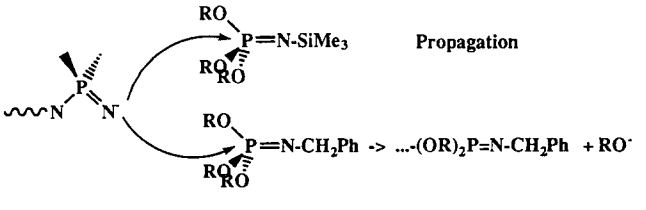
Molecular weights in the first chain growth stage are limited by transfer reactions to $M_n \approx 20000$. Moisture (water) acts as an efficient transfer reagent[14]. Molecular weights decrease to $M_n \approx 5000$ in the presence of $0.3\ mol\ l^{-1}$ of H_2O. At the same time, phosphates are formed as a product of hydrolysis. However, even when reactions were performed in the dry-box (<1 ppm of water) and with reagents dried over Na/K alloy, limited values of molecular weights from $M_n \approx 20000$ to 30000 were found. It is possible that growing anions may attack monomer not only at the phosphorus atom but also at the silyl moiety, resulting in transfer to monomer.



Molecular weights of polymers obtained in the first step strongly depend on the substituents on the silyl groups and on the structure of the alkoxy/aryloxy/alkyl groups.

Molecular weights can also be controlled by special additives which may provide functional end groups to the polyphosphazene chains[15]. One example is the use of *N*-alkyl phosphoranimines which have alkoxy leaving groups on the phosphorus and stable *N*-alkyl groups instead of a labile *N*-silyl group. *N*-Alkyl phosphoranimines were prepared by the Staudinger reaction of tris(trifluoroethyl)phosphite with four different alkyl azides: adamantyl, tert-butyl, benzyl and trityl. Polymerization slows down in the presence of *N*-alkyl phosphoranimines and a reduction in the molecular weights is detected. For example[15], addition of *N*-benzyl phosphoranimine to **1** in the ratio of 1:20 provides polymers with degree of polymerization, $DP \approx 20$ and in the ratio of 1:50 with $DP \approx 50$.

The decrease in the polymerization rate can be ascribed to the consumption of the more reactive *N*-silyl groups at the chain end. The alkoxy anions must attack less reactive silyl groups in the monomer to reinitiate polymerization.

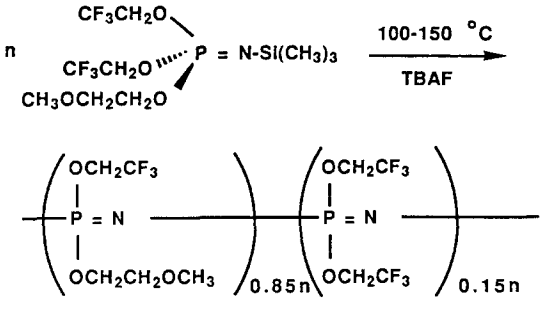


The benzyl groups have been observed by ^1H n.m.r. in the polymers precipitated from methanol. This method allows preparation of polyphosphazenes with reactive end groups which might be used as macromonomers for graft copolymers.

Polymerization of mixed phosphoranimines

A number of other polymerizable phosphoranimines can also be produced via the Staudinger reaction with trimethylsilyl azide[13,16]. Mixed phosphites bearing a wide variety of substituents (at least one of these must be a good leaving group) have been produced by nucleophilic displacement reactions on tris-(2,2,2-trifluoroethyl)phosphite with the appropriate alkoxide, the reaction of PCl_3 with alcohols in the presence of tertiary amines and/or the scrambling of two suitable phosphites in the presence of catalytic amounts of sodium. Using these methods, we have synthesized a wide variety of phosphites and phosphoranimines with various combinations of trifluoroethoxy, phenoxy, methoxy, 2-methoxyethoxy and 2-(2-methoxyethoxy)ethoxy groups.

$(CH_3OCH_2CH_2O)(CF_3CH_2O)_2P{=}N{-}Si(CH_3)_3$ was polymerized at temperatures ranging from 100 to 150°C using various concentrations of Bu_4NF (TBAF) or *N*-methylimidazole (NMI) initiators in bulk and in diglyme or toluene solutions.



^1H n.m.r. studies on the isolated polymers indicate that about 15% of the repeat units are bis-(2,2,2-trifluoroethoxyphosphazene) moieties. This indicates that trifluoroethoxy is approximately three times better as a leaving group than 2-methoxyethoxide. Both $CF_3CH_2OSiMe_3$ and $CH_3OCH_2CH_2OSiMe_3$ have been observed by gas chromatography–mass spectrometry (g.c.–m.s.). M_n was determined to be 12000–16000 for the bulk samples and 5000–8000 for the solution polymerizations by size exclusion chromatography (s.e.c.) *versus* polystyrene standards, and were independent of initiator concentration under the conditions studied. This might possibly indicate the presence of the aforementioned transfer or termination processes in this system. Lower molecular weights in comparison to $(CF_3CH_2O)_3P{=}N{-}Si(CH_3)_3$ at the end of the chain growth phase may result from inductive differences in the monomer, resulting in either a weaker Si–N bond or a lower phosphorus electrophilicity. This may lead to a higher rate of transfer to monomer. These polymers are optically clear, highly viscous oils with a glass transition temperature, T_g, of −62°C. Similarly, $(CH_3OCH_2CH_2O)_2(CF_3CH_2O)P{=}N{-}Si(CH_3)_3$ yields polymers with $M_n \approx 4000$ and $(CH_3OCH_2CH_2O)_3P{=}N{-}Si(CH_3)_3$ with $M_n \approx 1300$. This is consistent with the inductive trends mentioned above.

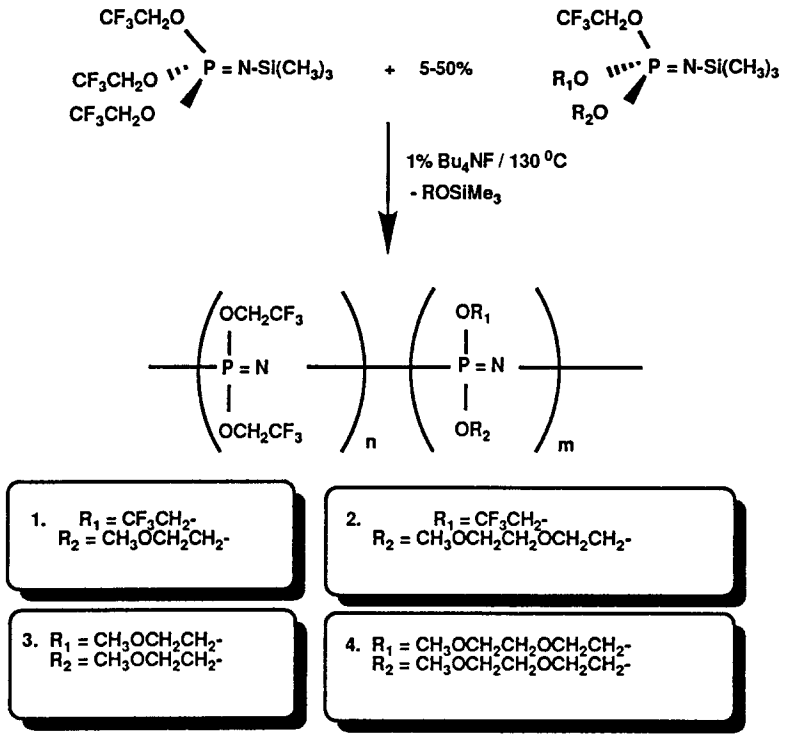
When the Staudinger reaction is performed between $(PhO)_3P$ and $(CH_3)_3SiN_3$, ^{31}P n.m.r. studies have shown that the phosphoranimine is produced and then decomposes *in situ* to form low molecular weight ($M_n \approx 3000$) poly(diphenoxyphosphazene), even at the lowest temperature at which the coupling reaction occurs (60°C). Up to 15% of the corresponding phosphoranimine has been observed spectroscopically, but has not been isolated. A trimethylsilyl peak has been observed by ^1H n.m.r. The molecular weight calculated from the integration of this peak is in reasonably good agreement (20%) with the s.e.c. results *versus* polystyrene standards. Long times and high temperatures have led to a gradual increase in the molecular weight of this polymer. For example, five days at 175°C leads to $M_n \approx 17000$. The presence of the trimethylsilyl end group indicates that a slow macromolecular condensation process may take place even after the complete consumption of phosphite and azide. Although it is possible to imagine propagation via phenoxy/azide ligand exchange, the hypothetical $(PhO)_2PN_3$ resulting from such a process has not been observed by n.m.r. and therefore it is possible that the phosphoranimine is unstable under these reaction conditions, owing to the lability of the phenoxy leaving group, and it condenses *in situ*. $(PhO)(CF_3CH_2O)_2P$ and $(PhO)_2(CF_3CH_2O)P$ yield similar results with $M_n \approx 4000$ and 16000, respectively. In these cases, both phenoxy and trifluoroethoxy are leaving groups. Although in the latter case, based on pK_a arguments one would not expect to see much incorporation of trifluoroethoxy groups into the polymer. N.m.r. studies indicate that approximately 25% of the repeat units bear this functional group. This suggests that phenoxy is seven times better as a leaving group than trifluoroethoxy.

Conversely, $(CH_3O)_2(PhO)P{=}N{-}Si(CH_3)_3$ and $(CH_3O)(PhO)_2P{=}N{-}Si(CH_3)_3$ are stable and are formed in the Staudinger reaction in addition to the *N*-methyl phosphoramidate isomers of those species. Both of these moieties will polymerize in the presence of 1% tetra-n-butylammonium fluoride at temperatures above 150°C, leading to relatively low molecular weight materials of $M_n = 2000$–5000. The isomer was inseparable from the phosphoranimine and, under the conditions studied, there was apparently some incorporation of the phosphoramidate $(PhO)(CH_3O)P(O){-}N(Si(CH_3)_3)(CH_3)$ into the backbone of the polymer. $(CH_3O)(CF_3CH_2O)_2{-}P{=}N{-}Si(CH_3)_3$ and $(CH_3O)_2(CF_3CH_2O)P{=}N{-}Si(CH_3)_3$ were not polymerizable in the presence of fluoride at 200°C. Methoxy groups, which are far less electron withdrawing than the other groups studied, may lead to increased electron density on the phosphorus and strengthen the N-Si bond. This might lead to decreased phosphorus electrophilicity and/or a much less labile bond. These inductive effects increase electron density on the nitrogen atom and may contribute to the formation of the phosphoramidate isomer side product in the Staudinger coupling reaction.

Random copolymers by simultaneous polymerization of various phosphoranimines

Polyphosphazene random copolymers were produced by simultaneously polymerizing two different phosphoranimines at 133°C using 1% TBAF[17,18] (*Scheme 1*). The purpose of these studies is to control the physical properties of the resultant materials by varying the monomer feed ratios. The monomers utilized in this investigation were chosen because of their similar reactivities.

For these random copolymer systems, *in situ* ^{31}P n.m.r. studies revealed simultaneous consumption of both monomers. Additionally, the precipitated polymers exhibited both types of repeating units in ^1H n.m.r., s.e.c. yielded monomodal distributions and there was a distinct



Scheme 1

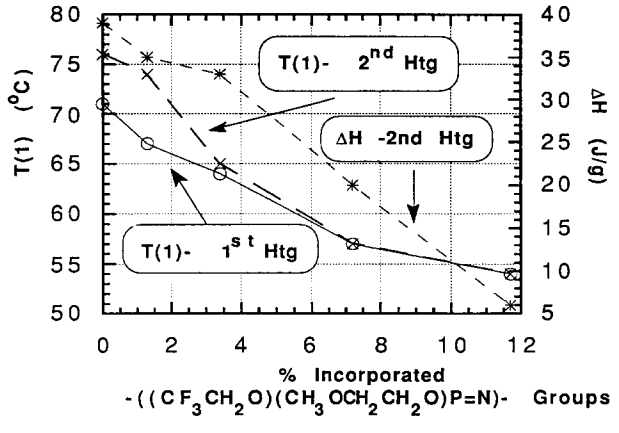


Figure 1 D.s.c. data on the random copolymers produced from $(CF_3CH_2O)_3P{=}NSiMe_3$ and $(CH_3OCH_2CH_2O)(CF_3CH_2O)_2P{=}NSiMe_3$

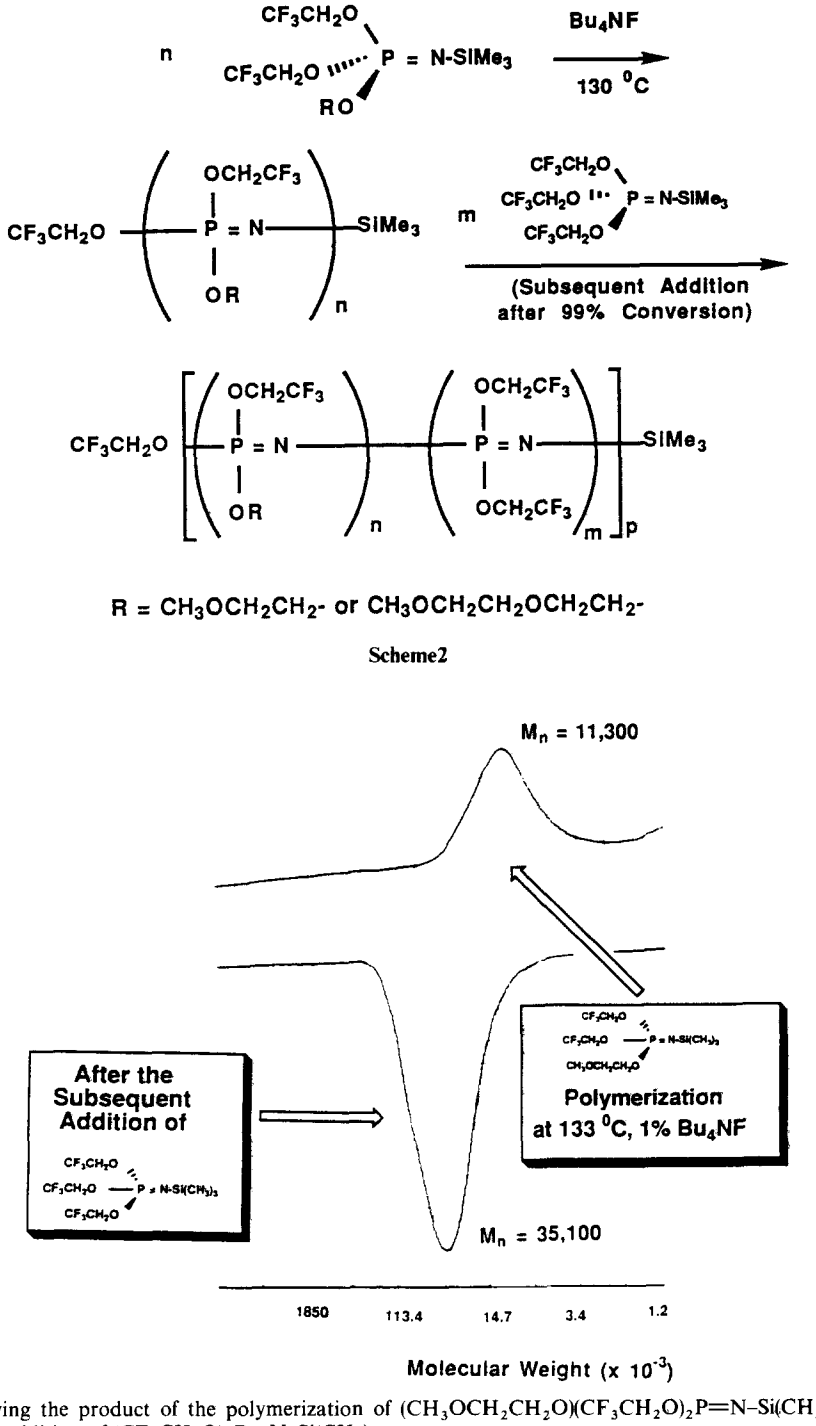
gradient in solubilities, thermal properties and physical properties which were proportional to the fraction of each repeat unit incorporated into the precipitated polymer. D.s.c. data on the polymers produced from the simultaneous 1% TBAF polymerization of various feed ratios of $(CF_3CH_2O)_3P{=}NSiMe_3$ and $(CH_3OCH_2CH_2O)(CF_3CH_2O)_2P{=}NSiMe_3$ at 133°C for 16 h are shown in *Figure 1*. A Seiko DSC 220 with two heating and cooling cycles at 10 and 20°C min^{-1} was utilized.

Molecular weights are dependent upon the monomers utilized. For example, the random copolymers produced from $(CF_3CH_2O)_3P{=}NSiMe_3$ and $(CH_3OCH_2CH_2O)(CF_3CH_2O)_2P{=}NSiMe_3$ range from $M_n = 30\,000$–$60\,000$, depending upon the feed ratios, while those synthesized from $(CF_3CH_2O)_3P{=}NSiMe_3$ and $(CH_3OCH_2CH_2OCH_2CH_2O)(CF_3CH_2O)_2P{=}NSiMe_3$ have $M_n = 9000$–$23\,000$. As previously discussed, this might be explained by increased rates of transfer to monomer. The materials become increasingly amorphous as more of the second monomer is incorporated into the chain. At low percentages, these copolymers are highly crystalline and, as the second monomer concentration is increased, they become increasingly tacky. The materials with 20% of the repeat units generated from the second monomer are gelatinous. This phenomenon is relatively independent of the molecular weight and can be attributed to decreasing regularity in the backbone which inhibits packing ability of the chains.

Polyphosphazene block copolymers

In situ ^1H n.m.r. studies have shown the presence of a singlet at 0.22 ppm which is present during the polymerization of the monomers used in this study. This peak is also present after removing the $ROSi(CH_3)_3$, condensates and residual monomer by vacuum distillation. This signal may be attributed to trimethylsilyl end groups on the polymer. The integration ratios of these signals agree reasonably well (usually to within about 10%) with s.e.c. studies (*versus* polystyrene standards). This assignment is also consistent with the dual chain/step growth mechanism discussed above. Since there are leaving groups on these polymers, it is possible to synthesize polyphosphazene block copolymers by making an addition of a second monomer after consumption of the first, see *Scheme 2*; this scheme has been simplified in that it does not show the presence of both possible repeating units after the first step.

Since the silyl group on the growing chain is easier to cleave than the one on the monomer, it is expected that a blocky structure with long runs of one type of repeating unit should be obtained. *Figure 2* exhibits s.e.c. curves obtained from the copolymers formed by the subsequent addition of 1.80 × molar excess $(CF_3CH_2O)_3P{=}N{-}Si(CH_3)_3$ using the products of the polymerization of $(CH_3OCH_2CH_2O)(CF_3CH_2O)_2P{=}N{-}Si(CH_3)_3$ with 1% TBAF initiator at 133°C at >99% conversion *versus* polystyrene standards using a refractive index detector. The first monomer was polymerized for 4 h and then the



Scheme2

Figure 2 S.e.c. traces showing the product of the polymerization of $(CH_3OCH_2CH_2O)(CF_3CH_2O)_2P{=}N{-}Si(CH_3)_3$ and the block copolymer formed after the subsequent addition of $(CF_3CH_2O)_3P{=}N{-}Si(CH_3)_3$

sample was heated at 133°C for additional 13 h after injection of the second monomer.

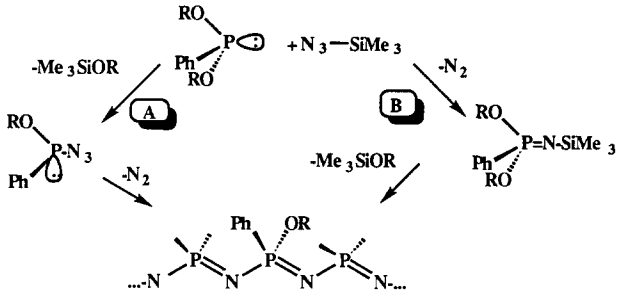
The refractive index of the polymer becomes increasingly negative *versus* tetrahydrofuran (THF) as the percentage of trifluoroethoxy side groups increases. There is no bimodality in the distribution as expected if both monomers were polymerizing independently.

The same types of molecular weight and thermal property trends which are noted in the case of the random copolymers are also seen in the blocky materials. However, there are distinct differences in the properties of the block and the random copolymers. For example, the random copolymer produced from 70% $(CF_3CH_2O)_3P{=}N{-}Si(CH_3)_3$ and 30% $(CH_3OCH_2CH_2OCH_2CH_2O)(CF_3CH_2O)_2P{=}N{-}Si(CH_3)_3$ has $M_n \approx 9200$. The analogous block copolymer has $M_n \approx 10\,400$. Both materials have 11% of the glycol ether pendent repeat units present, but the random copolymer is a soft, pliable material with little strength whereas the block copolymer is a much tougher, flexible material which forms films readily when cast from THF. These materials are the first reported examples of block copolymers formed between two polyphosphazenes.

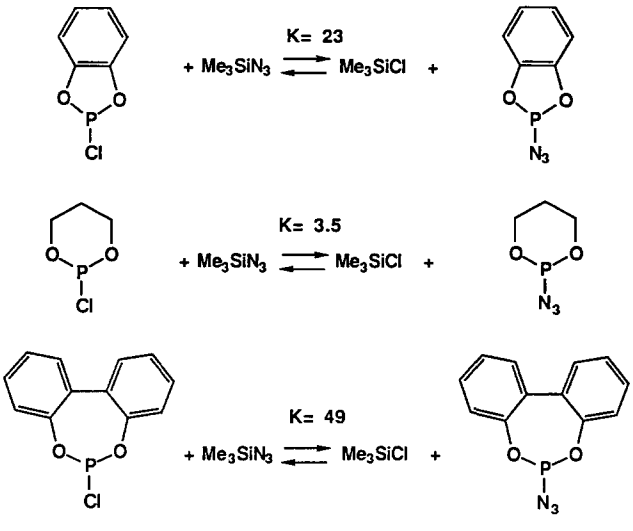
Soluble poly(diarylphosphazene)s

It has been previously demonstrated[19,20] that the reaction of trimethylsilyl azide with trivalent phosphorus compounds may proceed in two different ways: by the Staudinger reaction leading to phosphoranimines which

may be converted to polyphosphazene (route B), and by ligand exchange resulting in phosphine azides which may thermally decompose to provide the same polyphosphazene (route A).



The proportion of route A and B depends on ligands at phosphorus. Thus, three alkoxy substituents favour route B leading to phosphoranimine. When one alkoxy substituent is replaced by a phenyl group then approximately equal proportions of phosphine azide and phosphoranimine are formed. Two phenyl groups and one alkoxy substituent provide phosphine azides in high yield. Triphenylphosphine exclusively forms phosphoranimine because it has no leaving group to exchange ligands. The replacement of the alkoxy group by chloride apparently facilitates the exchange reaction. Phosphine azides are formed reversibly at ambient temperatures with equilibrium constants shown below as determined at 25°C in diglyme solution.



Exchange reactions are strongly catalysed by tetrabutylammonium salts and apparently obey overall first-order kinetics. The decomposition of phosphine azides shows internally first-order kinetics. However, the apparent rate constants of polymer formation increase with the initial monomer concentration. This may indicate that some kind of active sites are formed in a process which resembles chain growth polymerization.

It is even more interesting to apply the azide routes to the formation of poly(diarylphosphazene)s. These polymers cannot be formed by the ring opening of fully alkylated or arylated cyclic phosphazene moieties owing to the thermodynamic stability of such rings, or by nucleophilic displacement on the dichloro or difluoro substituted polymer owing to incomplete substitution and the resulting backbone degradation which takes place when using organomagnesium or organolithium compounds[20]. These materials are of interest because diarylphosphoranimines are thermally stable[21] at 250°C.

Poly(diphenylphosphazene) is intractable owing to high crystallinity. However, higher molecular weight polymers are formed in diphenyl ether as a solvent than in diglyme. No end groups could be found by n.m.r. and a higher mesophase transition temperature was observed (240°C compared to 210°C). X-ray crystallography revealed a columnar mesophase in the hexagonal packing[22]. No melting was found below the decomposition temperature of the polymer (420°C). When the polymer was annealed at >250°C and then rapidly quenched in liquid N_2, the mesophase was preserved. Polymer crystallized after heating to 70°C. This may be associated with sufficient chain segment mobility for crystalline packing and may be related to the apparent glass transition temperature.

In order to prepare soluble poly(diarylphosphazene)s, phenyl-*o*-tolyl chlorophosphine was synthesized using organocadmium reagents[23]. The exchange reaction with trimethylsilyl azide provides diarylphosphine azide in high yield[24]. Thermal polymerization results in the first high molecular weight soluble poly(phenyl-*o*-tolylphosphazene). N.m.r. spectroscopy shows no stereoregularity in the backbone. Surprisingly, a mesophase is not observed. There is apparently not enough long range order to pack chains into columns of sufficient length. S.e.c. shows a bimodal molecular weight distribution with a high polymer in the range of $M_n \approx 30\,000$ and low molecular weight material in the range of $M_n \approx 5000$. The reasons for the bimodal distribution are not yet known. More detailed mechanistic studies of the polymerization of diarylphosphine azides are currently being performed.

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