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Polyfluoroalkoxyphosphazenes—a Promising Class of Organoelemental Polymers

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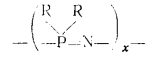
The results of the synthesis of polyfluoroalkoxyphosphazenes and also polyorganophosphazenes containing various non-fluorinated organic groups as substituents at the phosphorus atoms together with fluoroalkoxy-groups are surveyed. The characteristics of the formation of these polymers by the chemical modification of polydichlorophosphazene are examined. A systematic account is given of the literature data on the properties of polyfluoroalkoxyphosphazenes and their practical applications. The ways in which varieties of the macromolecules of these polymers arise and the influence of the nature and number of anomalous units on their properties are considered. Attention is drawn to a fundamentally important characteristic feature of polyfluoroalkoxyphosphazenes, namely the high sensitivity of their properties to anomalous units when the content of the latter is less than 1 mole %.
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I. INTRODUCTION

Among high-molecular-weight polyorganophosphazenes having the general structure



most attention has been attracted at the present time by polyfluoroalkoxyphosphazenes, where R = $OAlk_F$, which have properties of interest from the practical point of view. The chemical structure of their macromolecules has the following features. The main chain is made up of alternating phosphorus and nitrogen atoms and each second chain atom (nitrogen) has no substituents. Furthermore, the presence of fluoroalkoxy-groups as substituents at the phosphorus atom is responsible for a comparatively high fluorine content in these polymers (more than 40%). This ensures the following properties of polyfluoroalkoxyphosphazenes: flexibility and elasticity at low temperatures, effective resistance to oil and petrol, improved fire resistance, water- and dirt-repelling properties, etc.

During the last ten years, a comparatively large number of studies have been published on polyfluoroalkoxyphosphazenes, demonstrating the undoubted interest of investigators in these polymers. At the same time a series of the existing reviews[1-26] and monographs[27-34] deal with polyfluoroalkoxyphosphazenes either together with other polyphosphazenes, merely as one of the possible types of such polymers, or in terms of a specific aspect of their properties, so that the treatment is incomplete and insufficiently comprehensive.

This review surveys the main literature data on the synthesis, properties, and the most promising applications of polyfluoroalkoxyphosphazenes.

II. THE SYNTHESIS OF POLYFLUOROALKOXYPHOSPHAZENES

Polyfluoroalkoxyphosphazenes are comparatively new polymers. The first data concerning their successful synthesis were published almost simultaneously in the Soviet Union[35] and in the USA [36,37] as late as 1965–1966, when comparatively high degrees of nucleophilic substitution of the chlorine atoms in a high-molecular-weight fully soluble polydichlorophosphazene by fluoroalkoxy-groups were achieved and polyorganophosphazenes with an improved hydrolytic stability were obtained.

Later, attempts were made to synthesise polyfluoroalkoxyphosphazenes also by other procedures. Thus, Prons et al.[38] tried to carry out the thermal polymerisation of hexakis(3,3,3,2,2-pentafluoropropoxy)cyclotriphosphazene and Allcock et al.[39] attempted the synthesis of hexakis(trifluoroethoxy)cyclotriphosphazene in the melt at temperatures in the range 200–300 °C by analogy with the polymerisation of hexachlorotriphosphazene[36,37] However, it was found that fully substituted fluoroalkoxycyclotriphosphazene cannot be subjected to thermal polymerisation. On the other hand, it has been shown that rings with different degrees of substitution of the chlorine atoms nevertheless enter into both polymerisation and copolymerisation reactions[38] but with formation of a polymer having a lower molecular weight {the intrinsic viscosity $[\eta] = 0.5 - 0.6$ dl g^{-1} in organofluorine solvents} than in the polymerisation of hexachlorocyclotriphosphazene. The copolymerisation of partly substituted cyclic compounds with hexachlorocyclotriphosphazene[39] followed by the substitution of the residual chlorine by trifluoroethoxy-groups yielded polyorganophosphazenes with a much higher molecular weight (100000–400000). A polyphosphazene with a molecular weight of 110000 and $[\eta] = 0.71$ dl g^{-1} has been obtained in solution in tetrahydrofuran by Allcock et al.[39] and in the copolymerisation of hexakis(trifluoroethoxy)cyclotriphosphazene and hexachlorotriphosphazene.

Despite the fact that the above studies led to the discovery of the possibility, in principle, of the polymerisation of partly substituted cyclic compounds, this method of synthesis of polyfluoroalkoxyphosphazenes is of theoretical rather than practical interest owing to its more laborious nature and lower molecular weights of the resulting polymers than in the case where polydichlorophosphazene is used as the starting material.

Together with the attempt at the thermal polymerisation of fluoroalkoxycyclotriphosphazenes, studies have also been made of the possibility of their catalytic polymerisation[39,40].

However, the formation of a high-molecular-weight poly-[bis(trifluoroethoxy)phosphazene] from hexakis(trifluoroethoxy)cyclotriphosphazene in the presence of CsCl as the catalyst at 275 °C was not observed[39].

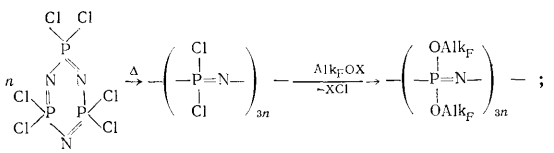
Kolkmann[40] studied the possibility of the polymerisation of hexakis(trifluoroethoxy)cyclotriphosphazene in the presence of acid catalysts such as BCl_3 (at 150 °C), BF_3, BBr_3, $TiCl_4$ (at 120–200 °C), CF_3SO_3H, $CF_3Se(O)OH$, and HCl, as well as basic catalysts such as K_2CO_3, Li_2O, MgO, CaO, BaO, CoO, and $N(C_2H_5)_3$, and also water (at 150 °C). The formation of a polyphosphazene with a molecular weight of 23000–33000, in which approximately half of the initial fluoroalkoxy-groups have been exchanged for chlorine, was observed only in the presence of an equimolar amount of BCl_3. Hexakis(hexafluoroisopropoxy)cyclotriphosphazene does not polymerise and does not react with BCl_3 at 225 °C according to Kolkmann's data[40].

Thus investigators have still not been able to find a realistic method for the polymerisation of fully substituted cyclic compounds—hexa(fluoroalkoxy)cyclotriphosphazenes.

Flindt and Rose[41] showed that poly[bis(trifluoroethoxy)-phosphazene] with a molecular weight of 10000 and soluble in acetone, isobutyl methyl ketone, tetrahydrofuran (THF), and ethyl acetate is formed from tris(1,1,1-trifluoroethoxy)-*N*-trimethylsilylphosphine imine at 200 °C.

Yet another procedure for the synthesis of linear oligomeric fluoroalkoxyphosphazenes from hexachlorocyclotriphosphazene and organosilanes having the formula $ROSiMe_3$, where R = $HCF_2CF_2CH_2$ or $HCF_2(CF_2)_3CH_2$, in the presence of a mixture of H_3PO_4 and pyridine and also polyphosphoric acid as catalysts, has been proposed[42–44].

Among the methods of synthesis of high-molecular-weight polyfluoroalkoxyphosphazenes known at the present time, the most promising is a two-stage procedure consisting of the thermal polymerisation of hexachlorocyclotriphosphazene with formation of polydichlorophosphazene and subsequent substitution of the chlorine atoms in the latter by fluoroalkoxy-groups in accordance with the mechanism



X = H, metal.

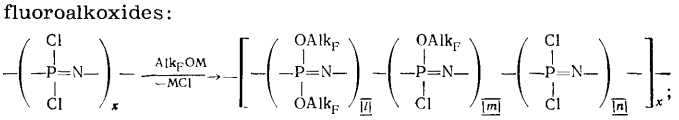
Before proceeding to a deeper analysis of the literature data on the synthesis of polyfluoroalkoxyphosphazenes by this method, it is useful to consider briefly the intermediate product—polydichlorophosphazene. In the early studies devoted to the polymerisation of hexachlorocyclotriphosphazene and considered in fair detail in a number of reviews[45–48], a cross-linked insoluble polydichlorophosphazene, virtually unsuitable for further reactions involving the substitution of chlorine by fluoro-alkoxy-groups, was mainly obtained. It was not until 1965–1966 that a fully soluble polydichlorophosphazene was obtained for the first time[35–37] and it was shown that the cross-linked polymer is not a direct polymerisation product but is formed from a non-cross-linked polymer[36]. It was also shown that a fully soluble polydichlorophosphazene can be obtained at a rigorously controlled temperature (250° ± 1 °C) by stopping the heating of the system when the polymerisation mixture loses its fluidity[28].

There is still no unanimous view among investigators concerning the chemical structure of the soluble polydichlorophosphazene. For example, Singler et al.[80] attribute a linear structure to the polymer, while Allcock[28] believes that the soluble polydichlorophosphazene obtained by the polymerisation of hexachlorocyclotriphosphazene by limiting the degree of conversion has almost certainly a branched structure. However, in both cases these are merely assumptions by the investigators, because polydichlorophosphazene was in no way characterised from this standpoint in their studies.

The influence of the heterounit structure of the initial polydichlorophosphazene, due to the branching of its macromolecules, on the synthesis and properties of polyorganophosphazenes was studied for the first time by Korshak et al.[49] It was shown experimentally in relation to the polymer-analogue substitution of chlorine atoms in the linear[50,51] and branched[52] polydichlorophosphazenes by trifluoroethoxy-groups that the presence of branches hinders the attainment of high degrees of substitution and has a significant influence on the solubility and thermomechanical properties of the polyorganophosphazene formed[49].

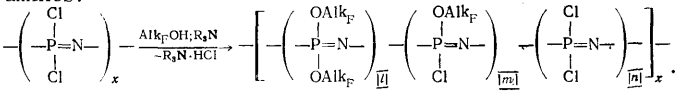
These data permit the conclusion that, in order to obtain reliable, satisfactorily reproducible results in the synthesis of polyfluoroalkoxyphosphazenes, it is necessary in the first place to characterise rigorously the initial polydichlorophosphazene not only in terms of the molecular weight but also in terms of the degree of branching.

The substitution of chlorine atoms in polydichlorophosphazene by fluoroalkoxy-groups in a series of organic solvents has been achieved in two ways—by condensation with fluoroalkoxides:



M=Na, Li, K; $l \gg m + n$

and with fluorinated alcohols in the presence of tertiary amines:



The characteristics of these reactions have still been little studied and most of the literature data on the synthesis of polyfluoroalkoxyphosphazenes reduce mainly to the description of methods for the preparation of specific specimens of such polymers.

Thus the synthesis of these polymers using sodium fluoroalkoxides as the nucleophiles has been described in a number of studies[36,37,53–67]. Some investigators used lithium[34,60,64,65] and potassium[65,70] fluoroalkoxides together with sodium fluoroalkoxides for the same purpose.

Unfortunately, analysis of the literature data does not permit a conclusion about the advantages of a particular alkali metal in the given polymer–analogue substitution reactions and systematic studies on these lines have not been carried out. At the same time, sodium fluoroalkoxides are used most often apparently mainly because sodium is most readily available and is easiest to handle.

According to Sharov and co-workers[60,65], the nature of the alkali metal can, however, influence the stage of aggregation of the fluoroalkoxyphosphazene polymers. In particular, under comparatively mild conditions of synthesis, when the polarity of the reaction medium (diethyl ether–toluene or dibutyl ether–toluene) is low and at reaction temperatures not exceeding 60 °C, amorphous polymers are formed when lithium fluoroalkoxide are used. The polymers obtained under the same conditions but using sodium and potassium fluoroalkoxides have a crystalline structure.

In the synthesis of polyfluoroalkoxyphosphazenes based on the macromolecular reaction of polydichlorophosphazene with sodium fluoroalkoxides, benzene[37,53–59,65,67], toluene[55–67],

chlorobenzene[55,57], and THF [57,61,62,67] were used as solvents for polydichlorophosphazene. Sodium fluoroalkoxides were obtained in solution in THF,[37,53-67] dioxane[55,67], diethyl ether[65], dibutyl ether[65], and diethylene glycol dimethyl ether[55]. In the course of the substitution of the chlorine atoms in polydichlorophosphazene by fluoroalkoxy-groups using sodium fluoroalkoxides, the polyorganophosphazenes formed are as a rule precipitated[37,53-60,65-67]. It has been suggested in the patent literature[61,62] that, in order to improve the rate of reaction and the degree of substitution of chlorine atoms by fluoroalkoxy-groups, the substitution reactions be carried out under homogeneous conditions in THF, in which certain polyfluoroalkoxyphosphazenes are readily soluble. The amount of unsubstituted chlorine in these compounds amounts to 0.06 wt.% under these conditions according to patent data[61,62]. Allcock and Cook[57] also obtained poly[bis(2,2,3,3-tetrafluoropropoxy)phosphazene] in solution in tetrahydrofuran but with a much higher content of unsubstituted chlorine (0.42 wt.%). At the same time, despite the precipitation of the polymer, a series of polyfluoroalkoxyphosphazenes whose chlorine content did not exceed 0.05 wt.% were successfully synthesised in mixtures of solvents such as benzene and THF.[56,59] Hence it is evident that the "homogeneity" or "heterogeneity" of the reaction mass is not always a decisive factor for the attainment of high degrees of the substitution reaction.

Among investigators there is no unanimous view concerning the optimum temperature for the successful polymer-analogue substitution of chlorine by fluoroalkoxy-groups. This reaction has been carried out most frequently by prolonged refluxing of the reaction mixtures[36,37,53,55,57,58,61,62] but in certain studies lower temperatures, for example 40 °C, have also been indicated[56,59].

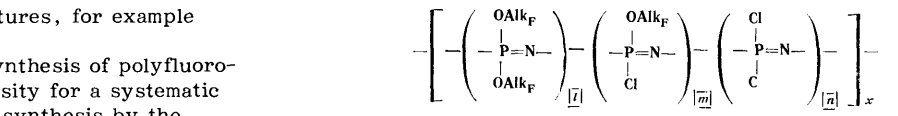
This state of the problem of the synthesis of polyfluoroalkoxyphosphazenes led to the necessity for a systematic study of the characteristics of their synthesis by the chemical modification of polydichlorophosphazene with fluoroalkoxides. In relation to the synthesis of poly[bis(trifluoroethoxy)phosphazene], we investigated the influence of various factors on the degree of the polymer-analogue substitution of chlorine atoms in polydichlorophosphazene by fluoroalkoxy-groups[67,69] and on the effectiveness of the hydrolytic side reactions during synthesis[66-68].

The investigation established that the main polymer-analogue reaction involving the substitution of chlorine by trifluoroethoxy-groups with the aid of sodium trifluoroethoxide is as a rule characterised by high degrees of conversion even in those cases where the polyfluoroalkoxyphosphazene does not dissolve in the reaction medium and precipitates after only a few minutes from the start of the reaction. On the other hand, the absolute amounts of the residual chlorine then depend on the temperature, the nature of the solvents, and the concentrations and ratios of the initial component. The highest degrees of the substitution reaction (up to 99.95 mole %) are obtained in solvent mixtures such as benzene–THF, toluene–THF or in solution in THF at room temperature for a reaction time of ~3 h, a concentration of the initial polydichlorophosphazene of ~20 g l^{-1}, and in the presence of a threefold excess of sodium trifluoroethoxide calculated per P–Cl group. The effectiveness of hydrolytic side reactions is determined by the nature of the solvent, the temperature, and the duration of the substitution reaction and depends significantly on the amount of water in the reaction system (even at the level of 10^{-2}–10^{-3} vol.%). Hydrolytic side reactions take place to the least extent at room temperature when the main reaction time is not more than 3 h and polyfluoroalkoxyphosphazene precipitates during the reaction, particularly from a toluene–THF mixture.

Since the unsubstituted P–Cl groups in polyphosphazenes are hydrolytically extremely unstable[28], the attainment of high degrees of the substitution reaction is naturally urgently required in the synthesis of polyfluoroalkoxyphosphazenes. Because of this, the degree of substitution is one of the most important characteristics of polymers of this kind. It can be inferred quantitatively from the content of unsubstituted chlorine.

Table 1 lists the contents of unsubstituted chlorine in polyfluoroalkoxyphosphazenes obtained by substituting the chlorine in polydichlorophosphazene by sodium, lithium, and potassium fluoroalkoxides under different substitution reaction conditions. It is seen that the authors of the relevant investigations did not always indicate the amount of unsubstituted chlorine in the polymer. Furthermore, in a number of instances, it was estimated extremely approximately and some workers[36,53,71] actually quote a zero chlorine content, which is unlikely, since polymer-analogue reactions do not as a rule take place to the extent of 100%. Overall, the polyfluoroalkoxyphosphazenes synthesised are usually characterised by a low content of residual chlorine by weight, which indicates a high degree of the given polymer-analogue substitution reaction.

Table 1. The polyfluoroalkoxyphosphazenes

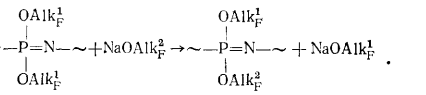


obtained by substituting the chlorine in polydichlorophosphazene by fluoroalkoxides.

Alk_F	Cl content, wt.%	Refs.
CF_3CH_2	Not detected	[36]
CF_3CH_2	0	[53,71]
CF_3CH_2	0.03	[56,59]
CF_3CH_2	0.057	[67]
CF_3CH_2	0.11	[57]
CF_3CH_2	<0.10	[60,65]
CF_3CH_2	<0.06	[62]
CF_3CH_2	Not quoted	[54,58,72–75]
$CF_3CF_2CH_2$	Not quoted	[2,12,28,35]
$CF_3(CF_2)_2CH_2$	0.05	[56,59]
$CF_3(CF_2)_2CH_2$	Not quoted	[28,35,55]
$CF_3(CF_2)_3CH_2$	<0.10	[60,65]
$CF_3(CF_2)_5CH_2$	Not quoted	[35]
$CF_3(CF_2)_6CH_2$	Not quoted	[54,72]
$HCF_2CF_2CH_2$	0.42	[57]
$HCF_2CF_2CH_2$	<0.10	[60,65]
$HCF_2CF_2CH_2$	Not quoted	[2,9,28]
$HCF_2(CF_2)_3CH_2$	0.03	[60,65]
$HCF_2(CF_2)_3CH_2$	<0.10	[60,65]
$HCF_2(CF_2)_5CH_2$	<0.10	[60,65]
$CF_3O(CF_2)_2CH_2$	Not quoted	[35]
$CF_3CHFCF_2CH_2$	0.10	[70]

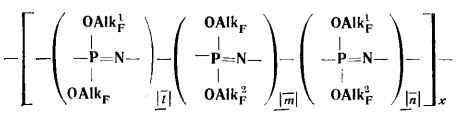
A large number of polyfluoroalkoxyphosphazenes containing various fluoroalkoxy-groups as substituents at the phosphorus atoms have now been obtained. These are, firstly, polyfluoroalkoxyphosphazenes in the synthesis of which mixtures of two different fluoroalkoxides were used for the reaction with polydichlorophosphazene[56,59,76-87] (Table 2). At the same time, the synthesis of polyfluoroalkoxyphosphazenes by the substituent exchange reaction

on heating in solution, in accordance with the following scheme, has been described[88,89]:



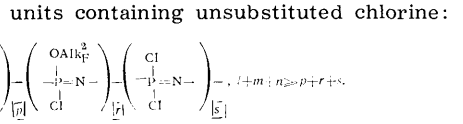
Using dihydric fluorinated alcohols, for example, 2,2,3,3,4,4-hexafluoropentanediol, the vulcanisation of polyfluoroalkoxyphosphazenes can be achieved by this reaction[89,90].

Table 2. Polyfluoroalkoxyphosphazenes with two different fluoroalkoxy-groups as substituents at the phosphorus atoms*.



Alk_F^1	Content, moles	Alk_F^2	Content, moles	Refs.
CF_3CH_2	1	$CF_3(CF_2)_2CH_2$	1	[56,59,76—81]
Ditto	1	ditto	3	[77]
»	2	»	1	[80]
»	3	»	1	[77]
CF_3CH_2	1	$CF_3(CF_2)_3CH_2$	1	[77]
CF_3CH_2	1	$HCF_2(CF_2)_2CH_2$	1	[82]
CF_3CH_2	1	$HCF_2(CF_2)_3CH_2$	1	[56,59,79,81, 83,84]
Ditto	0.64	ditto	0.36	[85,86]
»	0.65	»	0.35	[87]
CF_3CH_2	1	$CF_3CHFCF_2CH_2$	1	[70]
Ditto	1	ditto	3	[70]
»	3	»	1	[70]
$CF_3CF_2CH_2$	1	$CF_3(CF_2)_2CH_2$	1	[2,12]
$CF_3CF_2CH_2$	1	$CF_3(CF_2)_4CH_2$	1	[77]
$CF_3(CF_2)_2CH_2$	1	$CF_3(CF_2)_6CH_2$	1	[80]
$HCF_2CF_2CH_2$	1	$HCF_2(CF_2)_3CH_2$	1	[77]
$HCF_2CF_2CH_2$	1	$HCF_2(CF_2)_5CH_2$	1	[77,79,81]

*In reality the chemical structure of the copolymers is much more complex owing to the presence of a certain amount of anomalous units containing unsubstituted chlorine:



However, in most cases, the vulcanisable fluoroalkoxyphosphazene polymers contain a small amount of a third substituent at the phosphorus atoms with a reactive group which cross-links the polymer in subsequent chemical reactions, for example, double bonds, active HO and NH groups, silicon-containing groups, and other groups[91—98]. Secondly, polyphosphazenes containing comparable amounts of fluoroalkoxy- and non-fluorinated alkoxy or aryloxy-groups as a framework for the phosphorus atoms can be assigned to the same type.

Among polymers of this kind, a polyorganophosphazene with two different alkoxy-groups at the phosphorus atom, containing 1.6 moles of trifluoroethoxy-groups and 0.4 of a mole of ethoxy-groups[73,74], as well as polyphosphazenes with three different substituents, where the content of alkoxy-groups having less than 16 carbon atoms is up to 35 mole %,[99] have been described. Polyphosphazenes of the type indicated, with reactive hydroxy-groups in the alkoxy-substituents, which are capable of being hardened by reaction with di-isocyanates and tetracarboxylic acid dianhydrides, have been synthesised[100].

In the synthesis of polyphosphazenes with fluoroalkoxy- and aryloxy-groups, various investigators used sodium[101,102] or lithium[103—109] fluoroalkoxides and phenoxides. On the other hand, when polydichlorophosphazene was treated with 4-cyanophenol, Na_2CO_3 was used as the HCl acceptor, after which the partially substituted polyphosphazene was condensed with sodium trifluoroethoxide[110].

In a number of instances, where it was not possible to achieve high degrees of substitution of polydichlorophosphazene with the aid of various nucleophiles, further substitution was carried out very successfully with the aid of sodium trifluoroethoxide[111—119] and lithium 2,2,3,3-tetrafluoropropoxide[109,120,121]. Polymers containing ~50% of fluoroalkoxy-groups as substituents at the phosphorus atom were as a rule obtained under these conditions.

Allcock and co-workers[122—124] obtained coloured polyfluoroalkoxyphosphazenes by substituting some of the chlorine atoms in polydichlorophosphazene by chromophoric groups and the remaining chlorine atoms by trifluoroethoxy-groups. They used the sodium derivatives of 2-hydroxy-1-azonaphthalene, 4-phenylazoaniline, 2-amino-1-phenylnaphthalene, 1-phenylazo-4-*p*-hydroxyphenylazonaphthalene, etc. as the chromophoric reagents, the molar ratio of the usual and chromophoric substituents ranging from 1:1 to 15000:1.

Together with polydichlorophosphazene, Allcock and co-workers[125—127] also used polydifluorophosphazene as the starting material in the synthesis of polymers containing fluorinated and non-fluorinated groups at the phosphorus atom. In particular, the high reactivity of polydifluorophosphazene compared with polydichlorophosphazene made it possible to achieve a degree of substitution of 50—90% of fluorine atoms by alkyl and phenyl groups, while in polydichlorophosphazene phenyl-lithium substitutes only 10% of the chlorine[114]. The residual chlorine atoms were substituted in both cases by sodium trifluoroethoxide. However, studies with polydifluorophosphazene involve considerable experimental difficulties, because of its high sensitivity to hydrolytic side reactions.

As already mentioned above, several attempts to achieve the substitution of chlorine atoms in polydichlorophosphazene by fluoroalkoxy-groups by condensation with fluoroalcohols in the presence of tertiary amines have been described. Thus, as early as 1964, Lenton et al.[128] reported the synthesis of a cross-linked partly substituted polymer by treating dichlorophosphazene swollen in benzene with a mixture of trifluoroethanol and pyridine. According to patent data[53], a soluble polyfluoroalkoxyphosphazene containing ~2% of unsubstituted chlorine can be obtained from the insoluble polydichlorophosphazene by treating it with a mixture of trifluoroethanol and triethylamine.

It is noteworthy that despite the much smaller number of publications on the synthesis of polyfluoroalkoxyphosphazenes in the presence of tertiary amines, a series of important features of this process have already been discovered. In particular, a study has been made of the macromolecular reaction of polydichlorophosphazene with trifluoroethanol in the presence of triethylamine in tetrahydrofuran in the temperature range between −5° and 60 °C.[129,130] It was shown that, together with the substitution of chlorine atoms by trifluoroethoxy-groups, there is a side reaction in this instance between polydichlorophosphazene and triethylamine, leading to the formation of a heterounit polymer containing at best ~3% of unsubstituted chlorine.

Tate et al.[131] synthesised polyorganophosphazenes by substituting the chlorine in polydichlorophosphazene by trifluoroethanol and other non-fluorinated nucleophiles in the presence of triethylamine in THF at 80—120 °C. They

reported that fully substituted non-cross-linked polymers were obtained under these conditions. On the basis of these results, the authors concluded that in the early syntheses the side reactions accompanied by the cross-linking of the polyorganophosphazene were due to the presence of traces of moisture in the reaction medium and the incomplete substitution of chlorine atoms was caused by the short reaction time and mild reaction conditions.

This method of synthesis of polyorganophosphazenes was also used to obtain a large number of polyphosphazenes containing trifluoroethoxy- and various non-fluorinated groups at the phosphorus atom[132-147]. However, according to patent data, such polymers contain 2 wt.%[133] and more[138-140,146] of unsubstituted chlorine, which conflicts to a large extent with the report that the chlorine is fully substituted in the presence of triethylamine[131].

In the presence of triethylamine, other workers[148] obtained in addition phosphazene polymers containing substituents based on thienyl alcohols and trifluoroethoxy-groups at the phosphorus atoms.

Overall, the available literature data on the synthesis of polyfluoroalkoxyphosphazenes in the presence of tertiary amines show that the degree of this reaction is much lower than in the condensation of polydichlorophosphazene with fluoroalkoxides; on the other hand, it greatly exceeds 50% and the attainment of its limiting degree at the level of 90–95% cannot be explained either by a decrease of the reactivity of the second chlorine atom after the substitution of the first or by the increase of steric hindrance. We believe[130] that one can postulate that the effect is due to the properties of the macromolecules in solution, in particular the formation of associated species comprising partly substituted polyphosphazene macromolecules owing to the lower rate of substitution reactions in the presence of tertiary amines compared with alkoxides.

In order to elucidate the possibilities for the synthesis of graft copolymers on the basis of polyphosphazenes, polydichlorophosphazene was condensed with a high-molecular-weight poly(arylene sulphoxide), containing a reactive terminal hydroxy-group, in solution in THF in the presence of triethylamine with subsequent substitution of the chlorine atoms in the polyphosphazene fragments by fluoroalkoxy-groups with the aid of sodium fluoroalkoxides[149] or trifluoroethanol in the presence of triethylamine[150]. The graft copolymers thus obtained contain a comparatively large number of unsubstituted chlorine (2–3 wt.%) like the homofluoroalkoxyphosphazenes synthesised in the presence of tertiary amines.

The above survey of literature data on the synthesis of polyfluoroalkoxyphosphazenes shows that a comparatively large number of polyfluoroalkoxyphosphazenes and polyphosphazenes with various substituents, including fluoroalkoxy-groups, at the phosphorus atoms have already been synthesised. However, the majority of the data are presented in patents and the aim of the relevant studies was to obtain new polyphosphazene structures. The characteristics of the formation of these polymers have been studied mainly only for poly[bis(trifluoroethoxy)phosphazene]. This makes it difficult to survey the literature data in order to discover the general principles of the synthesis of polyfluoroalkoxyphosphazenes.

Nevertheless, detailed examination of specific experimental data obtained by various investigators permits the conclusion that the chlorine atoms in the fully soluble polydichlorophosphazene undergo most successful polymer-analogue substitution by fluoroalkoxides, in the first place sodium fluoroalkoxides. This method of synthesis actually ensures the formation of polyfluoroalkoxyphosphazenes having the highest molecular weights and with a comparatively high degree of substitution.

III. THE PROPERTIES AND APPLICATIONS OF POLYFLUOROALKOXYPHOSPHAZENES

Despite the fact that there are many obscure questions concerning the synthesis of polyfluoroalkoxyphosphazenes, requiring further study, a number of specific and extremely valuable, from the practical point of view, properties of these polymers have already been discovered. The available literature data on the properties of polyfluoroalkoxyphosphazenes mainly refer to polymers with identical or two different fluoroalkoxy-groups at the phosphorus atoms. The properties of polymers with fluorinated and non-fluorinated substituents have so far been very little studied. The literature data only for the properties of polyphosphazenes with fluoroalkoxy-groups will therefore be considered below.

According to the literature, polyfluoroalkoxyphosphazenes can have a partly crystalline or amorphous structure. Thus the polyfluoroalkoxyphosphazenes synthesised by the substitution of the chlorine atoms in polydichlorophosphazene with the aid of sodium fluoroalkoxides have as a rule a partly crystalline structure. This is indicated in particular by X-ray diffraction data for five fluoroalkoxy-substituted polyphosphazenes: $[NP(OCH_2CF_3)_2]_n$, $[NP(OCH_2C_2F_4H)_2]_n$, $[NP(OCH_2C_2F_5)_2]_n$, $[NP(OCH_2C_3F_7)_2]_n$, and $[NP(OCHC_2F_6)_2]_n$.[28,30] At the same time it has been stated in the literature that fully amorphous polymers are formed under comparatively mild conditions of synthesis when lithium fluoroalkoxides are used[65]. Amorphous poly[bis(trifluoroethoxy)phosphazene] has been obtained also in the polymer-analogue conversion of polydichlorophosphazene in the presence of triethylamine and LiCl.[49]

Table 3. The solubility of fluoroalkoxyphosphazene polymers.

No.	Polymer	Solvents	Refs.
1	$[NP(OCH_2CF_3)_2]_n$	Acetone, THF, ethyl methyl ketone, cyclohexanone, dimethylformamide	[8,36,37]
2	$[NP(OCH_2CF_2CF_3)_2]_n$	Ethyl trifluoroacetate	[2,28]
3	$\{NP[OCH_2(CF_2)_2CF_3]_2\}_n$	Freon TA*, Freon E-1	[28,59]
4	$\{NP[OCH_2(CF_2)_6CF_3]_2\}_n$	Solvent not found	[54]
5	$[NP(OCH_2CF_2CF_2H)_2]_n$	Acetone, tetrahydrofuran	[2,28]
6	$\{NP[OCH_2(CF_2)_3CF_2H]_2\}_n$	Acetone	[59]
7	$\{NP[OCH_2CF_3][OCH_2(CF_2)_2CF_3]\}_n$	Freon E-2***	[28,59,76]
8	$\{NP[OCH_2CF_3][OCH_2(CF_2)CF_2H]\}_n$	Acetone	[59,79]
9	$\{NP[OCH_2CF_3]_{0.64}[OCH_2(CF_2)_3\cdot CF_2H]_{0.36}\}_n$	Isobutyl methyl ketone, THF, ethyl methyl ketone, dimethylformamide, acetone, acetonitrile, dimethylacetamide, *N*-methylpyrrolidinone	[85]
10	$\{NP[OCH_2(CF_2)_2CF_3][OCH_2(CF_2)_6\cdot CF_3]\}_n$	Freon E-2	[80]
11	$\{NP[OCH_2CF_2CF_2H][OCH_2(CF_2)_5\cdot CF_2H]\}_n$	Acetone	[79]

*Freon TA = azotropic mixture of 1,2,2-trichloro-1,1,3-trifluoroethane and acetone.

**Freon E-1 = $F(CFCF_3CF_2O)CHFCF_3$.

***Freon E-2 = $F(CFCF_3CF_2O)_2CHFCF_3$.

The amorphous or partly crystalline structures of the polymers obtained using a mixture of sodium fluoroalkoxides depend on the chemical structure and proportions of the latter[77]. Depending on their chemical and geometrical structures, these fluoroalkoxyphosphazene polymers are soft plastics or elastomers[28,65,77,81].

Table 3 shows that certain fluoroalkoxyphosphazenes are easily soluble in readily available organic solvents such as acetone, THF, ethyl methyl ketone, etc. However, with increase of the number of CF_2 groups in the side substituents, the solubility of the polymers is significantly impaired. The replacement of the terminal CF_3 group by CF_2H in such substituents again ensures a high solubility of the polymers.

At the same time polyfluoroalkoxyphosphazenes are exceptionally resistant to liquid hydrocarbons[87]. They do not dissolve in hexane and benzene and are fairly resistant to the action of rocket fuel[151], which makes these polymers extremely promising for use as oil- and petrol-resistant rubbers.

The ready solubility of poly[bis(trifluoroethoxy)phosphazene] and also certain polymers with two different fluoroalkoxy-groups at the phosphorus atoms leads to the possibility of the study in greater depth of the hydrodynamic and rheological properties of the solutions and molecular weight characteristics of these polymers. A series of investigations devoted to these questions have already been published[31,78,80,85,152–155]. Table 4 presents the literature data for the molecular weight characteristics of polyfluoroalkoxy-phosphazenes. It is seen that all the test specimens are characterised by a very high molecular weight and a broad molecular weight distribution.

Table 4. Molecular weight characteristics of certain polyfluoroalkoxyphosphazenes.

No.	Polymer	$[\eta]$, dl g^{-1}	$10^{-6}\bar{M}_w$	$10^{-6}\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	Refs.
1	$[NP(OCH_2CF_3)_2]_n$	1.27*	1.5	—	—	[31]
2	$\{NP[OCH_2CF_3]_{0.65}[OCH_2(CF_2)_3CF_2H]_{0.35}\}_n$	1.9*	8.2	26.7	30.6	[85]
3	$\{NP[OCH_2CF_3][OCH_2(CF_2)_3CF_2H]\}_n$	2.1*	—	—	6.8	[153]
4	$\{NP[OCH_2CF_3][OCH_2(CF_2)_2CF_3]\}_n$	0.96**	3.1	11.7	26.5	[80]
5	$\{NP[OCH_2CF_3][OCH_2(CF_2)_2CF_3]\}_n$	1.06**	13.0	16.4	79.2	[80]
6	$\{NP[OCH_2CF_3][OCH_2(CF_2)_2CF_3]\}_n$	1.47**	10.00	15.8	63.2	[80]
7	$\{NP[OCH_2CF_3][OCH_2(CF_2)_2CF_3]\}_n$	1.26**	31.0	63.0	49.2	[80]
8	$\{NP[OCH_2CF_3]_{0.65}[OCH_2(CF_2)_2CF_3]_{0.35}\}_n$	0.90**	16.0	23.0	68.3	[80]
9	$\{NP[OCH_2(CF_2)_3CF_3]_2\}_n$	1.40**	10.0	64.0	15.5	[80]

*Solvent—tetrahydrofuran.
**Sovent—Freon E-2 (see footnote to Table 3).

According to Hagnauer and Schneider[80], the molecules of the polyfluoroalkoxyphosphazenes investigated are relatively linear and their broad molecular weight distribution must be attributed to the mechanism of the polymerisation of hexachlorocyclotriphosphazene and not to branching. However, this conclusion does not explain the appreciable discrepancies between the molecular weight distributions of specimens Nos.4–6 (Table 4) obtained from polydichlorophosphazene synthesised by the polymerisation of the same amount of the trimer (4 g) under identical conditions.

Carlson et al.[85] also failed to observe an appreciable branching of the macromolecules. They suggest that the broad molecular weight distribution indicates the presence in the polymer of a supermolecular structure of the type of associated species. Thus there is no unanimity among investigators concerning the causes of the broad molecular weight distribution in polyfluoroalkoxyphosphazenes.

In certain cases in the study of the concentration dependence of the intrinsic viscosities of solutions of polyfluoroalkoxyphosphazenes in Freon E-2 an anomalous character of such viscosity was observed, namely an increase of η_{int} with dilution[80]. Furthermore, many specimens had anomalously high Huggins constants (usually more than 1.0) in Freon E-2. The authors attribute these phenomena to the aggregation of the macromolecules owing to the presence in the polymer of groups such as P–OH, >NH, P–O–P, and P=O.

At the same time Aharoni[155] reported recently the discovery of a region of mesomorphous behaviour of solutions of poly[bis(trifluoroethoxy)phosphazene].

Estimates of the glass points of polyfluoroalkoxyphosphazenes yielded extremely interesting results. The data in Table 5 show that low glass points are characteristic of these polymers. This applies also to fluoroalkoxyphosphazene elastomers whose glass points are in the range between −64° and −77 °C.[31]

Table 5. The glass points of polyfluoroalkoxyphosphazenes.

No.	Polymer	T_g, °C	Method*	Refs.
1	$[NP(OCH_2CF_3)_2]_n$	−66	DTA	[36, 37]
	Ditto	−53	TA	[59]
	»	−73	TM	[65]
	»	−70	DTA	[72]
2	$[NP(OCH_2CF_2CF_3)_2]_n$	~−25	DTA	[2, 12, 28]
	Ditto	−76	TM	[65]
3	$\{NP[OCH_2(CF_2)_2CF_3]_2\}_n$	+14	DTA	[2, 12, 28]
	Ditto	−65	TA	[59]
	»	−79	TM	[65]
4	$\{NP[OCH_2(CF_2)_3CF_3]_2\}_n$	−80	TM	[65]
5	$\{NP[OCH_2(CF_2)_5CF_3]_2\}_n$	−63	TM	[65]
6	$\{NP[OCH_2(CF_2)_6CF_3]_2\}_n$	−40	DTA	[72]
7	$[NP(OCH_2CF_2CF_2H)_2]_n$	−75	TM	[65]
8	$\{NP[OCH_2(CF_2)_3CF_2H]_2\}_n$	−64	TA	[59]
	»	−89	TM	[65]
9	$\{NP[OCH_2(CF_2)_5CF_2H]_2\}_n$	−72	TM	[65]
10	$\{NP[OCH_2(CF_2)_2OCF_3]_2\}_n$	−99	TM	[65]
11	$[NP(OCH_2CF_2CHFCF_3)_2]_n$	−67	DTA	[70]

*Methods: DTA = differential thermoanalysis; TA = torsional analysis; TM = thermomechanical tests on A.I.Marei's apparatus[65].

Within the framework of the model of atom–atom potential functions, Allen and Allcock[156] studied the energy surface of polyorganophosphazenes and showed that the potential energy surfaces of polyalkoxyphosphazene molecules, including poly[bis(trifluoroethoxy)phosphazene], contain a large number of minima separated by low barriers. This explains the high flexibility of these polymers and their low glass points T_g. The results of the theoretical calculation are in satisfactory agreement with X-ray diffraction data available for poly[bis(trifluoroethoxy)phosphazene].

At the same time it is striking that the glass points determined by different investigators for the same phosphazene structures show large discrepancies in a number of instances (Table 5, polymer Nos.1, 2, 3, and 8). The causes of these discrepancies are so far obscure but one cannot rule out the possibility that they are associated to a large extent with the non-reproducibility of the results obtained in the synthesis of polyfluoroalkoxyphosphazenes, which has been frequently mentioned in the literature[8,30].

Another interesting feature was observed in the study of the physical transformations in polyorganophosphazenes by scanning calorimetry, the thermoanalytical method, nuclear magnetic resonance, and X-ray diffraction[30,32,59,65,72,157–162], namely the occurrence of two first-order transition temperatures. Table 6 presents the available data concerning this question as regards polyfluoroalkoxyphosphazenes. It is

seen that this aspect of poly[bis(trifluoroethoxy)phosphazene] has been mainly investigated among polyfluoroalkoxyphosphazenes. At the lower transition temperature $T(1)$ the crystalline phase is seen to melt with retention of a definite degree of order, i.e. at $T(1)$ the polymer passes to a mesomorphous state. The upper temperature, at which there is a transition to an isotropic liquid, is the true melting point T_m. In poly[bis(trifluoroethoxy)phosphazene], these two transitions are separated by an unusually wide temperature range amounting to 150 K.[30,32] According to data published recently[65], the width of this range can actually exceed 200 K for certain polyfluoroalkoxyphosphazenes.

Table 6. Thermal transitions in polyfluoroalkoxyphosphazenes.

Polymer	$T(1)$, °C	T_m, °C	Method*	Refs.
$[NP(OCH_2CF_3)_2]_n$	92	240	DSC	[30, 32, 157]
$[NP(OCH_2CF_3)_2]_n$	83	240	DTA	[72]
$[NP(OCH_2CF_3)_2]_n$	68	238	TA	[59]
$[NP(OCH_2CF_3)_2]_n$	83	242	DSC	[65]
$\{NP[OCH_2(CF_2)_2CF_3]_2\}_n$	131	241	DSC	[65]
$[NP(OCH_2CF_2CF_2H)_2]_n$	8	240	DSC	[65]
$\{NP[OCH_2(CF_2)_5CF_2H]_2\}_n$	1	240	DSC	[65]

*DSC = differential scanning calorimetry.

From the practical standpoint, the temperature $T(1)$ is the upper limit of the temperature range in which the polymeric materials can be used. Above $T(1)$, the polymer can be moulded as a thermoplastic, but this entails the displacement of a semirigid structure and not viscous flow.

A more detailed consideration of this phenomenon in polyfluoroalkoxyphosphazenes is not necessary in the present review, since several extremely detailed reviews have been devoted to this question[30,32].

In certain reviews published recently[29,30,32], in the discussion of the question of physical transitions in polyorganophosphazenes under the influence of heat, 360 °C is stated to be the temperature of the onset of the thermal degradation of poly[bis(trifluoroethoxy)phosphazene], determined by thermogravimetric analysis. In reality, the question of the temperature of the onset of the decrease of mass on heating of this polymer is more complex and not quite so unambiguous. This can be illustrated by the data obtained by Connelly and Gilhan[59] and also by Zeldin et al.[75] in a dynamic thermogravimetric analysis of poly[bis(trifluoroethoxy)phosphazene] in an atmosphere of nitrogen. The temperature of the onset of the decrease of mass obtained by the first set of investigators (at a heating rate of 2 K min^{-1}) is ~250 °C, while in the second study (at a heating rate of 5 K min^{-1}) it was close to 350 °C. Such a significant discrepancy between the results cannot naturally be explained solely by the difference between the rates of heating. This is most likely to be associated with definite differences between the chemical structures of the polymer specimens investigated in the two studies.

At the same time, the results of thermogravimetric analysis (TGA) reflect the decrease of mass and yield only preliminary information about the thermal stability of polyfluoroalkoxyphosphazenes. For a deeper investigation of the thermal stability of these polymers, a number of isothermal experiments have been performed with subsequent estimation of the molecular weight characteristics of the test polymers[57,71,82,86]. It was found that, in the temperature range 150–200 °C, polyfluoroalkoxyphosphazenes already undergo a comparatively rapid decrease of viscosity and molecular weight. The dissociation of the polyfluoroalkoxyphosphazene macromolecules in this temperature range takes place at random and is accompanied by a very slight depolymerisation[82].

Such behaviour of polyfluoroalkoxyphosphazenes at comparatively low temperatures is apparently associated with the presence of defective units in their molecules, in particular with the content of unsubstituted P–Cl bonds, branches, etc.

In order to increase the thermal stability of polyfluoroalkoxyphosphazene, zinc and magnesium di(8-hydroxyquinolates)[97,163], zinc and lead dimethyldithiocarbamates[164], and also the zinc derivative of 2-mercaptobenzothiazole[165] have been proposed as stabilisers. Their action involves the deactivation of the defective groups in the polyfluoroalkoxyphosphazene macromolecules by complex formation with units containing the P–Cl, P–OH, and P=O bonds[163].

The data obtained in the study of the photolysis of poly[bis(trifluoroethoxy)phosphazene][72,73] show that this polymer exhibits a high resistance to light. However, the residual unsubstituted P–Cl groups promote the degradation of the polymer, since they increase the amount of light absorbed by the specimen.

Fluoroalkoxyphosphazene polymers are extremely resistant to action of boiling water[55,151]. For example, there are data showing that certain vulcanisates retain ~85% of their initial strength characteristics after 900 h at 100 °C and in 100% relative humidity[151]. In the cold they do not change even after coming into contact with concentrated NaOH and KOH solutions for many months[28,55,151]. The data concerning the action of various acids on polyfluoroalkoxyphosphazenes are extremely contradictory. Thus Rose and Reynard[55] reported that these polymers do not react with concentrated H_2SO_4 at a low temperature. Allcock[28] noted their resistance to glacial acetic acid. However, in a later publication Vicic and Reynard[151] drew attention to the fact that strong inorganic acids and glacial acetic acid impair the mechanical parameters of these polymers. According to these investigators, even dilute acid solutions cause slight hydrolysis of polyfluoroalkoxyphosphazenes. It is noteworthy that all the considerations described above refer to polyfluoroalkoxyphosphazenes tested in the solid state.

Polyfluoroalkoxyphosphazenes do not burn in air. The oxygen index of the flammability of these polymers and materials based on them is 47–65,[83,166] reaching as much as 80 in certain cases[65].

According to Allcock's data[28], poly[bis(trifluoroethoxy)phosphazene] films have effective water repellent properties with a wetting angle of 100 °C and a critical surface tension of 19.7 dyn cm^{-1}. In terms of the latter characteristic, they approach Teflon (22 dyn cm^{-1}) and polydimethylsiloxane (18 dyn cm^{-1}).[28] Allcock[28] notes that poly[bistrifluoroethoxy)phosphazene] and poly[bis(pentafluoropropoxy)phosphazene] films are very flexible and can be readily oriented on extension, giving rise to material with a high tensile strength. At the same time, Singler et al.[8] characterised poly[bis(trifluoroethoxy)phosphazene] as an elastic but weak material. Materials having a tensile strength of 175 kg cm^{-1} with 200% elongation on rupture have been obtained on the basis of fluoroalkoxyphosphazene elastomers, but, overall, a tensile strength of ~100 kg cm^{-2} accompanied by 100–200% elongation is more characteristic of such vulcanisates[31].

As regards the possible applications of polyfloroalkoxyphosphazenes, one should note in the first place their likely usefulness as oil- and petrol-resistant elastomeric materials with an improved fire resistance over a wide range of working temperatures combined with an effective frost resistance. In particular, compositions based on vulcanised elastomers are being developed at the present time for sealing devices in oil seals, sleeves, washers, fuel hose, etc. in the working temperature range from −60 to +200 °C.[8, 31,83,151]. The application of polyfluoroalkoxyphosphazenes in the textile industry has been proposed. It involves the impregnation of textiles with these polymers in order to impart to them water- and dirt-repellent properties[167]. At the same time, there exist patent data according to which polyfluoroalkoxyphosphazenes can be used as binders in compositions for water-impermeable galvanic cells[168–171] and for electrodes in chemical cells[172].

Studies of the possible applications of poly[bis(trifluoroethoxy)phosphazene] in the solution of the problem of resistance to thrombosis and biocompatibility are of undoubted interest[33,34,172,173]. Preliminary selective tests *in vitro*[33] and also *in vivo*[34] enabled the authors to conclude that further studies of polyfluoroalkoxyphosphazenes from the standpoint of their possible use in medicine are desirable. At the same time it has been shown that the high resistance to thrombogenesis in contact with native blood and the contancy of the physicochemical and mechanical properties after prolonged contact with a medium close in composition to blood make these polymers extremely promising for vascular surgery[173].

Such a wide variety of properties, which are promising from the practical point of view, makes it possible to classify polyfluoroalkoxyphosphazenes as polymers with a wide range of purposes, which is apparently the reason for the increased interest in these polymers during the last 15 years.

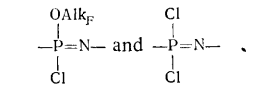
Overall, analysis of the literature data on the properties of polyfluoroalkoxyphosphazenes permits the following conclusions. On the one hand, polyfluoroalkoxyphosphazenes are undoubtedly interesting polymers with a wide variety of valuable properties. On the other hand, in the analysis of these properties attention is drawn in many instances to their very significant non-reproducibility. Therefore, some of the results achieved at the present time undoubtedly cannot as yet be regarded as optimal. The non-reproducibility of many properties of these polymers can be caused in the first place by the formation of anomalous units during synthesis which can influence their properties. This resembles the situation demonstrated by Korshak[174], for many heterounit organic polymers. Bearing this in mind, we thought it useful to consider this problem specially.

IV. THE INFLUENCE OF THE HETEROUNIT STRUCTURE OF POLYFLUOROALKOXYPHOSPHAZENES ON THEIR PROPERTIES

The heterounit structure of polyfluoroalkoxyphosphazenes can arise during their synthesis for several reasons and its chemical nature can be diverse. In the first place it is due to the branching inherited from the initial polydichlorophosphazene. This type of heterounit structure can, however, be virtually eliminated by employing as the starting material the linear polydichlorophosphazene obtained in accordance with the method developed recently for the polymerisation of hexachlorocyclotriphosphazene in a preheated polymerisation system[50,51].

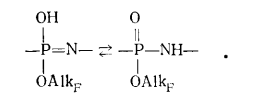
Another type of heterounit structure arises owing to the incomplete substitution of chlorine in the initial dichlorophosphazene, which, like, incidently, the majority of other macromolecular reactions[175], does not go to 100% completion. On this basis, one can assume that polyfluoroalkoxyphosphazene contain, together with units of the dominant type

also various amounts of intermediate and initial units:

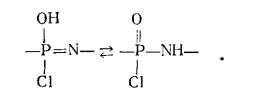


Since very high degrees of substitution (>99%) are nevertheless as a rule comparatively readily attained in the synthesis of polyfluoroalkoxyphosphazenes, it is natural to expect that their molecules contain mainly anomalous intermediate units with one unsubstituted chlorine atom at the phosphorus atom. However, in a study of the photolysis of poly[bis(trifluoroethoxy)phosphazene], Ferrar et al.[73] detected *gem*-1,1-$N_3P_3Cl_2(OCH_2CF_3)_4$ in the degradation products together with a cyclic trimer fully substituted by trifluoroethoxy-groups. This constitutes direct evidence for the presence in the polymer also of anomalous initial units with two unsubstituted chlorine atoms at the phosphorus atom. The amount of residual chlorine in polyfluoroalkoxyphosphazenes is a measure of the overall content of anomalous units with unsubstituted P–Cl groups.

We have shown[66–68] that yet another very significant type of heterounit structure can arise owing to the occurrence of hydrolytic side reactions in the synthesis of polyfluoroalkoxyphosphazenes. The anomalous units formed in this process can be present in the polymer in two tautomeric forms:



In addition, there is also a possibility of the combination of heterounit structures of different chemical types involving a single anomalous unit:

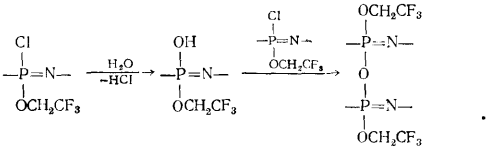


Such wide variety of anomalous units makes it significantly difficult to obtain stable readily reproducible results in the synthesis of polyfluoroalkoxyphosphazenes. This has led to the necessity for the investigation of the influence of the number and nature of the anomalous units on the set of properties of polyfluoroalkoxyphosphazenes. The study of hydrodynamic, conductimetric, and dielectric properties of dilute solutions of poly[bis(trifluoroethoxy)phosphazene] with different heterounit structures[176–178] by three independent methods led to the discovery of previously unknown polyelectrolyte properties of polyfluoroalkoxyphosphazenes in solution in organic solvents and showed that the presence of the specific amount of anomalous units with P–Cl and P–OH groups leads to the appearance of ionogenic groups in these polymers. An important feature of the polymers is the high sensitivity of their properties to small amounts of anomalous units (<1 mole %).

An electron microscope study of dilute solutions of poly[bis(trifluoroethoxy)phosphazene][179] made it possible to obtain more complete information about the character of the acquisition of polyelectrolyte properties by a polyfluoroalkoxyphosphazene, showing that, in dilute solutions in

polar and moderately polar solvents of the type of acetone and THF, poly[bis(trifluoroethoxy)phosphazene] exists in the form of individual macromolecules and that the formation of ionised groups in it is predominantly intramolecular.

The presence of anomalous units with residual P–Cl groups as well as very small amounts of P–OH and P(O)–NH groups, arising as a result of hydrolytic side reactions, reduces significantly the hydrolytic stability of poly[bis(trifluoroethoxy)phosphazene][66,67]. For example, the polymer containing ≥0.2 wt.% of unsubstituted chlorine is hydrolytically so unstable that it loses its solubility in organic solvents even at room temperature. The loss of solubility is associated in this instance with the formation of cross-links between the macromolecules of poly[bis(trifluoroethoxy)phosphazene] in accordance with the following scheme:



When the chlorine content is <0.2 wt.%, the polymer is hydrolytically more stable. However, when the chlorine content is in the range 0.06–0.20 wt.%, an appreciable decrease of [η] is nevertheless observed after boiling the polymer in aqueous acetone (at 56 °C), i.e. at a comparatively low temperature. Only in those cases where the amount of unsubstituted chlorine in poly[bis(trifluoroethoxy)phosphazene] does not exceed 0.06 wt.%, which corresponds (without taking into account other anomalous units) to a chlorine content of 0.21 mole %, is the polymer hydrolytically stable also on boiling in aqueous acetone.

All the factors described above are valid only when the polymer contains virtually no partly hydrolysed fragments. Their presence has the same unfavourable influence on the hydrolytic stability of polyfluoroalkoxyphosphazenes as the presence of unsubstituted P–Cl groups. Consequently, the hydrolytic stability of polyfluoroalkoxyphosphazenes at moderately high temperatures depends on the overall content of all the anomalous units with P–Cl, P–OH, and P(O)–OH groups. This conclusion has a direct bearing on the stability and reproducibility of the results, which had not been taken into account previously in the synthesis of polyfluoroalkoxyphosphazenes. To ensure the stability and high reproducibility of the results in the synthesis of such polymers, the overall content of the anomalous units should not exceed 0.2 mole %. Therefore, the valuable properties of polyfluoroalkoxyphosphazenes, characteristic of units of the dominant type, can be achieved only when a very far-reaching polymer-analogue substitution reaction is carried out under conditions ensuring a virtually total absence of hydrolytic side reactions and a minimal hetero-unit structure of these polymers.

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