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Open-chain poly(organophosphazenes). Synthesis and properties

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Abstract. Various methods for the synthesis of open-chain poly(organophosphazenes) are considered. The mechanism of polymerisation of hexachlorocyclotriphosphazene and the basic principles of formation of poly(organophosphazene) macromolecules by polymeranalogous reactions of poly(dichloro-phosphazene) with various nucleophilic reagents are analysed from a new viewpoint. The potential of this synthetic method for targeted design of poly(organophosphazenes) of various structures is shown. The possibility of synthesising poly(organo-phosphazenes) by polymerisation of cyclophosphazenes is also discussed. The problem of unit non-uniformity of poly(organophosphazenes) and its influence on the properties of these polymers are considered. The properties of poly(organo-phosphazenes) are considered in detail and it is shown that these polymers possess unusual valuable properties, which provide opportunities for their successful practical application. The bibliography includes 276 references.

I. Introduction

Open-chain poly(organophosphazenes) $[-PR_2=N-]_n$ constitute a relatively new class of organoelement polymers. They occupy a peculiar place among organoelement polymers. The inorganic nature of their backbone built of alternating phosphorus and nitrogen atoms and organic framing of the phosphorus atoms determine a number of specific properties in some of these polymers, namely, flexibility combined with elasticity at low temperatures; enhanced flame resistance and low smoke formation, resistance to hydrocarbon fuels and oils, low thrombogeneity, good biocompatibility, and others.

The first representatives of phosphazenes (halophosphazenes) were obtained back in the early XIX century; however, definite progress in the synthesis of poly(organophosphazenes) was achieved only in 1965 – 1966.

During the last two decades, studies dealing with poly(organophosphazenes) have been vigorously pursued. High-molecular-mass poly(organophosphazenes) with side groups of various structures have been synthesised. Considerable attention is being paid to the basic priciples of polymer formation and to comprehensive studies of the properties of poly(organophosph-azenes). The accumulated data certainly need to be generalised. Some aspects concerning the synthesis and properties of polyphosphazenes have been outlined in several reviews.[1 – 39]

In this review, we consider the synthesis of various poly(organophosphazenes) and the structure of their macromolecules. The properties of these polymers are discussed as functions of the molecular structure. The prospects for practical application of poly(organophosphazenes) are also presented.

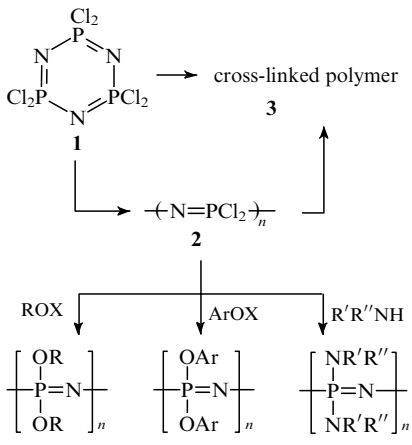
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II. Synthesis of polyphosphazenes

The search for new valuable synthetic materials has stimulated the intense development of the chemistry of polyphosphazenes during the last three decades. Considerable attention has been paid to halo-substituted polyphosphazenes, in particular poly(dichlorophosphazene) (PDCP), which is characterised by a broad high-elasticity region (from −30 to 300 °C), low glass transition temperature (−60 to −58°C), non-flammability, *etc.*[1, 32, 38, 40, 41] However, since PDCP contains chlorine, it suffers from a serious drawback, namely, instability to hydrolysis: during storage in air, it rapidly and irreversibly ages and loses its properties. However, it was found that the high reactivity of the chlorine atoms in PDCP offers wide opportunities for synthesising new polymeric materials based on it by polymeranalogous transformations. Analysis of the published data demonstrates that the two-stage synthetic scheme shown below (Scheme 1) is

Scheme 1



R = Alk, Alk_F; X = H, Na, K, Li; R′ = H, R″ = Alk, Ar; R′ = R″ = Alk.

currently the most realistic way for preparing high-molecular-mass open-chain poly(organophosphazenes).

In the first stage, high-molecular-mass soluble PDCP **2** is obtained by polymerisation of hexachlorocyclotriphosphazene (HCCTP) **1**. The second stage is a macromolecular reaction of the soluble PDCP with various nucleophilic reagents.

1. General features of the formation of PDCP

Polymerisation of cyclic halophosphazenes with ring opening is a very complicated process. Thermal polymerisation of HCCTP in the melt gives cross-linked PDCP **3** in a high yield (Scheme 1). However, this polymer is not suitable for the synthesis of poly(organophosphazenes), because of the low degrees of conversion of the P–Cl groups in reactions with nucleophilic reagents; hence, these reactions give poly(organophosphazenes) with low hydrolytic stability.

Allcock and Kugel [42] have shown that the cross-linked polymer **3** is not an immediate product of the polymerisation of HCCTP **1** but it is rather produced from non-cross-linked PDCP **2**. A completely soluble PDCP [42,43] was obtained by restricting the degree of conversion of HCCTP (heating was terminated at the instant when a decrease in the fluidity of the polymerisation mixture was observed) under strictly controlled temperature conditions. The data listed in Table 1 indicate that raising the temperature accelerates the formation of an insoluble cross-linked polymer.[44]

Table 1. Influence of the temperature and duration of the polymerisation of HCCTP on the yield of soluble PDCP.

Duration/ h	Yield of soluble PDCP (%)	Duration/ h	Yield of soluble PDCP (%)
250 °C		300 °C	
3	12.0	0.08	0
4	13.8	0.25	13.7
5	17.0	0.41	19.3
6	23.4	0.50	27.3
21	30.8	0.66	37.9
48	70.1	1.00	50.3
96	gel	1.17	gel

According to the data of Table 1, polymerisation at 250 °C affords the cross-linked polymer over a period of 96 h, while at 300 °C this product is formed in 1.17 h.

Numerous attempts have been made to select catalysts for the polymerisation of HCCTP that would enable conducting it under milder conditions.[1,8,9,32,37] However, these attempts have not met with success so far. Therefore, thermal polymerisation of chlorocyclophosphazenes still remains the main method for the preparation of PDCP.

Meanwhile, this method for the synthesis of PDCP suffers from one more serious drawback: the results of polymerisation are not reproducible. The yields of soluble PDCP obtained by various researchers under seemingly identical conditions vary over wide limits (from 5% to 70%).[2,44–47]

Various opinions about the structure of soluble PDCP have been expressed.[1–4,32] Apparently, the polymerisation product (before gelation) is a polymer with a fairly heterogeneous structure, characterised by variable and hardly controllable unit nonuniformity.[2] Most likely, this accounts for the irreproducibility of the yield and the properties of both PDCP itself and poly(organophosphazenes) based on it.[12,45,48–51] Therefore, it is important to study the mechanism of polymerisation of HCCTP and side reactions resulting in the formation of branched and cross-linked polymers, in order to find the ways of controlling these processes.

The possible mechanisms of polymerisation of HCCTP have been discussed in earlier reviews;[2,12] however, there is still no agreement on this point.[1,2,8,12,32,46,52–54] Here we discuss the mechanism that appears most probable from our viewpoint. A special study aimed at elucidating the influence of the residual water on the polymerisation of HCCTP in a closed system has revealed interesting and fundamental features of this process.[2,45] It was found that the intrinsic viscosity of the PDCP formed depends on the experimental conditions and on the amounts of water and the evolved hydrogen chloride in the system; this implies that polymerisation might be catalysed by hydrogen chloride.[2,45,50]

It has been found [55] that hydrolysis of the P–Cl bonds in HCCTP at 250 °C occurs only when the reaction mixture contains admixed higher chlorocyclophosphazenes, for example, octachlorocyclotetraphosphazene (OCCTP). Controversial opinions have been expressed in the literature about the role of this compound in the polymerisation of HCCTP. In fact, both accelerating [56] and inhibiting [57] effects as well as the absence of any activity during the polymerisation [58] have been reported for this tetramer.

Detailed study of this point has shown that the so-called 'non-catalytic' polymerisation of HCCTP [1] is catalysed, in reality, by the hydrogen chloride resulting from hydrolysis of the P–Cl bonds in OCCTP by the residual water.[55] There exist the optimum quantities of the tetramer and the residual water needed for successful polymerisation of the trimer. None of the reaction mechanisms proposed previously for the polymerisation of HCCTP did imply active participation of hydrogen chloride.[2]

It was found that highly pure HCCTP (containing $\sim 10^{-3}$ mol.% of OCCTP) neither undergoes hydrolysis nor polymerises at a noticeable rate under the conditions of formation of virtually linear poly(dichlorophosphazene) (250 °C, 50 h).[45,49] The optimum quantity of OCCTP is ~0.1 mol.% – 0.2 mol.% (Table 2), which corresponds to the amount of residual water in the polymerisation vessels. Larger amounts of the tetramer markedly retard the polymerisation of HCCTP.

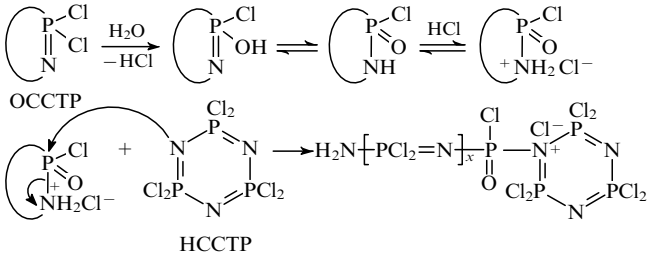
The known fact that the tetramer is more readily hydrolysed than the trimer **1** was rationalised based on electronic effects.[55] Study of the electronic structure by the extended Hückel method demonstrated that the P–Cl bond in OCCTP is weaker than that in HCCTP (the Mulliken populations are 0.687 and 0.724, respectively).

Table 2. Results of polymerisation of HCCTP in the presence of various amounts of OCCTP (250 °C, 50 h).

Amount of OCCTP mixed with HCCTP (mol.%)		Yield of PDCP (%)	Intrinsic viscosity of PDCP in toluene (25 °C)/ dl g^{-1}
total	specially admixed		
0.003	0	< 1	–
0.004	0	< 1	–
0.048	0	42	4.10
0.078	0.075	45	5.04
0.083	0.080	74	4.25
0.103	0.100	63	4.40
0.120	0	63	5.10
0.290	0	12	0.71
0.383	0.380	< 1	–
0.563	0.560	< 1	–

The above results provided grounds for the conclusion that OCCTP plays a dual role in the polymerisation of HCCTP: it acts as the source of the catalyst (hydrogen chloride) needed for the chain growth to start and as an inhibitor of the polymer growth. Thus, the process of HCCTP polymerisation could be controlled by varying the ratio of the residual water and OCCTP in the system.[55] The mechanism of polymerisation of HCCTP in the

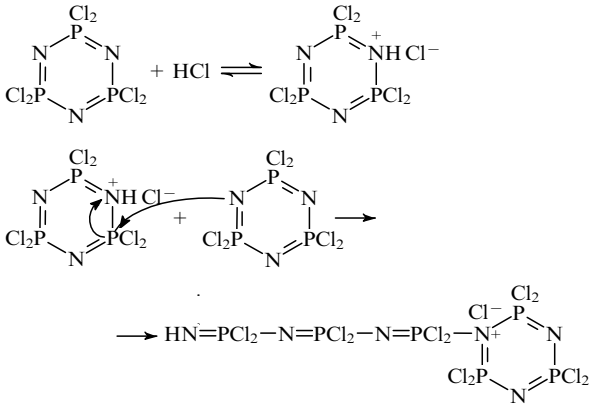
Scheme 2



presence of OCCTP, water, and hydrogen chloride[2, 12, 50] is presented in Scheme 2.

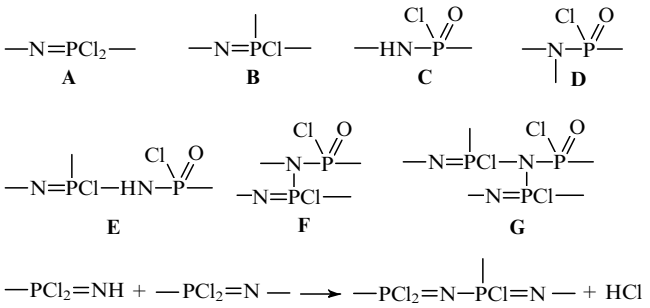
The first step of the reaction is hydrolysis of the P–Cl bonds in OCCTP by the residual water, which gives gaseous hydrogen chloride and hydroxyphosphazene, the latter being converted into the tautomeric oxophosphazane form. The subsequent protonation of the oxophosphazane ring with hydrogen chloride and the nucleophilic attack by the nitrogen atom of the phosphazene ring of HCCTP results in opening of the oxophosphazane ring and onset of the growth of a polymeric chain containing a terminal amino group. The chain growth occurs through subsequent addition of HCCTP molecules to the active site. When hydrolysis of the P–Cl bonds does not occur but HCl is present,[50] the phosphazene ring is also protonated; this yields molecules with terminal imino groups (Scheme 3).

Scheme 3



This mechanism of chain initiation and growth[45] is formally consistent with the view about the ionic character of the polymerisation of HCCTP but implies a completely different chemistry of this process. The possibility of polymerisation according to two pathways is fundamentally important, because it opens up way of controlling this process.[2, 12, 50] In fact, if the reaction starts with hydrolysis of the P–Cl bonds of the ring, this affords polymeric chains with terminal amino groups. These terminal groups can react with the P–Cl bonds of adjacent macromolecules; this accounts for side reactions. Due to these processes and also to the participation of oxophosphazane rings in the polymer chain growth, anomalous units of types **B**–**G** arise in the polymer, together with the predominant units of type **A**. Eventually, this leads to the formation of polydichlorophosphazene with a fairly high unit non-uniformity, to poor reproducibility of the experimental results, and to relatively low yields of the soluble polymer.

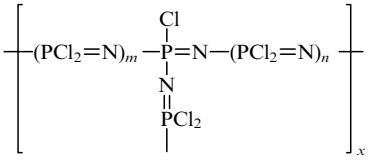
It is promising to carry out the polymerisation process under conditions permitting no hydrolysis; in this case, the reaction starts with protonation of the phosphazene ring with hydrogen chloride. This permits the preparation of PDCP with more inert terminal imino groups and, hence, with a more perfect defectless final chemical structure.



Elucidation of the mechanism of polymerisation of HCCTP made it possible to find a practical method for controlling the synthesis of PDCP; this method ensures good reproducibility of the results and the formation of a practically linear PDCP with molecular masses of about $(5-10)\times10^6$ and with a much narrower molecular-mass distribution ($M_w/M_n < 1.4$) compared to that of the polyphosphazenes described previously ($M_w/M_n \approx 7-79$[3, 33, 59–63]), its yield being more than 80%.[2, 12, 50]

The problem was solved by preliminary removal of water from the reaction system; for this purpose, the residual water was made to react with the P–Cl groups of chlorocyclophosphazene and then the resulting phosphazene derivatives containing hydrolysed fragments, which are the main source of side reactions, were separated from the reaction mixture. Polymerisation was carried out at 250 °C in an jointless Pyrex apparatus.[49] In this case, hydrogen chloride needed to initiate the polymer chain growth is retained in the reaction system.

The study of the polymerisation process has shown that the intrinsic viscosity of PDCP decreases, whereas the Huggins constant simultaneously increases following an increase in the polymerisation time. This apparently indicates that at larger degrees of conversion, branched PDCP molecules are formed.[50]



The content of branched molecules and the unit non-uniformity of the polymer depend on the experimental conditions [the extent to which the reaction tubes are filled with the monomer, quantity of the catalyst (hydrogen chloride), temperature, and reaction time].

The influence of the duration of the process in a preheated polymerisation system on the yield and intrinsic viscosity of PDCP and its fluoroalkoxy-derivatives has been studied.[63] A nearly quantitative degree of conversion of the trimer (97%) is attained when the polymerisation is carried out for 130 h (250 °C), the resulting PDCP being completely soluble in benzene and toluene. The high degrees of polymerisation [$(4-5)\times10^5$] and also the fact that the molecular-mass distribution curves of various PDCP samples at low degrees of conversion of the trimer virtually coincide, together with the narrow molecular-mass distribution of the polymer, imply that the chain growth reaction occurs much faster than competing side processes. The results obtained led the researchers[63] to the conclusion about a cationic mechanism of HCCTP polymerisation in the melt. The same mechanism was proposed for the polymerisation of the trimer carried out in solution in 1,2,3-trichlorobenzene in the presence of sulfamic acid, ammonium sulfamate, toluenesulfonic acid, and other catalysts.[64]

The polymerisation of HCCTP in the melt at 250 °C has been studied by electron microscopy.[65] In the early stages of the reaction, large spherical particles were detected, indicating a high

rate of chain growth. It was noted that poly(dichlorophosphazene) specimens prepared by the conventional procedure (method A) differ markedly from those obtained with preliminary removal of the residual water and the phosphazene products of hydrolysis from the reaction medium (method B).[49,50] The formation of an organised supermolecular structure in the polymer synthesised by method A is apparently hampered by the presence of cross-links between its macromolecules. On the contrary, in the case of the material prepared by method B, supermolecular associates of the lamellar type can be clearly seen in some parts of the electron photomicrography. Thus, the structure of PDCP in the aggregated state obtained at high degrees of polymerisation depends on the synthetic procedure used.

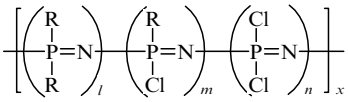
In general, it should be noted that despite the certain progress achieved in the synthesis of PDCP suitable for subsequent polymeranalogous substitution reactions, numerous important problems still need to be solved. The search for efficient catalysts for the thermal polymerisation of HCCTP, which would permit decreasing the reaction temperature and duration and increasing the yield of soluble PDCP, appears a promising and important aspect of investigations.

2. Synthesis of poly(organophosphazenes) based on poly(dichlorophosphazene)

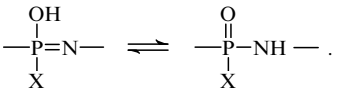
The commonest and most available method for the synthesis of poly(organophosphazenes) is the polymeranalogous substitution of chlorine in PDCP. It should be noted that the regularities of these reactions have not yet been adequately studied, and the majority of published data on the synthesis of poly(organophosphazenes) reduces mostly to the description of the procedures used to prepare one or another particular polymer.

An important characteristics of poly(organophosphazenes) is the possible unit non-uniformity.[2,3,12,14] The properties of these polymers are known to depend on the presence of a small number of anomalous units in their chains.

The anomalous units can arise for several reasons during the synthesis of poly(organophosphazenes) from PDCP and have different chemical structures. First of all, these are branching points, which were present in the initial polymer. The data on the influence of branching points on the properties of poly(organophosphazenes) available to date are scarce, probably, since there are no sufficiently strict characteristics for them. However, this type of unit non-uniformity can be virtually eliminated by using linear PDCP in the polymeranalogous transformations. Yet another type of anomalous units arises due to incomplete substitution of the chlorine atoms in PDCP. This affords non-uniform polymers, which contain partially substituted and non-substituted chain units, in addition to the completely substituted ones.



The presence of even small proportions of the anomalous units (< 1 mol. %) with non-substituted P–Cl groups substantially decreases thermal, hydrolytic, and thermohydrolytic stabilities of poly(fluoroalkoxy- and poly(aryloxy-phosphazenes) and also facilitates their decomposition during photolysis.[3,12] Hydrolysis proceeding as a side process can lead to the formation of anomalous partially hydrolysed units, which occur in the polymer chain as two tautomeric forms



These units are even less stable and promote destruction of the polymeric chains.

Due to the diversity of anomalous units arising during the synthesis of poly(organophosphazenes), it is difficult to obtain well-reproducible results. Therefore, to obtain poly(organophosphazenes) possessing valuable properties, one should conduct the polymeranalogous substitution up to very high degrees of conversion under conditions ensuring almost complete suppression of hydrolysis.

The polymeranalogous substitution of chlorine in PDCP by fluoroalkoxy groups has been studied in most detail (see early reviews[2,3]). Sodium,[3,42,44,46,47,66–76] potassium,[75,77,78] and lithium[36,74,75,77,79–81] alkoxides and also fluorinated alcohols (in the presence of triethylamine) have been used as nucleophilic agents.[3,48,82]

Since some regularities of the formation of poly(fluoroalkoxyphosphazenes) have been considered in our previous review,[3] we do not discuss them here. We only would like to mention that the degree of chlorine substitution and the occurrence of the extremely undesirable side reactions of hydrolysis during the polymeranalogous substitution of chlorine in PDCP by sodium trifluoroethoxide, depend appreciably on the experimental conditions.[69,76,83–85] The efficiency of these reactions is largely determined by the reaction medium, temperature, and duration of substitution. The amount of water in the reaction system (even at the level 10^{-2} vol.% –10^{-3} vol.%) is also significant. Hydrolysis is suppressed most efficiently when the reaction is carried out at room temperature and lasts for no more than 3 h when poly(-fluoroalkoxyphosphazene) precipitates, for example, from a toluene–tetrahydrofuran solvent mixture during the process, and when all the reactants and reaction vessels have been thoroughly dried before the process.[5,83] The latter problem has been successfully solved, for instance, by using molecular sieves as desiccants.[83,86] The molecular-mass characteristics of the resulting polymer remained unchanged during the subsequent high-temperature hydrolysis in boiling aqueous acetone, indicating that the use of molecular sieves as desiccants had ensured virtually complete suppression of hydrolysis during the synthesis of poly(-fluoroalkoxyphosphazenes). In particular, poly[bis(tri-fluoroethoxy)phosphazene] (PBTFEP) with a residual chlorine content of 0.04 mass % and a molecular mass of 10^7 was obtained in this way. The molecular-mass characteristics of the polymer did not change after boiling in 10% aqueous acetone for 10 h.[86]

Hydrolytic processes play a crucial role in the synthesis of poly(fluoroalkoxyphosphazenes) regarding the possibility of producing high-molecular-mass polymers. It has been noted (Table 3) that when the degree of hydrolysis of the P–Cl groups is less than 1×10^{-4}%, the molecular mass of PBTFPP is practically insensitive to hydrolytic destruction. The increase in the degree of conversion to $\sim1\times10^{-3}$% may decrease the molecular mass by a factor of two, and when the degree of conversion is $\sim1\times10^{-2}$%, even by a factor of ten.[14]

Table 3. Influence of the degree of conversion of P–Cl groups in side hydrolysis reactions on the molecular mass of poly[bis(tetrafluoropropoxy)phosphazene] (PBTFPP) according to Ref. 14.

Number of macromolecules (%)	Number of P–C groups in a macromolecule	Degree of conversion of P–Cl groups	$10^6\,\bar{M}_n$	Intrinsic viscosity $[\eta]$[a] of PBTFPP in THF/ dl g^{-1}
0	0	0	13.2	6.94
1	1	1.16×10^{-5}	13.1	6.89
10	1	1.16×10^{-4}	12.0	6.40
100	1	1.16×10^{-3}	6.6	3.85
100	10	1.16×10^{-2}	1.2	0.90

[a] $[\eta] = 6.15\times10^{-6}\,M^{0.85}$ (Ref. 59).

Table 4. Conditions of synthesis and characteristics of some poly(alkoxyphosphazenes) (PAP).

Nucleophilic agent	Reaction medium	T/ °C	[η] of PDCP/ dl g^{-1} (toluene, 25 °C)	Characteristics of PAP		
				[η]/ dl g^{-1} (THF, 25 °C)	Cl content[a] (mass %)	content of P–Cl groups[b] (mol.%)
C_3H_7ONa	$CH_3C_6H_5-C_3H_7OH$	95	4.10	3.30	< 0.01	< 0.02
C_4H_9ONa	$CH_3C_6H_5$ – THF	25	3.50	0.36	6.85	17.21
C_4H_9ONa	$CH_3C_6H_5$	25	5.74	0.53	5.26	11.40
C_4H_9ONa	$CH_3C_6H_5-C_4H_9OH$	110	5.74	4.03	< 0.01	< 0.02
$C_7H_{15}ONa$	$CH_3C_6H_5-C_7H_{15}OH$	110	4.10	5.62	< 0.01	< 0.03
$C_2H_5OC_2H_4ONa$	$CH_3C_6H_5$	25	5.74	0.98	0.70	1.80
$C_2H_5OC_2H_4ONa$	$CH_3C_6H_5-C_2H_5OC_2H_4OH$	60	4.40	7.90	1.23	3.80
$C_2H_5OC_2H_4OLi$	$CH_3C_6H_5-C_2H_5OC_2H_4OH$	100	4.40	Insoluble	< 0.01	< 0.03

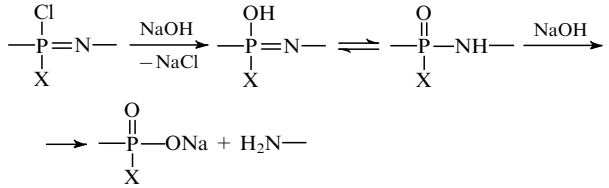
Note. Duration of the synthesis — 3 h; amount of sodium alkoxide — 3 moles per mole of P–Cl groups, concentration of PDCP in toluene — 0.17 mol litre^{-1}, concentration of the alkoxide in alcohol — 2.5 mol litre^{-1}. [a] Determined by coulometric titration. [b] Quantity of P–OH groups in the samples < 0.1 mol.%.

Whereas synthesis and properties of poly(fluoroalkoxyphosphazenes) have been considered in a large number of papers (see reviews [1,3]), non-fluorinated poly(alkoxyphosphazenes) (PAP) have been much less studied. However, since ordinary alcohols are more accessible than fluorinated ones, it was highly desirable to study the synthesis of this type of poly(organophosphazenes). Data on the synthesis and properties of PAP can be found in a number of publications.[44, 87–100]

To develop methods for the synthesis of high-molecular-mass PAP, a systematic study on the condensation of high-molecular-mass PDCP with several sodium alkoxides has been undertaken.[90] Data on the influence of the conditions of synthesis of PAP on the degree of conversion of the P–Cl groups in PDCP and on the intrinsic viscosity of the resulting polymers are listed in Table 4.[90, 91]

It was found that the extent of substitution of the chlorine atoms in PDCP by alkoxy groups is much more dependent on the temperature and duration of the reaction, on the chemical nature of the nucleophilic reagent, and on the polarity of the reaction medium than similar substitution by fluoroalkoxy groups. Thus under the conditions optimum for the synthesis of poly(fluoroalkoxyphosphazenes),[3] namely, when the reaction is carried out in a THF – toluene mixture at 25 °C for 3 h, the degree of conversion of the P–Cl groups into P–OC_4H_9 groups is only ~80%. This process was found to be best conducted in a mixture of toluene with the corresponding alcohol. In particular, in a mixture of toluene and butanol, the degree of conversion of the P–Cl groups at 110 °C is as high as >99.98% over a period of 3 h and, what is especially important, these results are well reproducible.

It should be taken into account that in the synthesis of PAP, the problem of side reactions of hydrolysis proves to be much more complicated. Unlike the acidity of fluorinated alcohols, that of ordinary alcohols ($pK_a \approx 16-18$, in water) is nearly equal to or less than the acidity of water. Therefore, the reaction of the residual water with alkoxides affords NaOH, which causes the side hydrolysis.



X = Cl, OAlk.

The efficiency of hydrolysis is determined by the amount of residual water in the reaction system and by the ratio of the main and side reaction rates. The side reactions occur to the least degree when all the reactants and equipment have been thoroughly dried prior to the reaction and when the experimental conditions employed ensure a high rate of the main reaction.[90]

The set of identified regularities made it possible to synthesise successfully high-molecular-mass PAP with a low content of defective units (P–Cl, P–OH, P=O)[90–93] as a result of the high degree of conversion of the P–Cl groups in the initial PDCP. The conditions used to synthesise PAP are presented in Tables 4 and 5.[90–92]

Table 5. Conditions of synthesis and characteristics of poly(alkoxyphosphazenes) $[-P(OR)_2=N-]_n$.

OR	Conditions of synthesis		[η] /dl g^{-1} (THF, 25 °C)	Content /mol.%	
	T/ °C	t/ h		P–Cl[a]	P–OH[b]
OCH_3	60	6	2.93	0.04	2.0
OC_2H_5	70	5	6.50	0.06	2.7
OC_3H_7	80	3	3.30	0.02	0.2
OC_3H_7[c]	80	3	1.36	0.02	2.1
OC_4H_9	110	3	3.70	0.03	0.1
OC_4H_9[c]	110	3	2.70	0.03	2.7
OC_5H_{11}	110	3	4.08	0.03	0.1
OC_6H_{13}	110	3	5.62	0.03	0.1
OC_7H_{15}	110	3	4.50	0.04	0.1
OC_8H_{17}	110	3	6.07	0.04	0.1

Note. The reaction medium was $CH_3C_6H_5$ – ROH (0.18 mol of RONa and 72 ml of ROH; 0.02 moles of PDCP in 116 ml of toluene); the intrinsic viscosity of PDCP in toluene at 25 °C was 4.1 dl g^{-1}. [a] Calculated from the content of chlorine found by coulometric titration. [b] Found by ^{1}H NMR. [c] Content of water in the system was $> 3 \times 10^{-3}$ vol.%; in other cases, it was $< 3 \times 10^{-3}$ vol.%.

A significant factor influencing the rate and the degree of substitution in the alcoholysis of PDCP is the reactivity of the P–Cl groups in the polyphosphazene, which can vary during the reaction under the influence of converted groups:[14, 101, 102] the neighbouring group at the same phosphorus atom ('close neighbour' effect) and groups at the adjacent phosphorus atoms ('far neighbour' effect). The effects of neighbouring groups determine the structure of anomalous non-substituted units in the chain. Thus it has been found that fluoroalkoxy groups exert an accelerating 'close neighbour' effect in the alcoholysis of PDCP.[102] Consequently, the resulting poly(fluoroalkoxy-phosphazenes), in addition to the completely substituted units, contain the original units with two chlorine atoms attached to phosphorus (–PCl_2=N–) even at high degrees of conversion of the P–Cl groups (> 99.9%). The results of quantum-chemical calculations led to

the suggestion that the accelerating influence of the neighbouring fluoroalkoxy groups during the polymeranalogous substitution in poly(dichlorophosphazene) is mostly due to polar effects.[102] Unlike fluoroalkoxy groups, ordinary alkoxy groups exert a decelerating 'close neighbour' effect; as a result, the PAP formed contain partially substituted units of the type –PCl(OAlk)=N–. Thus, for the same degree of conversion of the P–Cl groups in PDCP, the number of anomalous units in PAP is twice that in poly(fluoroalkoxyphosphazenes). In addition, extensive substitution of chlorines in PDCP by ordinary alkoxides requires more drastic conditions including elevated temperatures.[90] Due to the high activity and equal reactivity of chlorine atoms in the initial PDCP, the 'far neighbour' effect in the alcoholysis reactions is less pronounced than the 'close neighbour' effect. Like the behaviour in alcoholysis, the hydrolytic stability of the anomalous units with non-substituted P–Cl groups and, hence, the stability and reproducibility of the properties of poly(organophosphazenes), also depend on the effect of neighbouring groups.[14]

The microstructures of three specimens of PBTFPP with different degrees of conversion of the P–Cl groups, prepared at molar ratios of the P–Cl groups to sodium 2,2,3,3-tetrafluoropropoxide of 1 : 0.25, 1 : 0.50, and 1 : 0.75, have been studied by ^{31}P NMR spectroscopy.[101] It was found that the distribution of the $-PCl_2=N-$ (A) and $-P(OR)_2=N-$ (B) units along the chain can be sketched as follows:

(a) for 25% degree of conversion

... AAAAAAAA... ⟶ ...BAAABAAA...BBAAAAAA... ,

(b) for 50% degree of conversion

...AAAAAAAA... ⟶ ...BBAABBAA... ,

(c) for 75% degree of conversion

...AAAAAA... ⟶ ...BBBABBBA... .

When the degree of conversion is 25%, the polymer consists mostly of AAA triads and B units, small proportions of BB diads and AAAAAA hexads being also present. In the case of 50% conversion, alternation of AA and BB diads predominates in the chain. At 75% conversion, triads BBB are separated by the initial A units.

The presence of the initial units A in poly(fluoroalkoxyphosphazenes) even at high degrees of conversion of the P–Cl groups is in good agreement with the data[103] on the photolysis of poly[bis(trifluoroethoxy)phosphazene]. According to these data, the destruction products contain chloro(trifluoroethoxy)-cyclotriphosphazene with two geminal chlorine atoms.[103]

The course of the polymeranalogous substitution of chlorine in PDCP depends appreciably on the chemical nature of the substituting reagent.[80, 81, 101–109]

Fig. 1 presents the results of interaction of PDCP with lithium 2,2,3,3-tetrafluoropropoxide, phenoxide, and *o*-allylphenoxide.[105] It can be seen that a 96% degree of substitution of the chlorine in PDCP by tetrafluoropropoxy groups is attained as soon as after 15 min. The replacement of chlorine by phenoxy groups under similar conditions occurs efficiently during the first 2 h up to 50% degree of conversion. After 24 h, the degree of substitution increases only to 60%, and then the reaction sharply slows down. When lithium *o*-allylphenoxide is used in this reaction, the process is decelerated as soon as after a 25%–30% degree of substitution.[105, 106] A ^{31}P NMR study of the nucleophilic substitution of the chlorine atoms in PDCP by the phenoxy groups has shown that one chlorine atom at each phosphorus atom is replaced first, and the polymer formed after 24 h is mostly built of $[-N=PCl(OC_6H_5)-]$ units. The substantial decrease in the reaction rate observed with phenoxides is apparently due to the fact that the chlorine atoms, the close environment of which consists of phenoxy groups, are less reactive towards subsequent nucleophilic attacks of both the phenoxide groups and other nucleophiles. In fact, unlike the initial PDCP, poly[chloro-(phenoxy)phosphazene] is relatively stable to hydrolysis.[105] When it is made to react with lithium tetrafluoropropoxide under the conditions outlined above (reaction time 24 h), the polymers formed contain much more chlorine (6.64%) than poly(tetrafluoropropoxyphosphazene) (chlorine content < 1.00%). This indicates that chlorine in poly[chloro(phenoxy)-phosphazene] is less reactive than that in poly[chloro(tetrafluoro-propoxy)phosphazene].[105]

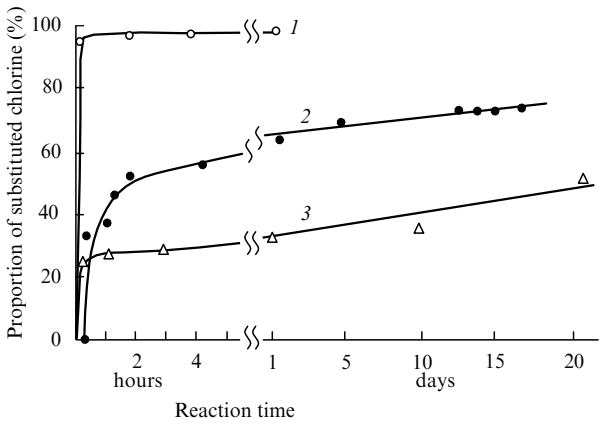


Figure 1. Dependence of the degree of substitution of chlorine atoms in PDCP (THF solution, concentration 0.5 mol litre^{-1}) on the duration of its reaction with a threefold molar amount of lithium tetrafluoropropoxide (*1*), phenoxide (*2*), and *o*-allylphenoxide (*3*) (THF solutions, concentration 2 mol litre^{-1}) at 20 °C.

When poly(organophosphazenes) are synthesised by simultaneous addition to PDCP of a mixture of lithium tetrafluoropropoxide and lithium phenoxide, taken in a molar ratio of 1 : 1, a large portion of lithium phenoxide remains unreacted, and according to elemental analysis, the repeating unit of the resulting polymer can be represented as $NP(OC_6H_5)_{0.5}(OCH_2CF_2CF_2H)_{1.3}Cl_{0.2}$. Thus, under the conditions of competitive nucleophilic substitution, the probability of formation of the $-N=P(OCH_2CF_2CF_2H).(OC_6H_5)-$ units or, especially, the $-N=P(OC_6H_5)_2-$ units dramatically decreases,[80, 105] and thus the polymer becomes enriched in units containing the more reactive nucleophilic reagent; in this particular case, it is tetrafluoropropoxide. Based on the data of ^{31}P NMR spectroscopy,[80] it can be assumed that competitive substitution yields a random heterounit polymer containing phosphorus atoms with different environments.

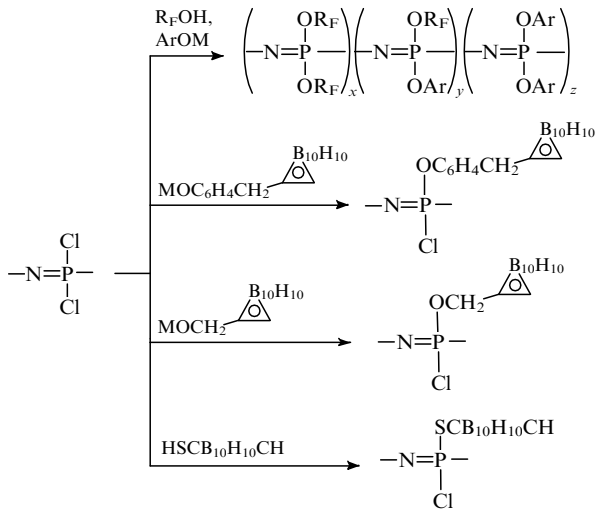
$$[-P(OR)(OAr)=N-]_k-[-P(OR)_2=N-]_m-[-PCl(OAr)=N-]_n$$

OR = $OCH_2CF_2CF_2H$, OAr = OC_6H_5.

It was shown[80] that the final structure of poly(organophosphazenes) depends on the order in which nucleophilic reagents are introduced in the reaction medium. To prepare a poly(organophosphazene) with mixed phosphorus environments of a specified composition, the less reactive reagent should be introduced first in the reaction area, and the process should be carried out until the desired degree of substitution is attained. Then the more reactive component should be added (the first equation in Scheme 4).

Let us consider a particular aspect concerning the synthesis of poly(organophosphazenes) with mixed structures. Recently it has been reported[107] that the reaction carried out in the presence of tetra-n-butylammonium bromide or 15-crown-5 ether is complicated by the fact that the phenoxy groups in the $-NP(OCH_2CF_3)(OC_6H_5)-$ fragments formed can be replaced by trifluoroethoxy groups and that an excess of sodium trifluoroethoxide results in replacement of the phenoxy groups in the $-NP(OCH_2CF_3)(OC_6H_5)-$ units but not in $-NP(OC_6H_5)_2-$. This

Scheme 4



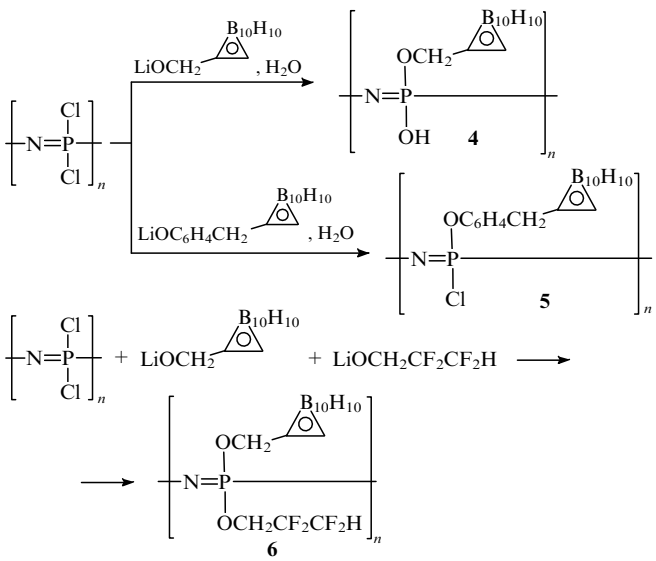
R_F = $CH_2CF_2CF_2H$, CH_2CF_3;
Ar = C_6H_5, C_6H_4Cl, $C_6H_4CH_2-CH=CH_2$;
M = Na, Li.

exchange is markedly retarded after a certain number of phenoxy groups have been substituted. The same investigators noted that tetra-n-butylammonium bromide can be successfully used as an agent accelerating the synthesis of poly(organophosphazenes) with bulky side groups or in those cases where chlorine is substituted by weak nucleophiles.

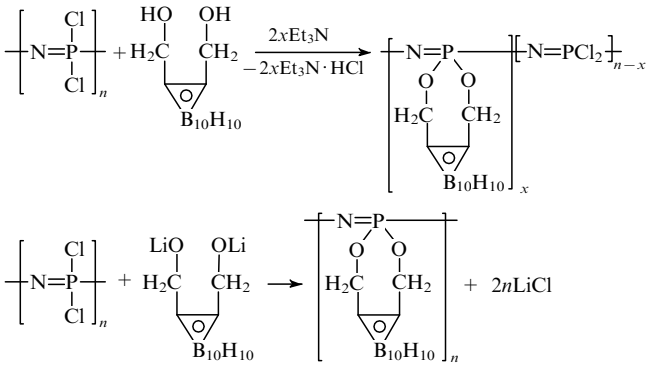
Carborane-containing poly(organophosphazenes) have been synthesised using lithium derivatives of phenyl-*o*-carborane and -*m*-carborane, *m*-carboranethiol, lithium *o*-carboranylmethoxide, and lithium *o*-carboranylmethylphenoxide, as well as bis(hydroxymethyl)-*o*-carborane and its lithium derivative as the nucleophilic reagents.[108–112] The reactions involving lithium derivatives of phenyl-*o*-carborane and -*m*-carborane yielded products, the structure of which could not be determined, since they were highly unstable.[108] The use of lithium *m*-carboranylthiolate, lithium *o*-carboranylmethoxide, and lithium *o*-carboranylmethylphenoxide (see Scheme 4) resulted in the synthesis of carborane-containing polyphosphazenes in 60%–70% yields.[108] The highest degree of chlorine substitution attained in these reactions was only 50%, evidently, due to the steric influence of the carborane substituents.

The chlorine atoms remaining in poly(chlorophosphazenes) containing *m*-carboranylthio and *o*-carboranylmethoxy groups in the side chains are hydrolytically unstable.[108] During the isolation of these polymers, the chlorine atoms contained in them are partially or completely hydrolysed (Scheme 5, polymer **4**). The chlorine atoms in polymer **5** are not hydrolysed under similar conditions.

Scheme 5

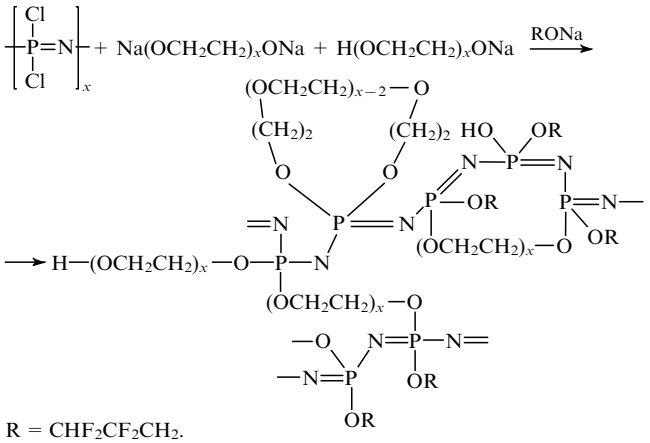


When lithium *o*-carboranylmethoxide and lithium tetrafluoropropoxide are added successively to PDCP, a polymer with carboranylmethoxy and tetrafluoropropoxy groups attached to the same phosphorus atom is produced (polymer **6**). The reaction of bis(hydroxymethyl)-*o*-carborane with PDCP was carried out in THF in the presence of triethylamine at 20–50 °C or by the alkoxide method at 20–22 °C.[109, 110, 112] The results obtained indicate that the two chlorine atoms at the same phosphorus atom in PDCP can, in principle, be replaced by a carborane-containing group yielding cardo-type polymers; this is accomplished using bis(hydroxymethyl)-*o*-carborane as the nucleophilic agent.



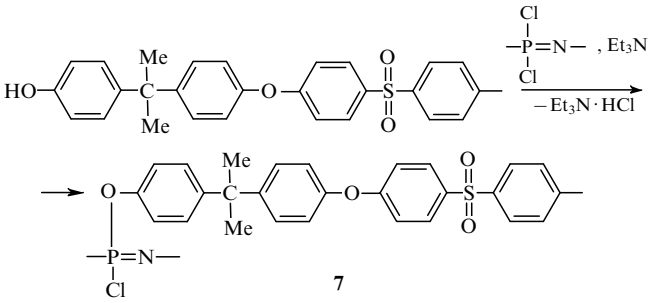
It should be mentioned that a higher degree of substitution of the chlorine atoms in PDCP is achieved in the presence of lithium alkoxide. However, in this case, the *o*-carborane rings are partially converted into dicarbaundecaborate groups, which are unstable with respect to hydrolysis and oxidation. Therefore, triethylamine appears to be the reagent of choice for trapping the hydrogen chloride evolved during the synthesis of carborane-containing polyphosphazenes. Replacement of the remaining chlorine atoms in these polymers by tetrafluoropropoxy groups (without isolation of the product formed in the first stage) has given poly(organophosphazenes) in which the surrounding groups are represented by fluoroalkoxy groups in addition to the cardo carborane groups.[110]

Poly(dichlorophosphazene) is a highly reactive initial compound for the synthesis of insoluble polymeric catalysts containing oligooxyethylene fragments.[14, 113–115] The reaction is carried out with stirring in a mixture of anhydrous THF with toluene.



R = $CHF_2CF_2CH_2$.

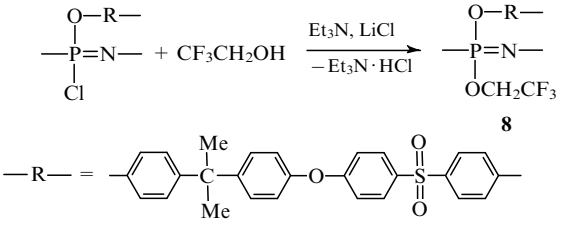
PDCP has also served as the starting compound in the synthesis of graft copolymers. Thus copolymer **7** was synthesised by the reaction of PDCP with a polyarylene sulfone oxide, prepared from 2,2-bis(4-hydroxyphenyl)propane and 4,4′-dichlorodiphenyl sulfone, and containing a reactive terminal hydroxy group.[116, 117]



7

The results obtained attest that this macromolecular reaction is fairly complicated. However, the fact that it yields graft copolymer, the composition of which is close to the specified one and the amount of which is no less than 45% of the total amount of the initial compounds indicates that this method can be used to prepare graft copolymers based on PDCP.

Since the copolymer **7** obtained in this way proved to be hydrolytically unstable, an attempt was made to replace the remaining chlorine atoms in the phosphazene moiety (one-pot procedure) by trifluoroethoxy groups in the presence of triethylamine and lithium chloride.

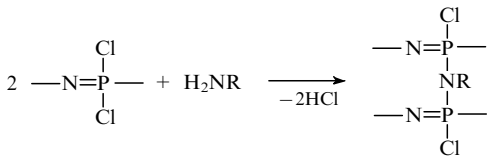


8

It was found that the polyarylene sulfoxide fragments present in the macromolecule of the graft copolymer **7** hamper the attainment of high degrees of the additional substitution of chlorine by the trifluoroethoxy groups. The substitution product **8** in which the residual chlorine content does not exceed 3 mass % is much more resistant to hydrolysis than the copolymer **7**.

Graft polyphosphazenes of yet another type have also been reported. Free radical reaction of poly[bis(4-ethylphenoxy)phosphazene] with maleic anhydride carried out in the presence of peroxides or with heating [118] afforded a graft copolymer, poly[bis(4-ethylphenoxy)phosphazene-*g*-succinic anhydride, containing up to 14% of grafted succinic anhydride groups.

As shown in Scheme 1, amines can also be used as reagents replacing the chlorine atoms in PDCP. This yields poly(aminophosphazenes).[1, 9, 10, 17, 25, 32, 42, 91, 119–126] Non-branched primary amines substitute the chlorine atoms relatively easily; however, in this case, it is difficult to obtain a soluble polymer because of the possible cross-linking of macromolecules.



A detailed study of the aminolysis of linear PDCP by secondary amines made it possible to find conditions for the formation of poly(di-n-alkylaminophosphazenes) possessing highly chemically uniform structures with low contents of defective units and molecular masses of more than 10^6.[91, 119, 120] In particular, a homologous series of these polymers, $[-N=P(NHC_nH_{2n-1})_2-]_x$, where $n = 1-7$, was successfully synthesised in this way.[119]

3. Synthesis of poly(organophosphazenes) by polymerisation of cyclophosphazenes

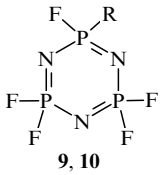
Preparation of poly(organophosphazenes) by polymerisation of completely substituted organocyclophosphazenes would make it possible to avoid the undesirable side processes, which occur when these polymers are synthesised from PDCP because of the hydrolytic instability of chlorine. In addition, this method would permit preparation of poly(organophosphazenes) with a regular arrangement of substituting groups at the phosphorus atoms along the polymeric chain. However, as has been noted in a number of reviews,[1, 3, 10, 11, 32] most of the numerous attempts to synthesise poly(organophosphazenes) by this approach were unsuccessful. The attempts to accomplish thermal polymerisation of alkyl-, aryl-, alkoxy-, and aryloxy-substituted cyclotriphosphazenes at 150–350 °C either failed or resulted in the formation of only low-molecular-mass polymers.[127–131] The completely substituted fluoroalkoxycyclotriphosphazenes containing pentafluoropropoxy [132] and trifluoroethoxy [133] groups could not be involved in thermal polymerisation at 200–300 °C, or at 200 °C under an elevated pressure.[64]

Attempts have been made to carry out polymerisation of fluoroalkoxycyclotriphosphazenes [64, 133, 134] in the presence of various catalysts. However, only in the presence of an equimolar amount of BCl_3, did this give a polyphosphazene with a molecular mass of 23 000–33 000; however, in this case, too, half of the fluoroalkoxy groups were replaced by chlorine.[134]

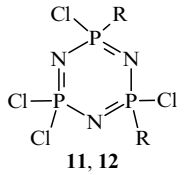
Nevertheless, chlorocyclophosphazenes with various degrees of substitution of chlorine by organic groups do enter into polymerisation and copolymerisation.[132, 133, 135] Thus a polyphosphazene with a molecular mass of 110,000 was obtained by copolymerisation of hexakis(trifluoroethoxy)cyclotriphosphazene and hexachlorocyclotriphosphazene.[133] A rubber-like polymer has been prepared by copolymerisation of a mixture of trichlorotrimethylcyclotriphosphazene and tetrachlorotetramethylcyclotetraphosphazene.[135] Thermal bulk polymerisation of geminally substituted cyclotriphosphazenes $C_6H_5(X)P_3N_3Cl_4$ (X = Cl, Br, CH_3, C_4H_9) has been studied.[136] At 250 °C, the compound with X = Cl polymerises over a period of 20–56 h, and that with X = Br reacts over a period of 4.5–24 h. The products of polymerisation of the monomers with X = CH_3 and C_4H_9 comprise a broad range of substances including both oligomers and polymers.

Allcock and Turner [137] have considered the thermal behaviour of substituted cyclotriphosphazenes of complex structures. It was found that thermolysis of these compounds at temperatures above 200 °C in the absence or in the presence of hexachlorocyclotriphosphazene, which could initiate polymerisation, affords only low-molecular-mass poly(organophosphazenes).

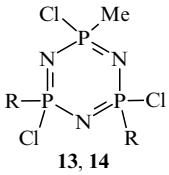
Below we present a number of substituted cyclic phosphazenes, products of their polymerisation and copolymerisation with hexachlorocyclotriphosphazene, and also poly(organophosphazenes) based on them; the latter were prepared by polymeranalogous substitution of the residual halogen atoms in the polymerisation products by the trifluoroethoxy groups.[138] Polymerisation of chlorocyclophosphazenes was carried out at 210–250 °C, while that of fluorine-substituted cyclophosphazenes was conducted at 250–300 °C. The molecular masses of the resulting polymers amounted to $(2.8-12.0)\times10^5$.[138]



9, **10**

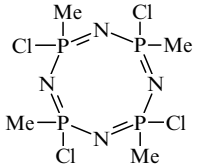


11, **12**

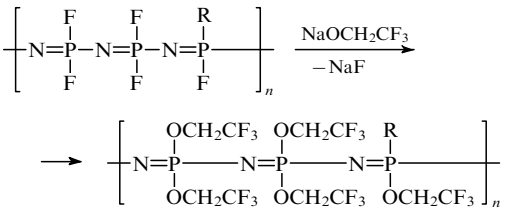


13, **14**

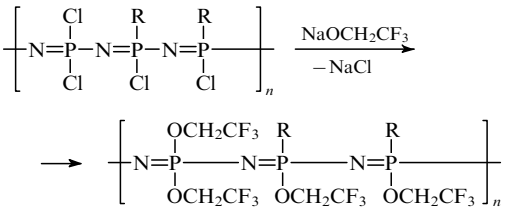
R = Bu^t (**9**), Ph (**10**), Me (**11**, **13**), Et (**12**, **14**).



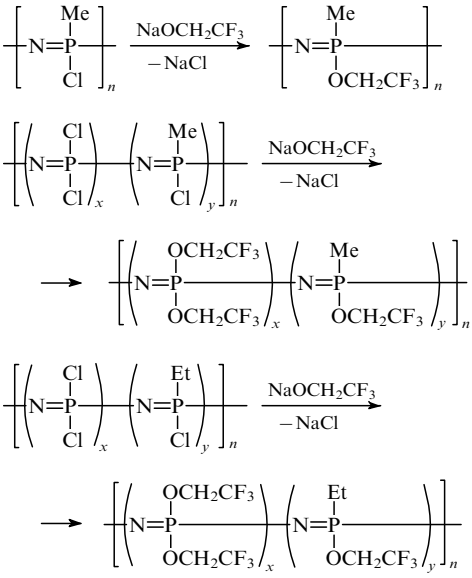
15



R = Bu^t, Ph.

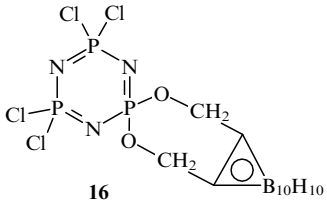


R = Bu^t, Et.

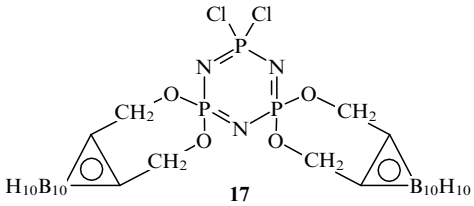


Allcock and Ngo [139] have synthesised a number of new phosphazene polymers by thermal polymerisation of 1,1-bis-(trichlorophosphazo)tetrachlorocyclotriphosphazene followed by replacement of the residual chlorine atoms in the polymerisation product by various organic pendent groups. Polymerisation was carried out at 150 °C at a reduced pressure for 2 h. Thermal polymerisation of phenylpentafluorocyclotriphosphazene at 300 °C for 48–72 h was used to synthesise poly(phenylfluorophosphazene) $[-N=PPhF-N=PF_2-N=PF_2-]_n$.[140] Polymeranalogous substitution of fluorine in this compound resulted in the synthesis of poly(organophosphazenes) with Me_3SiCH_2 side groups and poly(organophosphazenes) with mixed phosphorus environments containing trifluoroethoxy groups in addition to Me_3SiCH_2 groups.

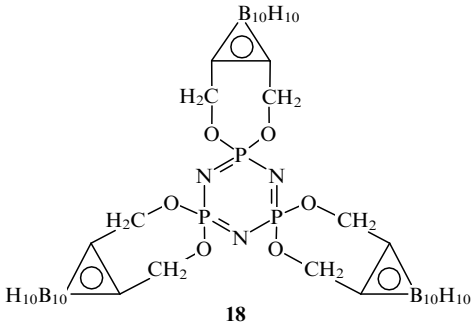
Mono- (**16**), bis- (**17**), and tris- (**18**) *o*-carboranyl-substituted cyclotriphosphazenes have been prepared in order to synthesise carborane-containing polyphosphazenes.[110, 141, 142] This polymer is formed under milder conditions than those resulting from polymerisation of hexachlorocyclotriphosphazene and previously known carboranecyclophosphazenes.[143] To increase the



16



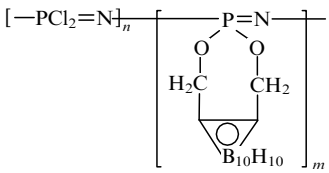
17



18

hydrolytic stability of this carborane-containing polymer, the remaining chlorine atoms were substituted by tetrafluoropropoxy groups.[141]

Only polymerisation of mono-substituted derivative **16** gave a polymer (yield 60%) completely soluble in THF and having a reduced viscosity of 0.52 dl g^{-1} in this solvent.[141] Polymerisation of this monomer was carried out in the melt at 220 °C for 2 h. The data obtained by ^{31}P NMR spectroscopy suggested an irregular arrangement of phosphorus atoms carrying the carboranyl groups. Apparently, the macromolecule of this polymer contains the following fragments, which are randomly distrubuted along the chain:

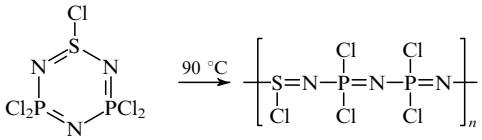


n = 1–4, m = 1–2.

This polymer is formed under milder conditions than those resulting from polymerisation of hexachlorocyclotriphosphazene and previously known carboranecyclophosphazenes.[143] To increase the hydrolytic stability of this carborane-containing polymer, the remaining chlorine atoms were substituted by tetrafluoropropoxy groups.[141]

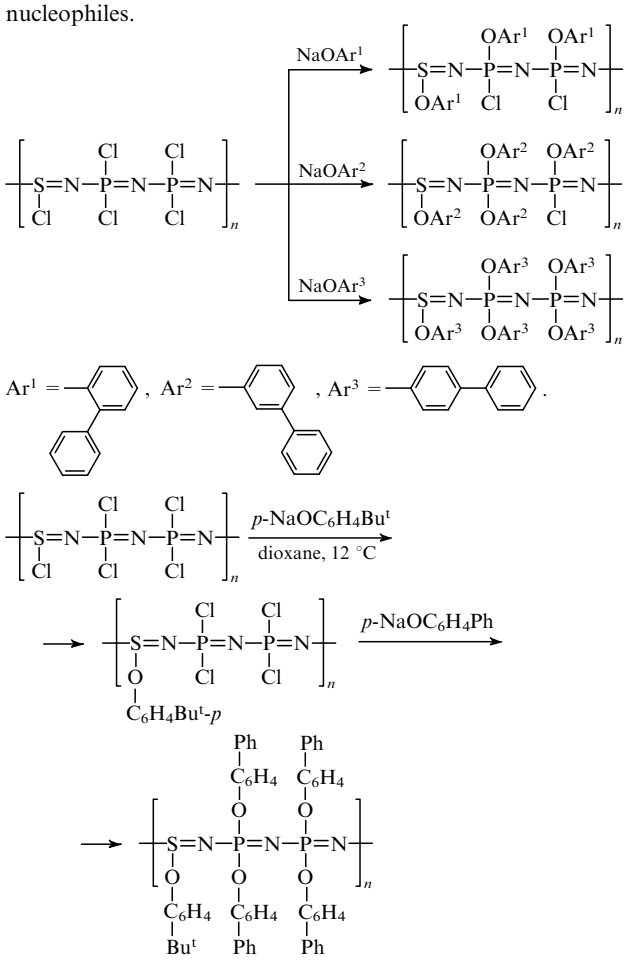
The synthesis of cyclic and polymeric phosphazenes with methyl- and phenyl-*o*-carboranyl groups has also been reported.[144, 145] Thermal polymerisation of (methyl-*o*-carboranyl)- or (phenyl-*o*-carboranyl)-pentachlorocyclophosphazenes was conducted at 250 °C for 120 h. The chlorine atoms remaining in the polymer and susceptible to hydrolysis were replaced by trifluoroethoxy groups.

Let us discuss one more type of polyphosphazenes, namely, poly(thiaphosphazenes), the polymeric chains of which incorporate sulfur-containing fragments in addition to the –P=N– units. Poly(chlorothiaphosphazene) has been prepared by polymerisation of cyclic thiaphosphazene $N_3P_2SCl_5$.[146]



The process was carried out in Pyrex tubes at 90 °C or at room temperature. It is of interest that polymerisation of a freshly distilled specimen requires several days at 90 °C, whereas a specimen that has been first kept overnight at room temperature polymerises over a period of 4–5 h. The yield of the polymer

after two reprecipitations was 32%. Poly(chlorothiaphosphazene) proved to be readily hydrolysable. It was involved in polymer-analogous transformations with various aryloxy-containing nucleophiles.



It should be noted that some of the chlorine atoms in polymers of this type still remain unsubstituted. Their molecular masses are $> 10^5$.

Thus, the data presented above demonstrate that despite the numerous attempts to prepare poly(organophosphazenes) directly from completely substituted organocyclophosphazenes, conditions for their successful polymerisation have not yet been found. More reassuring results have been obtained when halocyclophosphazenes, in which chlorine has been partially substituted by organic groups, were subjected to polymerisation. However, due to hydrolytic instability of the resulting polymers, subsequent replacement of the residual halogen atoms by organic groups of one or another type is required. Certainly, studies on the polymerisation of organo-substituted cyclophosphazenes require further development. Currently the two-stage procedure considered above is undoubtedly the most efficient method for the synthesis of poly(organophosphazenes).

III. Properties of poly(organophosphazenes)

1. Chemical properties

In a number of publications,[1–3,9] it has been noted that poly(organophosphazenes) are chemically stable; however, their stability depends substantially on the structure and defectiveness of their chemical structure. Thus the presence of anomalous units in poly(organophosphazenes) markedly decreases their hydrolytic stability. Completely substituted poly(organophosphazenes) with inert alkoxy and aryloxy pendent groups are stable to atmospheric moisture and to weak acids and bases.[1,4,9] Poly(diphenoxy)phosphazene remains unchanged after refluxing in 1 M HNO_3 or 1 M aqueous KOH for 48 h.[147]

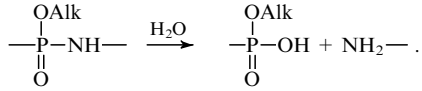
Data concerning the behaviour of poly(fluoroalkoxyphosphazenes) on treatment with various acids are contradictory. It has been reported that in the solid state, these polymers are resistant to concentrated sulfuric [67] and glacial acetic [1] acids at low temperatures. However, it has also been reported that strong inorganic acids or glacial acetic acid diminish their mechanical properties.[148] Cured poly(fluoroalkoxyphosphazenes) have been noted to be stable on treatment with boiling water [67,148] and to remain unchanged when in contact with concentrated solutions of KOH or NaOH for many months in the cold.[1,67,148] The hydrolytic stability of poly(fluoroalkoxyphosphazenes) at moderately elevated temperatures depends on the overall contents in the polymer of all the anomalous units with P–Cl, P–OH, and P(O)–NH groups (Table 6).[3,66,76]

Table 6. Some characteristics of poly[bis(trifluoroethoxy)phosphazene] containing predominating units $-P(OCH_2CF_3)_2=N-$ and anomalous units $-P(OCH_2CF_3)Cl=N-$, $-PCl_2=N-$, $-P(OCH_2CF_3)(OH)=N-$, $-P(O)(OCH_2CF_3)-NH-$, $-P(OH)Cl=N-$, and $-P(O)Cl-NH-$.

Characteristics	Specimen	
	A	B
Total contents of anomalous units x, mol.%	< 0.18	$0.2 < x < 1.0$
Molecular mass	10×10^6	3×10^6
$[\eta]$ in acetone/ dl g^{-1}		
after the synthesis	3.70	1.64
after 20 h	3.63	0.14
after 3 years	3.68	0.65
σ_r[a]/ kgf cm^{-2}		
after the synthesis	1920	810
after 3 years	2260	80
ε[b]/ %		
after the synthesis	680	510
after 3 years	760	13

[a] σ_r is the tensile strength of a nonoriented film; [b] ε is relative elongation at break.

Table 6 presents some characteristics of poly[bis(trifluoroethoxy)phosphazene]. Two specimens of this polymer are considered: one of them (specimen A) contained < 0.18 mol.% of anomalous units, while the other one (specimen B), 0.2 mol.% $< x <$ 1.0 mol.%. For polymer B, the intrinsic viscosity substantially decreases (from 1.64 to 0.14 dl g^{-1}) after a 20-h refluxing in aqueous acetone, while in the case of polymer A, it remains virtually the same.[79] This indicates that at a particular content of anomalous units, polyphosphazene undergoes hydrolytic destruction, which can occur, for example, as follows:



Poly[bis(trifluoroethoxy)phosphazene] containing $\geqslant 0.2$ mol.% of residual chlorine is so hydrolytically unstable that even at room temperature, it becomes insoluble in organic solvents, apparently, due to cross-links between macromolecules arising from its chemical transformations.[3,66,76]

Poly(organophosphazenes) can undergo various chemical transformations under appropriate conditions. Reactions of poly[bis(4-methoxyphenoxy)phosphazene] and poly[bis(benzyl-oxyphenoxy)phosphazene] with BBr_3 to give the polymer $[-N=P(OC_6H_4OH)_2-]_n$ have been reported.[149] The pendent substituents in this polymer contain free OH groups, which enable its subsequent chemical modification.

The possibility of exchange reactions of poly[bis(trifluoroethoxy)phosphazene] with esters and hydroxyl-containing com-

pounds has been studied.[150] It was found that the substitution of trifluoroethoxy groups by alkoxy groups carried out in a saturated solution of polyphosphazene and dibutyl adipate containing tetrabutoxytitanium at 240 °C occurs by 10% over a period of 20 h. When polyphosphazene is made to react with *m*-cresol and undecyl alcohol at temperatures below 240 °C, the exchange hardly takes place. The replacement of trifluoroethoxy groups in polyphosphazenes by alkoxy groups occurs successfully only when the corresponding metal alkoxides are used. Thus treatment of the polyphosphazene $[=NP(OR)_2-]_n$ with R′ONa, where R and R′ are monovalent radicals of the type $F(CF_2)_xCH_2$ or $H(CH_2)_yCH_2$ (x and y vary from 0 to 9) yielded polymers with mixed environments, $[=NP(OR)(OR')-]_n$.[107, 151–153] The reaction was carried out by mixing solutions of the initial compounds in dry THF at 25 °C followed by refluxing the mixture for 4 h.[152, 153] The use of bifunctional alcoholates, for example, the disodium hexafluoropentanediolate, permits curing of polyphosphazene.[151]

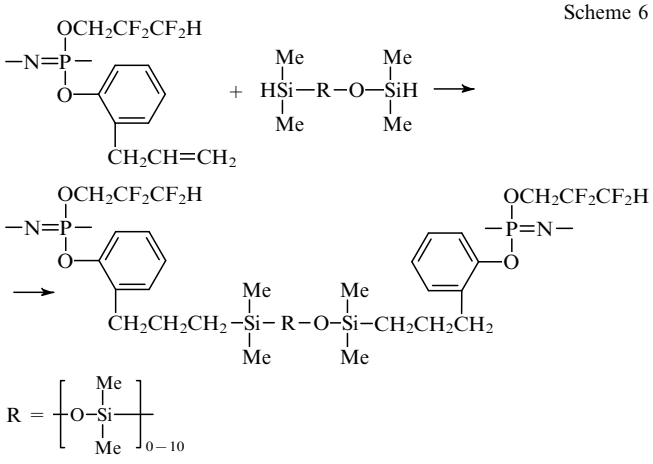
Poly(organophosphazenes) with mixed environment containing free hydroxyl groups in some of the pendent substituents, which can be cured by diisocyanates, dicarboxylic acid anhydrides, *etc.*, have been described.[154]

Poly(organophosphazenes) containing 0.5 mol.%–35 mol.% of organic radicals with NH bonds, in addition to side alkoxy, fluoroalkoxy, or aryloxy groups, can be cured at room temperature by cross-linking reagents containing epoxy, anhydride, or NCO groups.[155] Poly(fluoroalkoxyphosphazenes) containing a small amount (0.1%–5%) of OC_6H_4Alk-*o* groups in the lateral chain can be cured in compositions with various filling agents by peroxides and sulfur on exposure to high-energy radiation giving tough compounds.[156] Poly(organophosphazenes) with the residues of allyl, n-butenyl, and isobutenyl alcohols[157–159] and allyl hydroxybenzoate[160–162] as the P-substituents have been synthesised. Under appropriate conditions, these polyphosphazenes can be cured or involved into copolymerisation with unsaturated monomers.[162]

The attempts to cure poly(fluoroalkoxyphosphazenes) by procedures used in vulcanisation of fluorinated rubbers have not been a success.[163] However, the polymers obtained upon introduction of reactive *o*-allylphenoxy groups, $[-N=P(CH_2CF_2CF_2H)_{2-x}(OC_6H_4CH_2CH=CH_2-)_x]$ where $x = 0.02-1.00$, acquire the ability to undergo thermal curing in the presence of initiators as well as radiation-induced and chemically induced curing.[163] It was found that organosilicon hydrides of various structures can serve as the curing agents for these polyphosphazenes. Curing with these agents was accomplished in the presence of hydrogen hexachloroplatinate both in solution and in films at 20–65 °C for 0.25–10 h.[163, 164] The curing process may occur according to Scheme 6.

However, the fact that polyphosphazenes are cured by organosilicon monohydrides suggests that interaction by a free radical mechanism is also possible.[163]

Scheme 6



A method for the preparation of hybrid polyphosphazene copolymers has been developed. The method includes the reaction of poly(tetrafluoropropoxyphosphazenes) containing 2 mol.% and 5 mol.% of *o*-allylphenoxy groups, or poly(chlorophenoxyphosphazene) containing 2 mol.% of *o*-allylphenoxy groups with polysiloxanes.[165] The role of the latter component was played by a poly(dimethyl-)(or methylphenyl-) (or methylvinyl)siloxane rubber (the content of methylphenylsiloxane units was 8.0 mol.%, that of methylvinylsiloxane units was 0.3 mol.%) and also by a siloxane polymer of the composition $[OSiHEt]_m$, where $m = 10-15$. In the former case, the reaction was carried out by heating films containing 2 mol.% of benzoyl peroxide at 90 °C. After 5 h of heating, the content of the insoluble fraction amounted to ~30%–70% depending on the particular polyphosphazene used. The reaction of polyphosphazenes with siloxanes containing terminal Si–H groups was carried out in films in the presence of hydrogen hexachloroplatinate, by heating the films to 65 °C. In some cases, as soon as after 2 h, the content of insoluble fraction in the reaction products was ~90%. Judging from thermomechanical testing, polyphosphazene–siloxane hybrid systems of this type surpass poly(organophosphazenes) in elasticity and heat resistance.[165] Poly(aryloxyphosphazenes) are capable of self-extinguishing in air with only moderate smoke evolution.[33, 166] The limiting oxygen index of their inflammability is 24–65. Poly(fluoroalkoxyphosphazenes) do not burn in air; the oxygen index of their inflammability is 47–65, and in some cases, it is as high as 80.[3, 77, 167, 168]

It has been found that the probability of decomposition of polyalkoxy- and polyaryloxyphosphazenes during photolysis[103, 169] depends on the content of unsubstituted P–Cl groups. In the absence of these groups, poly(organophosphazenes) possess high light resistance.

Data on the influence of high temperatures on poly(organophosphazenes) have been reported in numerous publications.[1, 3, 8, 9, 11, 32, 34, 36, 44, 47, 104, 121–123, 131, 170–180] Allcock[1] has noted that heat treatment of poly(organophosphazenes) is accompanied by depolymerisation and decomposition and that the size of the pendent groups attached to phosphorus has an appreciable influence on the polymer stability with respect to depolymerisation. Thus poly(aryloxyphosphazenes) are more thermally stable than alkoxy-substituted compounds. The latter completely decompose at 550 °C, whereas aryloxy-derivatives loss only 50% of their weight when the temperature reaches 600 °C (for a heating rate of 10 deg min^{-1}).[47] The decomposition of poly(aryloxyphosphazenes) affords mostly linear and cyclic oligomers.[104, 170] Tables 7 and 8 contain thermal characteristics of some poly(diaryloxyphosphazenes) and poly(diarylaminophosphazenes).

Table 7. Thermal characteristics of some poly(diaryloxyphosphazenes) $[-N=P(OAr)_2-]_n$.[34, 122]

Ar	Decomposition temperature/ °C	
	under argon	under oxygen
C_6H_5	380	400
p-MeC_6H_4	310	310
m-MeC_6H_4	350	340
p-ClC_6H_4	400	385
m-ClC_6H_4	380	375
p-EtC_6H_4	285	250
p-$MeOC_6H_4$	340	233
p-$Bu^tC_6H_4$	350	–
3,4-$Me_2C_6H_3$	315	–
3,5-$Me_2C_6H_3$	340	–

Note. Thermogravimeteric analysis was carried out at a heating rate of 10 deg min^{-1}.

Table 8. Thermal characteristics of some poly(diarylaminophosphazenes) $[-N=P(NHAr)_2-]_n$.[123]

Ar	T/ °C	Ar	T/ °C
p-MeC_6H_4	250	*p*-$MeOC_6H_4$	266
m-MeC_6H_4	262	*p*-ClC_6H_4	265
p-EtC_6H_4	245	*m*-ClC_6H_4	253
m-EtC_6H_4	243	*p*-FC_6H_4	260
p-$Bu^nC_6H_4$	253	*m*-FC_6H_4	249

Note. Thermogravimeteric analysis was carried out at a heating rate of 20 deg min^{-1}.

The data presented demonstrate that the temperatures of the onset of decomposition of arylamino derivatives are lower than those for poly(aryloxyphosphazenes). According to viscosimetric measurements, destruction of many poly(organophosphazenes) starts in the temperature range 100–200 °C.[9, 69, 104, 170, 177] Thus a decrease in the molecular masses of poly(diphenoxy- and poly(di-*m*-chlorophenoxy-phosphazenes) can be observed even at 130–160 °C.[170, 177] Apparently, the destruction processes in poly(organophosphazenes) are strongly influenced by the end groups in the polymer chains as indicated, for example, by the fact that the rate of destruction of poly(dibutoxyphosphazene) at 200 °C *in vacuo* increases with a decrease in the molecular mass of the polymer and with an increase in the concentration of the P=O and P–OH groups.[9, 180]

Some studies contain results of thermogravimetric analysis and thermal stability of poly(fluoroalkoxyphosphazenes); however, these data are sometimes contradictory.[3, 70, 171] Thus it has been reported [70] that the weight loss of poly[bis(trifluoro-ethoxy)phosphazene] starts at ~200 °C, whereas other researchers [5, 6, 34, 171] give values of 350–360 °C. Molecular-mass characteristics of these polymers have been estimated.[69, 172–174] It was found that the molecular mass of poly(fluoroalkoxyphosphazenes) decreases relatively rapidly at 150–200 °C, probably due to the presence of defective units in their macromolecules. An attempt has been made to elucidate more precisely the nature of the defective groups and the active sites, which initiate destruction of the polyphosphazene chain in poly[bis(trifluoroethoxy)phosphazene].[176] It was shown that thermal depolymerisation of this polymer corresponds to a depolymerisation model with two-stage initiation at which normal phosphazane units are first transformed into defective ones. The latter may be represented by oxophosphazene units like –P(O)(CH_2CF_3)–NH– and –P(O)(CH_2CF_3)–N(Cl)–. They induce the appearance of active sites for depolymerisation, and, hence, the polymer in question undergoes complete thermal destruction even about 200 °C. Defective oxophosphazane units can arise during the synthesis of the polymer upon hydrolysis of P–Cl bonds and subsequent tautomeric rearrangement; they also can appear upon thermal transformations of normal phosphazene groups at temperatures about 400 °C. It has been suggested [176] that this mechanism of depolymerisation is common to all poly(alkoxy- and aryloxyphosphazenes).

It order to elucidate the possibility of increasing the thermal stability of poly(organophosphazenes), polymers of this type containing carboranyl groups have been synthesised.[108–111, 141] It was found that a 5% decrease in the weights of these polymers in air is observed at moderate temperatures (200–270 °C). However, the positive influence of the carboranyl groups is manifested at higher temperatures. The coke residue of these polymers in air at 500 °C amounts to 50%–80% and that in a helium atmosphere can be as high as 100% even at 900 °C, whereas the initial poly(dichlorophosphazene) and some poly(organophosphazenes) completely decompose even at 500–570 °C.[121]

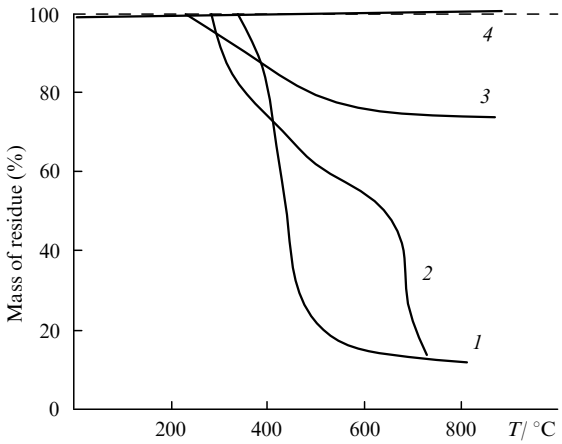


Figure 2. Thermogravimetric curves for polyorganophosphazenes with mixed environments recorded in air (curves *1*, *2*, *3*) and under helium (*4*); heating rate 4.5 deg min^{-1}.

(*1*) $[-N=P(OCH_2CF_3)(OC_6H_4Cl)-]_n$, (*2*) $[-N=P(Cl)(OC_6H_5)-]_n$,

(*3*, *4*) $[-N=P(Cl)(OC_6H_4CH_2-B_{10}H_{10})-]_n$.

Figure 2 compares thermogravimetric curves for a carborane-containing polyphosphazene (*3* and *4*) with those for polymers containing no carborane groups (*1* and *2*). It can be seen that during heating in air, the weight of carborane-containing polymers changes to a much lesser degree than that of the polyphosphazenes $[-N=P(OCH_2CF_3)(OC_6H_4Cl)-]_n$ and $[-N=P(OC_6H_5)Cl-]_n$. Heating in a helium atmosphere does not result in any change in the weight of the carborane-containing polymer up to very high temperatures.

Thus, thermal stability of poly(organophosphazenes) depends on a number of factors, namely, on the chemical structure of groups linked to the phosphorus, on the presence of defective fragments in the polyphosphazene chain, on the terminal groups in the macromolecules, and on the molecular mass. The thermal stability of poly(organophosphazenes) can be changed by varying the above factors or by adding special stabilising compounds to materials based on these polymers.[3, 8, 9, 181–185]

2. Physical properties

Physical properties of poly(organophosphazenes) are intimately connected to their chemical structure. The data of Table 9 give an idea of the influence of chemical structure of poly(organophosphazenes) on their solubility. It can be seen that some poly(organophosphazenes) are readily soluble in ordinary organic solvents, which provides opportunity for investigation of their hydrodynamic, rheological, and molecular-mass characteristics and other properties, which have been dealt with in a number of publications.[1, 3, 9, 33, 48, 59–63, 87, 91, 121–126, 177, 186–193] Studies of the molecular-mass distribution of polyphosphazenes have led to ambiguous results. Some researchers have noted broad molecular-mass distributions.[1, 3, 60–62, 121–126, 177] Thus polydispersity factors of about 7–79 have been reported for poly(fluoroalkoxyphosphazenes).[3, 60–62] However, in relation to poly[bis(tetra-fluoropropoxy)phosphazene], it was shown that the synthesis carried out under controlled conditions can lead to poly(fluoro-alkoxyphosphazenes) with narrow molecular-mass distributions (M_w/M_m = 1.03, 1.39).[63] A relatively low polydispersity factor, equal to 1.09, has been reported for poly[bis(octafluoropentyl-oxy)-

Table 9. Solubility of polyorganophosphazenes $[-N=PR_2-]_n$.

R	Soluble in	Insoluble in	Ref.
OEt	alcohols, benzene, ethers, ketones	water, ethanol, aliphatic hydrocarbons	1, 32, 44, 92
OBu	hexane, benzene, chloroform, THF, cyclohexane, ethyl acetate	methanol, water	90–92
OCH_2CF_3	acetone, ethyl acetate, THF, dimethyl ether, DMF, ethylene glycol, methyl ethyl ketone	ethanol, diethyl ether, aromatic and aliphatic hydrocarbons	1, 3, 4, 42, 44, 48, 143
$OCH_2C_2F_4H$	THF, acetone	aliphatic hydrocarbons	1, 3, 16
$OCH_2C_7F_{15}$	no solvents were found		3, 47
OPh	benzene, toluene, DMF, dioxane, chloroform, chlorobenzene, THF	acetone, hexane, ethanol, water, DMSO	1, 32, 44
NHC_6H_{13}	THF	methanol	120

phosphazene].[13] In another study, it was noted that for poly(aryloxyphosphazenes), the polydispersity factor can be as high as 30.[121] According to the results of gel-permeation chromatography, these polymers are typically characterised by bimodal molecular-mass distributions.[9, 177, 191] The polydispersity factor of poly[bis(phenylamino)phosphazene] is 13.4.[124]

For a number of poly(fluoroalkoxy- and poly(alkoxyphosphazenes), the parameters of the Mark–Kuhn–Houwink equations and dependences of the sedimentation constants in THF solutions on their molecular masses have been determined (Table 10).[13, 91, 192]

Table 10. Parameters of the equations $[\eta] = k_\eta M^a$ and $S_0 = k_S M^{1-b}$ for polyphosphazenes $[-N=P(OR)_2-]_n$.

R	k_η	a	$10^{14} k_S$	$1-b$	Range $10^{-3} x_{S_\eta}$	Ref.
CH_2CF_3	1.77×10^{-4}	0.59	35.20	0.47	45.0–122.1	13, 192
$CH_2(CF_2)_2H$	6.10×10^{-6}	0.85	1.17	0.39	3.6–63.1	13, 192
$CH_2(CF_2)_4H$	6.74×10^{-7}	1.00	2.95	0.33	7.1–23.7	13, 192
$(CH_2)_2CH_3$	2.03×10^{-4}	0.65	27.00	0.45	4.8–20.9	91
$(CH_2)_3CH_3$	1.17×10^{-4}	0.70	33.30	0.43	2.7–28.7	91
$(CH_2)_5CH_3$	9.36×10^{-6}	0.88	56.00	0.37	4.0–16.1	91

For the same polymers, conformational parameters were calculated and it was shown that the statistical Kuhn segment values increase with an increase in the length of the pendent substituent.[91, 192] Thus the Kuhn segments for the polyphosphazenes with R = $-(CH_2)_2CH_3$, $-(CH_2)_3CH_3$, and $-(CH_2)_5CH_3$ amount to 53×10^{-8}, 72×10^{-8}, and 110×10^{-8} cm, respectively. The same values for poly[bis(fluoroalkoxy)phosphazenes] with R = $-CH_2CF_3$, $-CH_2(CF_2)_2H$, and $-CH_2(CF_2)_4H$ are equal to 44×10^{-8}, 122×10^{-8}, and 160×10^{-8} cm, respectively. These results permitted the conclusion that the equilibrium rigidity of poly(alkoxyphosphazene) macromolecules is much lower than that of poly(fluoroalkoxyphosphazene) macromolecules, provided that the lengths of the lateral groups are comparable. The replacement of the oxygen atom in the side chain of poly(dihexyloxyphosphazene) by an NH group increases the Kuhn segment by a factor of about three; thus the Kuhn segment of poly(dihexylaminophosphazene) is 350×10^{-8} cm.[91]

In several studies[2, 3, 48, 62, 186, 193, 194] dealing with the concentration dependence of the reduced viscosity of solutions of poly(alkoxy- and poly(fluoroalkoxy-phosphazenes), an abnormal character of this dependence has been observed, namely, the reduced viscosity increases upon dilution, as is normally observed for dilute solutions of polyelectrolytes. Viscosity, electrical conductivity, and dielectric properties of dilute THF solutions of four poly[bis(fluoroethoxy)phosphazene] samples were studied.[193] The following unusual properties were discovered:

(1) the reduced viscosity markedly depends on the shear rate;

(2) the reduced viscosity increases upon a decrease in the polymer concentration in the solution;

(3) the magnitude of the reduced viscosity of a polymer solution decreases and the pattern of its concentration dependence changes in the presence of various amounts of a salt (KI);

(4) the magnitude of the reduced viscosity and sedimentation constants S_0 of solutions decrease on passing from a more polar solvent to a less polar one.

This type of combination of hydrodynamic properties is quite typical of linear polyelectrolytes.[195]

The polyelectrolyte character of some poly(organophosphazenes), for example, poly[bis(trifluoroethoxy)phosphazene], is caused by anomalous units such as $-PCl(OCH_2CF_3)=N-$ and $-P(OH)(OCH_2CF_3)=N-$ present in the polymer chain.[2, 186, 193, 194]

The appearance of ionised groups can be explained by intra- or intermolecular interactions between two different units, for example, by formation of quaternary nitrogen atoms with chloride anions as counter-ions.[186] According to the results obtained by electron microscopy for dilute solutions of polymers in polar and moderately polar solvents such as acetone and tetrahydrofuran, ionised groups in these polymers result mostly from intramolecular interactions.[196]

Several studies[197–200] have been devoted to the Kerr effect in solutions of poly(fluoroalkoxyphosphazenes). Thus investigation of dynamic and electrical birefringence of solutions of the polyphosphazenes $-P[OCH_2(CF_2)_2H]_2=N-$, $-P[OCH_2(CF_2)_4H]_2=N-$, and $-P(OCH_2CF_3)_2=N-$ showed that the specific Kerr constants for these polymers in ethyl acetate are 4.8×10^{-8}, 5.7×10^{-8}, and 7×10^{-8} $cm^5\ g^{-1}\ (300\ V)^{-2}$, respectively. It was shown that polyphosphazene molecules are oriented in an electric field owing to their permanent dipole moment, which is collinear with the vector connecting the ends of the macromolecule. This accounts for the substantial contribution of large-scale motion to the orientation of macromolecules of polyphosphazene in an electric field.

The heat resistance of poly(organophosphazenes) depends appreciably on their chemical structure. Previously, glass transition temperatures for a number of poly(fluoroalkoxyphosphazenes) have been reported; for many of these polymers, these values are fairly low.[3] For example, the glass transition temperature of $\{-N=P[OCH_2(CF_2)_2OCF_3]_2-\}_n$ determined by the thermomechanical method is -99 °C.[77]

Tables 11–14 contain data on the glass transition and melting temperatures of a series of poly(organophosphazenes) with different substituents. These data show that poly(alkoxy- and poly(fluoroalkoxy-phosphazenes) possess the lowest glass transition temperatures. On passing to aryloxy substituents, glass transition temperatures of polyphosphazenes increase; finally, poly(diarylaminophosphazenes) possess the highest glass transition temperatures (Table 14). It can be seen from Table 13 that the glass transition temperatures of polyphosphazenes with mixed environments can be varied by changing both the chemical nature of substituents at the phosphorus atom and their ratio.

The heat resistance of polyorganophosphazenes with reactive side groups can also be changed by their chemical modification,[163] which is illustrated by Fig. 3.

Data on the physical state, in particular the phase composition, of poly(organophosphazenes) have been presented in numerous publications (see, for example, Refs 3, 19, 34, 34, 70, 77, 93, 94,

Table 11. Glass transition and melting temperatures of poly(dialkoxyphosphazenes) $[-N=P(OR)_2-]_n$.[92]

R	Physical state of polymers at 20°C	T_{gl} /°C	T_{melt} /°C
Me	amorphous	−77	does not crystallise
Et	"	−97	–
Pr	mesomorphic	−107	–
Pr	amorphous	−107	–
Bu	mesomorphic	−107	–
Bu	amorphous	−108	–
C_5H_{11}	mesomorphic	−110	–
C_6H_{13}	amorphous	−104	–
C_7H_{15}	"	−96	−17
C_8H_{17}	"	−77	4

Note. Glass transition and melting temperatures were determined by differential scanning calorimetry (DSC).

Table 12. Melting and glass transition temperatures of some poly(diaryloxyphosphazenes) $[-N=P(OAr)_2-]_n$.

Ar	T_{gl}/ °C [a]	T_{melt}/ °C [b]	T_{melt}/ °C [c]
C_6H_5	−1 (5.5)	160	390
p-$CH_3C_6H_4$	3 (0.3)	152	340
m-$CH_3C_6H_4$	−25 (−25)	90	348
p-ClC_6H_4	5 (4)	167	365
m-ClC_6H_4	−37 (−24)	66	370
m-$C_2H_5C_6H_4$	−30 (−18)	43	–
p-$CH_3OC_6H_4$	6 (13)	125	–

[a] T_{gl} were determined both by DSC and by thermomechanical analysis (values in parentheses);[122] [b] T_{melt} were determined by DSC at a heating rate of 20 deg min^{-1} (see Ref. 122); [c] T_{melt} were determined by the penetration method.[34]

Table 13. Glass transition temperatures of poly[(aryloxy)fluoroalkoxyphosphazenes] $[-N=P(OR')(OR'')-]_n$.

OR′	OR″	Content of groups (%) [a]		T_{gl}/°C	Ref.
		OR′	OR″		
OC_6H_5	OC_6H_5	100	–	−8	1
OC_6H_5	OCH_2CF_3	41	46	−30 [b]	81
OC_6H_5	$OCH_2CF_2CF_2H$	37	53	−50 [b]	81
OC_6H_4Cl-*p*	OC_6H_4Cl-*p*	100	–	−12	121
OC_6H_4Cl-*p*	OCH_2CF_3	78	8	−20 [b]	81
OC_6H_4Cl-*p*	OCH_2CF_3	52	47	−25 [b]	81
OC_6H_4Cl-*p*	$OCH_2CF_2CF_2H$	59	33	−40 [b]	81
$OCH_2CF_2CF_2H$	$OCH_2CF_2CF_2H$	–	100	−60 [b]	81
OCH_2CF_3	OCH_2CF_3	–	100	−66	1

[a] According to elemental analysis. [b] According to thermomechanical tests at a load applied to the sample of 0.8 kgf cm^{-2} and a heating rate of 1 deg min^{-1}. The T_{gl} was taken to be the temperature of 2% deformation of the specimen.

100, 121, 201–246). Studies of physical transformations of poly(organophosphazenes) carried out by scanning calorimetry, thermoanalytical methods, nuclear magnetic resonance, and X-ray diffraction [3, 19, 34, 70, 77, 121, 202–208] demonstrated that some of them exhibit two temperature transitions, despite the fact that they are flexible-chain polymers and contain no mesogenic groups. The lower-temperature transition T_1 corresponds to melting of the crystalline phase with retention of a certain degree of ordering, *i.e.* at T_1 the polymer passes into a mesomorphic state.

Table 14. Glass transition temperatures of some poly(diarylamino-phosphazenes) $[-N=P(NHAr)_2-]_n$.[36, 123]

Ar	T_{gl} /°C	Ar	T_{gl} /°C
C_6H_6	105	*p*-$Bu^nC_6H_4$	53
p-MeC_6H_4	97	*p*-$MeOC_6H_4$	92
m-MeC_6H_4	76	*p*-ClC_6H_4	85
p-EtC_6H_4	88	*m*-ClC_6H_4	80
m-EtC_6H_4	61	*m*-FC_6H_4	80

Note. T_{gl} were determined using a thermal analyser at a heating rate of 10 deg min^{-1}.

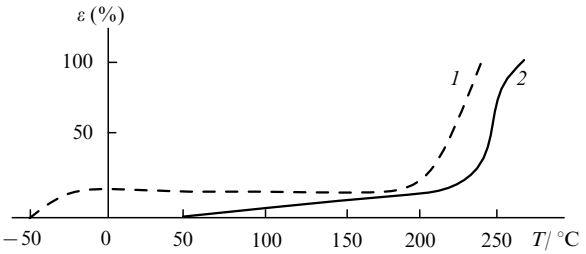


Figure 3. Thermomechanical curves for poly(tetrafluoropropoxy)(*o*-allylphenoxy)phosphazene $-N=P(OCH_2CF_2CF_2H)_{1.96}(OC_6H_4CH_2.CH=CH_2)_{0.04}-$.
(*1*) before curing; (*2*) after curing with tetramethylhydrodisiloxane in a film at 65 °C for 4 h in the presence of hydrogen hexachloroplatinate. The load applied to the specimen was 0.8 kgf cm^{-2}, the heating rate was 1 deg min^{-1}.

The upper temperature at which it transforms into an isotropic liquid is the true melting temperature (T_{melt}). For some poly(organophosphazenes), these two transitions are separated by an unusually broad temperature range; in some cases, it reaches 150–250 °C or even more.[6, 34] For example, T_1 and T_{melt} for poly[bis(trifluoroethoxy)phosphazene] are approximately ∼90 °C and 240–250 °C;[13, 34] those for poly[chloro(phenoxy)-phosphazene] are 169°C and 356 °C.[34]

The physical state of poly(dialkoxyphosphazenes) has been studied in a number of publications.[92–94, 244] The influence of the length of the pendent alkoxy groups (ranging from methoxy to octyloxy) in polyphosphazenes on their glass transition temperatures, crystallisation, and the ability to form mesophases has been analysed (see Table 11). For poly(dibutoxyphosphazene), it was found that a mesophase is formed only when the total content of defective units in the polyphosphazene is < 0.1 mol.%.[93, 94] Thus, the mesomorphic properties of poly(organophosphazenes) are crucially dependent of the chemical homogeneity of their structure. The transition of poly(butoxyphosphazene) from the mesomorphic to the isotropic state occurring at 200 °C is accompanied by a small thermal effect (1.3 J g^{-1}). It was shown for poly(dipentyloxyphosphazene) that the formation of the mesophase depends not only on the content of defective units in the polymer but also on the conditions under which the sample was prepared: when the solvent (benzene, THF, chloroform) is slowly evaporated from a polymer solution, the mesophase is formed, whereas fast evaporation or precipitation of the polymer yields an amorphous phase.[94]

IR and Raman spectra of poly(dialkoxyphosphazenes) $[-N=P(OC_mH_{2m+1})_2-]_n$, where m = 1–9, have been studied over a wide temperature range (from −100 to 100 °C).[247, 248] It was suggested that the backbone has a helical structure. Some temperature-induced spectral changes were attributed to conformation transitions in the side chains. When the temperature is lowered, the content of *trans*-isomers increases, whereas that of *gauche*-isomers decreases.

Various aspects concerning the physical state of poly(fluoroalkoxyphosphazenes) have been studied.[6, 13, 34, 201, 208, 210–232, 244, 245] For the homologous series of poly(fluoroalkoxyphosphazenes) with various lengths of the pendent groups,[231, 245] it was shown that the glass transition temperatures of the polymers increase with increase in the length of the side group, whereas the temperatures of the transition to the mesomorphic state, characterised by a hexagonal packing of the macromolecule backbones, scarcely change. The increase in the range of existence in the mesomorphic state for polymers with longer pendent groups is due to higher temperatures at which the polymer passes into the isotropic melt.

It has been noted in a review[13] that poly(fluroalkoxy-phosphazenes) are characterised by labile structures, which depend on the conditions of preparation of the polymer and its thermal prehistory. The main reason for the formation of the mesomorphic state in these polymers is specific interaction between the backbone and the pendent groups containing a large number of electronegative fluorine atoms. Primary attention was devoted to poly[bis(trifluoroethoxy)phosphazene]. It was noted that a peculiar structure of the mesophase of this polymer accounts for its ability to flow like a liquid in the mesomorphic state. The structure of the isotropic melt of the polyphosphazene retains the main features of the mesophase structure but is distinguished by a coil conformation of macromolecules.[212] In the 453–493 K temperature range, rheological properties and structural characteristics of the mesophase melt of the polymer substantially change, which is accompanied by a thermal effect.[213] It is believed that this change corresponds to a conformational transition of macromolecules into a structure intermediate between one-dimensional layered and two-dimensional pseudo-hexagonal structures. The mesophase in poly[bis(trifluoro-ethoxy)phosphazene] was found to be highly sensitive to external pressure; when the pressure increases (up to 400 MPa), the temperature (T_1) of the polymer transition from the crystalline state into the mesophase increases, the range of existence of the mesophase is sharply extended, and the mesophase becomes more ordered.[211]

Temperature transitions and the orientational order in the near-surface layers of poly[bis(trifluoroethoxy)phosphazene] films have been studied.[230] The glass transition temperature of this polymer is equal to -70 °C, the temperature of transition of the mesophase into a new modification is 120 °C, and the temperature of isotropisation and transition of the polymer into the amorphous state is 225 °C. It was found that the segment optical anisotropy of poly[bis(trifluoroethoxy)phosphazene] in the bulk is twice that in solution. This points to a strong orientational interaction of the macromolecules, resulting in the higher thermodynamic rigidity of polymer chains in the bulk than that in solution. It was noted that the structure of uniaxially oriented fibres of poly[bis(trifluoroethoxy)phosphazene] is fundamentally modified upon annealing at a temperature above the mesomorphic transition. The type of packing changes, namely, non-equilibrium α-phase passes into a thermodynamically stable γ-orthorhombic form.[216] It has been suggested that macromolecules of this polymer spontaneously straighten out in the mesomorphic state.

The phase transitions in poly(organophosphazenes) with partially fluorinated alkoxy groups $\{-N=P[OCH_2.(CF_2)_xCF_2H]_2-\}_n$, where $x = 1, 3, 5$, from the crystalline phase to the mesophase, which can be regarded as a conformationally disordered crystal, have been studied in detail by various physical methods.[217–220, 224] The temperatures of phase transitions in these polymers decrease linearly following an increase in the length of the pendent groups. The structure of poly[bis(pentafluoropropoxy)phosphazene] has been studied over a broad temperature range.[221, 222] It was found that the polymer macromolecules in the mesomorphic state undergo orientation during extrusion. The studies confirmed the condis-crystalline type of the mesophase with a pseudo-hexagonal packing.[222] It was established that poly[bis(heptafluorobutoxy)phosphazene] is capable of existing in the condis-crystalline and mesomorphic states. The mesophase of this polymer possesses high orientational and positional orders in the basis plane but is conformationally disordered.

The physical structure of poly[bis(halophenoxy)-phosphazenes] has been considered in a number of studies.[208, 233, 243] It was noted that the structures of their mesophases belong to the pseudo-hexagonal type. The physical structures of these polymers are markedly influenced by the thermal prehistory of a particular specimen.[243] The mesophase state can also occur in poly(organophosphazenes) with the following side groups: 4-n-$C_5H_{11}OOCC_6H_4-$, 4-n-$C_4H_9OOCC_6H_4-$, and 4-n-$C_{10}H_{21}OOCC_6H_4-$.[234]

Study of the structures and phase transitions of poly(dialkylaminophosphazenes) has demonstrated that linear highly chemically homogeneous polyphosphazenes of this type form thermally reversible, ordered phases.[119] An additional driving force for the self-organisation of these polymers is the formation of hydrogen bonds between the NH groups.[244]

A number of publications contain data on gas permeability of poly(fluoroalkoxyphosphazenes).[235–240, 246] In particular, it was noted that gas transfer through poly[bis(trifluoroethoxy)-phosphazene] is characterised by high selectivity parameters and, hence, this polymer is a promising material for gas separating membranes, for example, for separation of CO_2-containing mixtures.[235] The penetrability factor of this polyphosphazene in relation to the CO_2/CH_4 pair is ~ 10. Of particular interest is the mesophase of poly[bis(trifluoroethoxy)phosphazene], which can ensure production of membranes operating reliably at elevated temperatures.[235]

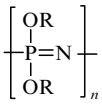
The physical state of poly(organophosphazenes) has a considerable influence on the properties of composite materials based on these polymers. Blends of poly[bis(trifluoroethoxy)-phosphazene] with polyethylene[13, 241, 242] and with the ABS plastic (a ternary copolymer of acrylonitrile, butadiene, and styrene) have been studied.[215] It was found that the unusual rheological properties of isotropic and mesomorphic polyphosphazenes can be used to modify the technological properties of ultra-high-molecular-mass polyethylenes. Polyphosphazenes added in small amounts sharply decrease the viscosity of polyethylene during extrusion and permit production of extrudates with good surface quality.[241] A decrease in the melt viscosity by approximately 40% was observed for mixtures of the ABS plastics with 10% of poly[bis(-trifluoroethoxy)phosphazene]. The increase in the elasticity of samples, formed from these mixtures, at 225–240 °C (processing temperatures) is presumably due to the orientation effect induced by the mesomorphic character of polyphosphazene in this temperature range.

Many poly(organophosphazenes) possess good film-forming properties; naturally, this requires that these polymers should have high molecular masses and homogeneous chemical structures. In particular, it has been noted[83] that high tensile strengths (about 2000 kgf cm^{-2}) of poly[bis(trifluoroethoxy)phosphazene] films are realised only when the molecular mass of the polymer is about 10×10^6. In addition, the data of Table 6 clearly demonstrate the influence of the unit non-uniformity of the polymer on the strength of polyphosphazene films. Films of poly[bis(trifluoroethoxy)phosphazene] with high molecular masses and chemically homogeneous macromolecules were found to possess long-term climatic stability under conditions of cold (Yakutsk, Russia)[249] and tropical[250] climates. Thus the service life of these films in the Arctic environment was found to be about 18 years, whereas for polyethylene, this period is only 2 years.

3. Medical and biological properties

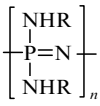
The high reactivity of poly(dichlorophosphazene) provides broad opportunities for preparing diverse poly(organophosphazenes) with specific biological properties, which can be used for the development of materials meant for medical purposes. They include thromboresistant,[14, 251, 252] self-resolvable,[253] biologically inert,[35, 36] and biologically active materials,[254–260] medi-

cines,[35,254–256] *etc*. In particular, biocompatibility of eight different poly(organophosphazenes) was tested *in vivo* in rat muscles.[36]



19–22

R = CH_2CF_3 (**19**), C_6H_4Me-*p* (**20**), $C_6H_4Bu^i$-*p* (**21**), $C_6H_4Bu^t$-*p* (**22**)



23–26

R = Ph (**23**), C_6H_4Me-*p* (**24**), $C_6H_4(CH_2)_3Me$ (**25**), $C_6H_4C_6H_4Cl$-*m* (**26**)

It was found that the influence of these substances on a living organism is as minor as that of the widely used silicone materials. These poly(organophosphazenes) can be applied as film coatings onto parts to be implanted, or introduced into various compositions.

Especially interesting results have been obtained in a study of medical and biological characteristics of poly[bis(trifluoro-ethoxy)phosphazene][14,251,261–263] with a molecular mass of about 16×10^6 and the minimum unit non-uniformity (the concentration of anomalous units with non-substituted P–Cl groups was as low as 5.8×10^{-4} mole fraction).[251] Thromboresistant properties of more than 100 poly(organophosphazene) samples as films and sutureless tubes have been assayed *ex vivo* by platelet tests and the dynamics of parietal thromogenesis in dogs.[14,262] The results presented in Fig. 4 indicate that in thromboresistance (the number of platelets adhered to the surface of the polymers studied upon contact with blood), poly[bis(trifluoroethoxy)phosphazene] substantially surpasses poly(tetrafluoroethylene) and polyethylene

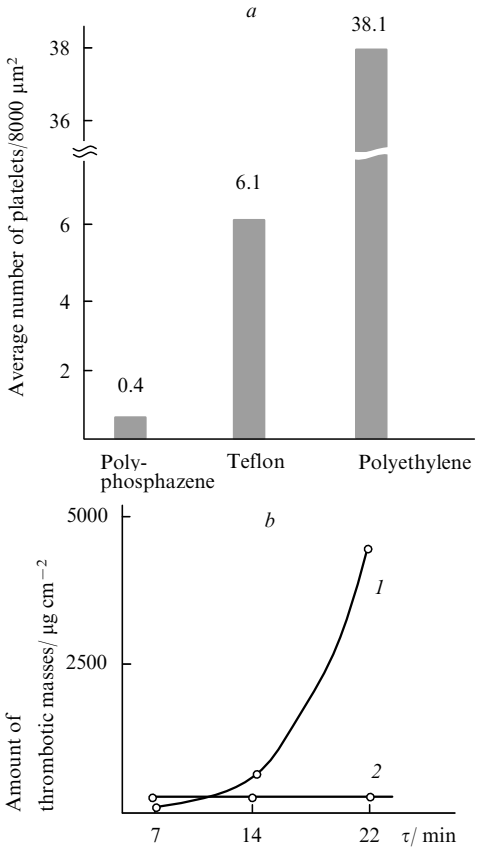


Figure 4. Thromboresistant properties (*a*) and dynamics of parietal thrombogenesis (duration of the contact of the polymer with blood — 1 min) (*b*) of 100 samples of poly[bis(trifluoroethoxy)phosphazene] ($M = 16 \times 10^6$, proportion of anomalous units 0.06 mol.%) tested in 10 mongrels.
(*1*) polyethylene, (*2*) polyphosphazene.

Table 15. Mechanical properties of nonoriented poly[bis(trifluoro-ethoxy)phosphazene] films after contact with blood serum at 40 °C.

Duration of the contact (months)	$[\eta]$/ dl g^{-1} (acetone)	σ_{tc} / kgf cm^{-2}	σ_{tr} / kgf cm^{-2}	ε (%)	E/ kgf cm^{-2}
0	4.00	190	1160	530	725
3	2.90	215	1400	580	910
6	2.70	230	1370	505	1000
8	3.02	170	840	395	1120
12	2.73	160	840	415	1600
16	2.60	140	700	390	1550
24	2.68	146	653	347	1200

Note. σ_{tc} and σ_{tr} are conventional and real tensile stresses related to the initial and ruptured cross-sections of the specimen, respectively; ε is the relative elongation at break; E is elasticity modulus.

meant for medical purposes.[14,251] Polyphosphazene is also superior to polyethylene as regards the dynamics of parietal thrombogenesis.

The strength characteristics of poly[bis(trifluoroethoxy)-phosphazene] films (Table 15) remain at a good level even after a 2-year contact with blood serum (the results were obtained *in vitro*).[261] Toxicological assays carried out with an isolated frog heart, male genital cells of animals, and isolated erythrocytes have also demonstrated that films of this polyphosphazene are free from general toxicity; they are highly chemically stable and exert no toxic effect on organs.[262]

Biological assays of a polyphosphazene[264] as monofilament threads was carried out *in vivo* for 6 months in 12 rats, 4 rabbits, and 2 dogs. Suturing polyphosphazene threads were used in surgical operations in various tissues. These sutures do not cause inflammation in tissues; they are quickly covered by a conjunctive tissue and do not adsorb the tissue liquid. In addition, they are antiseptic and non-toxic and are resolved in living tissues at a controllable rate (from 2 weeks to more than 6 months).[264] A fluorinated alcohol, phosphate, and ammonia are the final products of destruction of polyphosphazene filaments. It was concluded that the set of medical and biological properties of polyphosphazene suturing materials permit them to be widely employed in surgery. Polyphosphazene filaments can also be employed to produce a special reinforced jersey fabric for sutureless tubes used in endoprosthetic appliances for the restorative surgery of the upper respiratory tract and for other purposes.

IV. Conclusion

Nowadays, the most widespread method for the synthesis of poly(organophosphazenes) is the polymeranalogous substitution of the chlorine atoms in poly(dichlorophosphazene) by various organic groups. This opens up way for targeted design of polymeric chains and, hence, for the preparation of polymers with diverse properties. However, this synthetic route is characterised by poor reproducibility of experimental results. Nevertheless, these difficulties can be overcome provided that the regularities of the formation of poly(dichlorophosphazene) and polymeranalogous substitution are known. In this case, the method can be used successfully to prepare high-quality poly(-organophosphazene) materials with long service lives.

Poly(organophosphazenes) possess a broad range of specific properties and may be of interest for various practical purposes.[1,3,8,9,12,14,24,31,33,35,36,265–276] There are prospects for using them as materials operating at low temperatures (non-freezing elastomers, lubricants, *etc*.). Vulcanisates of poly(fluoro-alkoxyphosphazene) elastomers are resistant to fuels, oils, and hydraulic fluids; they are also highly stable with respect to oxygen and ozone and can operate over a wide temperature range, from −65 to 175 °C. Regarding their resistance to repeated low-

temperature deformations, these materials surpass vulcanised materials based on fluorine-containing and fluorosilicone rubbers.[266] They can be used to manufacture antivibration and packing gaskets, rings and sleeves, fuel pipes, and other parts for air and space engineering, petrochemical industry, and other branches of industry.[3, 4, 14, 31, 33, 148, 168, 265, 266, 268] In regions with a cold climate, poly(fluoroalkoxyphosphazenes) can be used both by themselves and as low-temperature modifiers for other materials.[249]

Some poly(organophosphazenes) can be useful as flame-retardant articles.[33] Thus poly(aryloxyphosphazenes) are highly fire-resistant, and simultaneously they evolve only little smoke. These elastomers appear to be promising as insulating materials for closed spaces such as submarines and planes; they can be used to insulate electric cables and to produce insulating foam plastics.[265–267]

There are data on using poly(organophosphazenes) as elastic hermetic adhesives for inert materials [164] and for impregnation of textiles in order to impart water- and soil-repelling properties to them.[272] Being used to modify other polymers, polyethylene and ABS plastics,[13, 241, 242] polyvinylphenylsiloxane rubber,[270, 271] polyesters, phenolic and epoxide polymers,[10, 24] *etc*., poly(organophosphazenes) improve in some cases technological properties, elasticity, flame resistance, and thermal stability of these materials.

Poly(organophosphazenes) present considerable interest as polymers used for specific non-trivial purposes, for example, in polymeric catalytic systems,[14, 113, 254] as solid electrolytes,[273, 275] or as electrodes in chemical cells.[274]

Poly(organophosphazenes) are undoubtedly promising for medico-biological purposes, for example, as self-resolvable suture materials meant for diverse purposes in surgery, anaesthetic preparations, and medicines,[14, 35, 36, 251–264, 276] thromboresistant materials for reliably operating artificial organs (prosthetic blood vessels, heart valves, and ventricles of heart, endoprosthetic respiratory tracts, *etc*.)

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