Translated from *Uspekhi Khimii*, 51 266 - 284 (1982) U.D.C. 541.64:547.241

Polyphosphazens

V.V.Kireev, G.I.Mitropol'skaya, and Z.K.Zinovich

The main features of the catalytic and thermal polymerisation of chlorocylophosphazens are examined, with a possible mechanism of rearrangement of rings in the thermal polymerisation of mixtures of cyclic chlorophosphazens. Research on the influence of side-groups on the chemical and physicochemical properties of polyorganophosphazens (polydialkoxyphosphazens, polydiaminophosphazens) is discussed, as well as aspects of the vulcanisation and stabilisation of these polymers. The chemical properties, structure, molecular-mass characteristics, and thermal stability of polyphosphazens are surveyed, and also the application of these polymers in the national economy. A list of 151 references is included.

CONTENTS

I. Introduction 149
II. Polyhalogenophosphazens 149
III. Polyorganophosphazens 152
IV. Properties of polyphosphazens 154
V. Applications 157

I. INTRODUCTION

Interest in polyphosphazens has increased considerably during recent years, as a consequence of the undoubted practical value of this interesting class of hetero-organic polymers. The large quantity of experimental results and the many original investigations following publication of Allcock's monograph[1] and a review[2] have made it necessary to summarise some of the most important aspects of the chemistry of polyphosphazens. We have now attempted to systematise work appearing during recent years on the synthesis and properties of linear homopolyphosphazens, a most interesting and industrially important type of phosphazen polymers. The survey of published data has taken into account recent reviews[3-10], most of which cover only part of the field or are essentially advertising material.

II. POLYHALOGENOPHOSPHAZENS

The only method for synthesising linear macromolecular polyphosphazens has been to replace halogen atoms in polydihalogenophosphazens by various groups. Since polydichlorophosphazen is most often used for this purpose, establishment of the laws and mechanism of its formation in the polymerisation of chlorocyclophosphazens is a most urgent problem of phosphazen chemistry.

The polymerisation of cyclic chlorophosphazens

$$(PNCl_2)_n \xrightarrow{200-300^\circ} -\left[\begin{array}{c} Cl \\ | \\ -P=N- \\ | \\ Cl \end{array}\right]_x -$$

$n=3-8,\ x \lesssim 15\,000$

known long ago from the work of Stokes[11], can be accomplished either thermally or catalytically. Research during recent years on the catalytic polymerisation of hexachlorocyclotriphosphazen has determined the most effective range of catalysts for subsequent investigation. Alkali-metal phenoxides and alkoxides[12], inorganic acids, and hetero-organic Lewis acids (e.g. ethylaluminium halides)[13] enable the temperature to be lowered to 200 °C. Use of 1 mass % of phosphoric acid[17] also permits the above chlorocyclophosphazen to be polymerised in a solvent (1,2,4-trichlorobenzene) at this temperature; the resulting polydichlorophosphazen has a lower molecular mass and a broader distribution thereof than has that obtained purely thermally[7,14].

The use of metal chlorides[15], known some time ago for the splitting of chlorocyclophosphazens[16,17], enables the temperature of polymerisation to be lowered to 175–200 °C, but also leads to a decrease in molecular mass that is larger the greater the quantity of catalyst.

Ring opening occurs in hexachlorocyclotriphosphazen under mild conditions in the presence of phenylmagnesium bromide[18] or diphenylmagnesium[19], and especially readily (at 20 °C) on treatment with phenyl-lithium[20]. In the last case the first stage involves formation of a linear product $C_6H_5PCl_2NPCl_2$. $.NPCl_2NLi$, which undergoes further phenylation by excess of phenyl-lithium (mainly from the end), but in the presence of a deficiency of this compound branched structures are formed owing to interaction with other similar molecules, the resulting oligomer having molecular mass up to 2000 and relative composition

$$(C_6H_5)_3P : (C_6H_5)_2P : PCl_2 = 5 : 2 : 22.$$

Low-temperature opening of phosphazen rings is fundamentally possible[18-20], but the catalysts used must be inert towards phosphorus–chlorine bonds.

Since effective catalysts for the polymerisation of chlorocyclophosphazens have not yet been found, thermal polymerisation mainly of a cyclic trimer remains the chief method for obtaining polydichlorophosphazen. Despite the large amount of research on thermal polymerisation[1,2] methods are not yet available for conducting the process under controlled conditions, which would yield reproducible results; nor can the yield, solubility, and molecular-mass characteristics of the products be controlled.

It now seems highly likely that the usual thermal polymerisation of hexachlorocyclotriphosphazen and other chlorocyclophosphazens is not a truly thermal process, but is determined in considerable measure by the presence of impurities in the initial cyclic compound and on the walls of the reaction vessels. Thus hexachlorocyclotriphosphazen that has been thoroughly purified by successive recrystallisation, boiling with barium oxide in a stream of nitrogen at 130 °C, passage of the vapour over phosphorus pentoxide, and vacuum sublimation does not polymerise below 300 °C,[21] but rapid polymerisation begins after the introduction of oxygen. The reason for this and the nature of the active centres were not discussed[21]. An effective method for purifying the trimer is first to heat it under polymerisation conditions (200–250 °C) for 15–180 min and then distil[22]: polymerisation of the purified product gives a higher yield

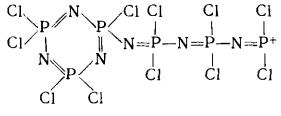
of soluble polydichlorophosphazen, but the rate of the process is lowered.

The now preferred ionisation mechanism of the thermal polymerisation of hexachlorocyclotriphosphazen[23-25] involves as initial stage heterolysis of a phosphorus–chlorine bond with formation of a cyclic azophosphonium cation

$$P_3N_3Cl_6 \rightleftarrows P_3N_3Cl_5^+ + Cl^-$$

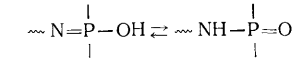
that initiates chain growth. It was confirmed in later work[26,27], and agrees well with conductivity measurements on the trimer and on polydichlorophosphazen[28].

Examination of the effects of pH at the surface of the glass ampoules, temperature, and duration[29], indicating an increase in the rate of polymerisation of hexachlorocyclotriphosphazen with increase in acidity of the glass, suggested in terms of the ionisation mechanism[26] that chain growth begins with protonation of a trimer molecule. The cation $P_3N_3Cl_6H^+$ then reacts with a second trimer molecule to eliminate hydrogen chloride and form the cyclolinear cation

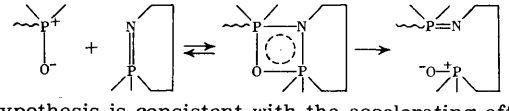


which is responsible for further chain growth, as in the usual ionisation polymerisation[26].

However, the hydrogen chloride not only does not catalyse polymerisation but is even capable of inhibiting it slightly[30]. Phosphorus pentachloride is a stronger inhibitor of this process, and also acts as a telogen[30,32]. The accelerating effect of small additions of water (10^{-5}–10^{-1} mole mole^{-1} trimer) also indicates that the main role in initiating polymerisation is played by acid centres of the type

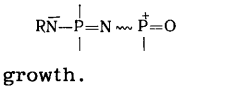


formed at the same time as hydrogen chloride[30,31]. Allcock's results[30] indicate that chain growth in the polymerisation of chlorocyclophosphazens is effected not only by an azophosphonium cation but also by a terminal phosphoryl group:



(1)

This hypothesis is consistent with the accelerating effect of phosphoric acid[17] and alkoxy-derivatives of the trimer[12] on its polymerisation; it is assumed in the latter case that phosphazen–phosphazan rearrangement takes place, and the resulting phosphazan is converted into a zwitterion



which initiates chain growth.

Although formation of cationic centres seems to be generally accepted as initiating chain growth in the thermal polymerisation of hexachlorocyclotriphosphazen, information on the laws of chain growth and termination has hitherto been almost completely lacking, and the reasons for the wide molecular-mass distribution in particular have remained obscure.

Interesting results have been obtained from investigation of the copolymerisation of hexachlorocyclotriphosphazen with other chlorocyclophosphazens. Although a patent report[33] that the rate and the yield of soluble polydichlorophosphazen in the polymerisation of this trimer are increased by the presence of 5–25% of octachlorocyclotetraphosphazen has not been confirmed[34], and additions of other higher chlorocyclophosphazens only slightly raise the yield of soluble product[35], study of the thermal copolymerisation of the trimer with its higher cyclic homologues has revealed the phenomenon of ring rearrangement, mostly involving increases in the proportion of tetramer and other homologues in the initial stages of polymerisation[36,37] (Table 1). This was first detected by Allen et al.[75], who synthesised polydichlorophosphazen by the thermal polymerisation (at 250 °C) of the trimer containing 2.9% of the tetramer, and found that increasing the duration of the process from 20 to 62 h not only raised the yield but also increased the content of higher homologues—especially pentamers and hexamers—in the mixture that had not reacted. However, at the time due attention was not paid to this interesting observation.

Table 1. Variation in composition of mixture of cyclic chlorophosphazens $(PNCl_2)_n$ during thermal block polymerisation at 250 °C[37]*.

3:4:5:6:7	W,%	ΔG, %			
		n=4	n=5	n=6	n=7
77 : 23 : 0 : 0 : 0	8	330	—	—	—
95 : 0 : 0 : 5 : 0	26	—	—	300	—
95 : 0 : 1 : 0 : 4	20	—	—	—	240**
95 : 0 : 1 : 0.1 : 3.9	14	—	126	730	260
90 : 0 : 2 : 1 : 7	8	—	92	300	120
85.5 : 9.5 : 1 : 0.25 : 3.75	24		106	450	210

*Column headings: 3:4:5:6:7 = proportions by weight in initial mixture of homologues having n = 3–7; W = yield of polydichlorophosphazen; ΔG = change in content of chlorocyclophosphazens (% on initial quantity of each ring).
**Total quantity of pentamer and heptamer.

Interconversions of rings have in general been known in phosphazen chemistry for a comparatively long time. Thus as early as 1960 Korshak et al.[38] observed the conversion of octaphenylcyclotetraphosphazen at 320–500 °C into a mixture of tri-, tetra-, penta-, and hexa-mers; hexakisheptafluorobutoxycyclotriphosphazen when boiled at 340 °C for 50 h is 50% converted into a tetramer[39]; and the reverse conversion of a tetrameric into a trimeric ring takes place when octachlorocyclotetraphosphazen is phenylated with phenylmagnesium bromide[40]. Interconversions of mixtures of cyclic chlorophosphazen homologues from trimer to heptamer during their vacuum distillation and in certain low-temperature (20–80 °C) nucleophilic substitutions have been reported recently[41], and also those of trimeric into tetrameric dimethylcyclophosphazens over the range 200–350 °C.[42] However, a distinguishing feature of this work[38-42] is that interconversions of chlorocyclophosphazens at 20–500 °C are not accompanied by polymer formation (except in the vacuum distillation of mixtures[41]).

In addition to the above work[36,37] formation of higher cyclic homologues from trimeric phosphazens has been observed by Allcock et al.[43] in a study of the thermal polymerisation of trifluoroethoxychlorocyclotriphosphazens $P_3N_3Cl_n(OCH_2CF_3)_{6-n}$ and the copolymerisation of hexachlorocyclotriphosphazen with the hexakistrifluoroethoxycyclotriphosphazen (I) (Table 2). Among the most important aspects of this work[43] pure (I) does not polymerise below 300 °C, but when heated at 275 °C for > 46 h, small quantities of the corresponding

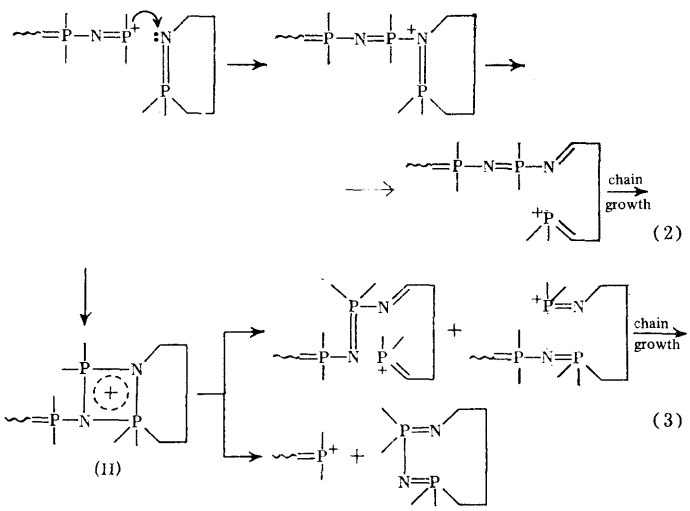
tetramer and pentamer are formed; copolymerisation of hexachlorocyclotriphosphazen and (I) takes place at 200 °C, at which temperature neither of the pure individual compounds polymerises; among partly substituted trifluoroethoxychlorocyclotriphosphazens only those having $n = 5-3$ undergo polymerisation; above 230 °C polycondensation takes place with the evolution of 2-chloro-1,1,1-trifluoroethane; and the molecular masses of the products of the above copolymerisation are lower than those resulting from the polymerisation of pure hexachlorocyclotriphosphazen.

Table 2. Copolymerisation of equimolecular quantities of hexakistrifluoroethoxycyclotriphosphazen (I) and hexachlorocyclotriphosphazen (III) at 200 °C[43]*.

t, h	(III):(I)	(I + III):(IV)	$PNCl_2$:$PN(OCH_2CF_3)_2$	t, h	(III):(I)	(I + III):(IV)	$PNCl_2$:$PN(OCH_2CF_3)_2$
24	1:1.3	1:0.024	—	32	1:2.0	1:0.:55	1:0.9
27	1:1.5	1:0.025	1:1.3	36	1:2 1	1:0.130	1:0.9
30	1:1.7	1:0.041	1:0.8	50	1:2.4	1:0.160	1:1.0

* Here t = duration of process; (I) and (III) given in mole proportions; (IV) = proportion by weight of (I + III) and other cyclic oligomers; and $PNCl_2 : PN(OCH_2CF_3)_2$ = mole proportions of $PNCl_2$ and $PN(OCH_2CF_3)_2$ units in copolymer.

The considerable increase in the content of higher chlorocyclophosphazens accompanying formation of polydichlorophosphazens in the initial stage of their copolymerisation with hexachlorocyclotriphosphazen has been explained[37] by specific interaction of the growing macrocation with cyclophosphazen molecules. The usual interaction (2) leading to further chain growth may be accompanied by an anomalous reaction involving formation of a cyclic transition state (II):



Localisation of the positive charge on either phosphorus atom of the four-membered ring (II) will entail its cleavage with increase in the length of the macrocation by the number of units of the initial ring. In view of the great stability of four-membered cyclic systems in phosphazen chemistry[44], however, it may be postulated that the transition state (II) can also break down at an exocyclic phosphorus–nitrogen bond (3). The additional structural units expanding the chlorophosphazen rings are thus provided by growing macrocations, which as a consequence of specific interaction with cyclic molecules (3) become one unit shorter, and this unit is incorporated into the ring under attack, which becomes larger.

Reaction (3) can evidently take place also with $-N=P<$ units of linear macromolecules that have already been formed, and the proportion of such interaction will increase with the degree of conversion. It may provide one reason for the observed wide molecular-mass distribution of polydichlorophosphazen. Determination of the proportions of reactions (2) and (3) in an actual process must obviously take into account both structural and thermodynamic factors. The strain in a ring, which governs the energy of its vapour-phase polymerisation, may differ substantially for different conformers[45]. For example, the difference in strain between crenulated planar and buckled C_2 forms of the cyclic pentamer, which characterise crystalline and liquid states respectively, is 18.75 kJ mole^{-1}.

Table 3. Polymerisation of fluoroalkoxychlorocyclotriphosphazens[46].

Cyclophosphazen	R_FO:Cl	T, °C	t, h	W *, %	$[\eta]$, dl g^{-1}
$(C_2F_5CH_2O)_2P_3N_3Cl_4$ (V)	0.5:1	200	80	70.5	0.55
$(C_3F_7CH_2O)_2P_3N_3Cl_4$	0.5:1	200	120	73.0	0.50
(V) + $(C_2F_5CH_2O)_6P_3N_3$ **	1.24:1	260	90	76.2	***
$(C_2F_5CH_2O)P_3N_3Cl$	5:1	270	100	0	
$(C_2F_5CH_2O)_nP_3N_3Cl_{6-n}$ ****	2.23:1	270	100	0	

* Yield of polymer.
** Mixture of 53% (V) + 47% $(C_2F_5CH_2O)_6P_3N_3$.
*** Polymer swells strongly but does not dissolve.
**** Contents of homologues having n = 3–6 respectively 25%, 50%, 10%, and 15%.

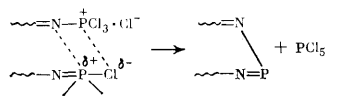
The presence of ring substituents other than chlorine atoms will also influence the probability of formation of transition state (II), so that the capacity of partly substituted chlorocyclophosphazens for thermal polymerisation becomes significant. Even before the appearance of Allcock's work[43] it had been reported[46,47] that fluoroalkoxychlorocyclotriphosphazens can polymerise at 200 °C. The process occurred only when $R_FO : Cl \leq 2 : 1$ (Table 3). When mixtures of hexachlorocyclotriphosphazen with hexakisperfluoroalkoxycyclotriphosphazen or other mixtures satisfying the above ratio are used, polymerisation is apparently preceded by exchange of substituents[48], which is not excluded by Allcock et al.[43]

In the polymerisation of fluoroalkoxychlorocyclotriphosphazens, however, the proportion of polycondensation processes accompanied by separation of a fluoroalkyl chloride increases with rise in temperature[43]. Such processes take place at lower temperatures with non-fluorinated alkoxyphosphazens—e.g. at 150–170 °C with butoxychlorocyclotriphosphazens[49]—although polycondensation of the latter with separation of butyl chloride and formation of polymers containing P–O–P links between phosphazen rings is also accompanied[50] by polymerisation with ring opening.

It is therefore more interesting, from the point of view of capacity for polymerisation, to investigate alkylchlorocyclotriphosphazens containing the more stable phosphorus–carbon bonds. Trimethyltrichlorocyclotriphosphazen, tetramethyltetrachlorocyclotetraphosphazen, and their mixtures are polymerised[51] at 200–220 °C after 15–20 h, with formation of a rubberlike product having viscosity $[\eta] = 0.5–0.7$ dl g^{-1}. Use in the thermal polymerisation of hexachlorocyclotriphosphazen of additions of its partly substituted derivatives of general formula $R_xP_3N_3Cl_{6-x}$ (R = CH_3, CF_3CH_2O, or other fluoroalkoxyl; $x \leq 1.5$) not only shortens the process but also raises the yield of soluble polydichlorophosphazen[52].

In an investigation of the thermal polymerisation of a series of phenylhalogenocyclotriphosphazens Allcock and Moore established[53] that only the phenylpentafluoro-compound is capable of homopolymerisation at 300 °C: geminal and non-geminal compounds $(C_6H_5)_nP_3N_3Cl_{6-n}$ having $n = 2–6$ do not polymerise at this temperature, although at 250 °C homologues in which $n = 2$, 3 copolymerise with an equimolecular proportion of hexachlorocyclotriphosphazen, but products in which $n = 4–6$ inhibit polymerisation of the latter. The copolymers have a considerably lower molecular mass than has the polydichlorophosphazen obtained by its homopolymerisation. Results[47,53] are fully consistent with the above mechanism of chain growth (schemes 2 and 3). Attempts to effect the catalytic polymerisation of hexaphenyl- and hexaphenoxy-cyclotriphosphazens in the presence of strong acids gave only a low yield of oligomeric products, whose formation involves intermediate detachment of side-groups[54–56]. Yet a report appeared on the thermal polymerisation of an aryloxypentachlorocyclotriphosphazen[57], essentially by a modification of the method of Ref. 12.

Among other methods for obtaining polydichlorophosphazen is its synthesis from linear oligomers $Cl_3P{:}N.[PCl_2{:}N]_n.PCl_4$ ($n = 3–15$) by prolonged heating at 240–260 °C. The process is accompanied by separation of phosphorus pentachloride, obviously by the reaction of terminal groups[58]:



Thermal degradation of polydichlorophosphazen is a first-order reaction having activation energy 92.11 kJ mole^{-1} and yielding a large number of oligomeric linear and cyclic homologues[59]. It is assumed to involve ionic terminal groups, which is consistent with the known[1,2] equilibrium character of the polymerisation of chlorocyclophosphazens.

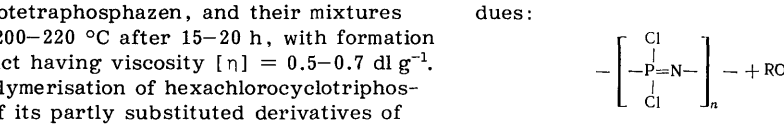
X-Ray examination of polydifluorophosphazen–the phosphazen polymer having the smallest of known side-groups–has yielded interesting results[60]. This polyphosphazen can be present as two conformers: conformer A exists between −36 and +25 °C, and has a repeat distance of 6.49 Å; conformer B is observed at around −56 °C, and has repeat distance 4.86 Å (for polydichlorophosphazen 4.96 Å). The latter conformer has a *cis–trans* planar chain conformation with P–N–P and P–F bond lengths 1.52 and 1.47 Å, and PNP, NPN, and FPF angles 136°, 119°, and 95° respectively. The density of polydifluorophosphazen at 25 °C is 1.84 g cm^{-3}.[60]

III. POLYORGANOPHOSPHAZENS

Interest in the synthesis of macromolecular linear polyphosphazens has grown considerably during recent years[61–63] in connection with the problem of producing thermostable and non-flammable rubbers having good resistance to cold.

1. Polydialkoxyphosphazens

These polyphosphazens are obtained by replacing chlorine atoms in polydichlorophosphazen by alcohol of phenol residues:



where R = Alk, Ar and M = alkali metal. The main trends in research during recent years have been the synthesis of polyperfluoroalkoxyphosphazens as potential fire-resistant and thermostable rubbers having high chemical stability and resistance to cold, investigation of the effect of the nature of side-groups on the chemical and physicochemical properties of such polymers, study of the possibilities of using polydialkoxyphosphazens for biomedical purposes, and a search for methods of vulcanisation and stabilisation.

It had been shown earlier[1] that polyphosphazens having identical lower perfluoroalkoxy-groups in the side-chain are in most cases crystalline. In order to obtain elastomeric products, therefore, the synthesis of polymers containing various groups–perfluoroalkyl[65–70] or mixed alkoxy-substituents[71,73,79–83]–has been investigated.

Table 4. Some properties of polyphosphazen copolymers $-[N{:}P(OR)(OR')]_n-$*.

R	R′	R:R′	$10^{-5}M$ ([η], dl g^{-1})	T_{gl}, °C	T_{decomp}, °C**	Ref.
CF_3CH_2	$C_3F_7CH_2$	1:1	50(1.46)	−71(−77)	300	[67]
CF_3CH_2	C_6H_5	1:1	(3.50)	—	460	[65]
CF_3CH_2	C_6H_5	1:1	(1.14)	−35	—	[105]
CF_3CH_2	$HC_6F_{12}CH_2$	1:1	(1.50)	−64	—	[67,69]
CF_3CH_2	$HC_4F_8CH_2$	1:1	—	−67	—	[67,69]
CF_3CH_2	$HC_4F_8CH_2$	1.9:1	(1.20)	−68	—	[92]
CF_3CH_2	$C_6H_4C_6H_4O$-*p*	1:0	—	−70	260	[70]
CF_3CH_2	$C_6H_4C_6H_4O$-*p*	0.4:1.6	—	−10	355	[70]
CF_3CH_2	$C_6H_4C_6H_4O$-*p*	0:1	—	43	320	[70]
$H(CF_2)_2CH_2$	C_6H_5	1:1	(1.32)	−50	—	[105]
CF_3CH_2	C_6H_4Cl-*p*	1:3	(1.03)	−20	—	[105]
CF_3CH_2	C_6H_4Cl-*p*	1:1	(0.84)	−25	—	[105]
$H(CF_2)_2CH_2$	C_6H_4Cl-*p*	1:1	(0.92)	−40	—	[105]

* Macromolecules may contain doubly and singly substituted phosphorus atoms.

** T_{decomp} = temperature at which decomposition begins.

Polyperfluoroalkoxyphosphazen copolymers are most often obtained from mixtures of trifluoroethoxides with fluorinated higher alkoxides[65–69] and also with phenoxides[65,81,105]. Sodium alkoxides are usually employed, although in some cases the lithium compounds are more effective[74]. Substitutions are conducted predominantly in oxolan, dioxan, diglyme, and their mixtures with benzene; the last is usually employed to dissolve polydichlorophosphazen. In order to increase the conversion the concluding stages are carried out at high temperatures, especially when aryloxy-groups are introduced[70,75–77]. Almost complete replacement of chlorine can thus be achieved, although this is influenced by various uncontrollable factors, assumed[78] to be connected mainly with the stage of polymerisation of hexachlorocyclotriphosphazen in the synthesis of polydichlorophosphazen.

By varying the nature and the proportions of side-groups it is possible to change within wide limits such properties of polydialkoxyphosphazens as solubility, glass temperature,

molecular mass and molecular-mass distribution, thermal stability, processability by various methods, etc.[78-85,89,91,92]. For this purpose substitution is effected with mixtures of alcohols and phenols[65,70,81,89], fluorinated C_{4-12} alcohols[79], and mixtures of phenols[80,83]. The properties of homoaryloxyphosphazens can be controlled by varying the nature and the position of constituents in the initial phenol[76,77,82]. Table 4 lists some of the properties of polyalkoxyphosphazen copolymers, among the most interesting of which are those of trifluoroethoxy- and octafluoropentyloxy-phosphazens. Thus a copolymer containing 65 mole % of CF_3CH_2O groups and 35 mole % of $H[CF_2]_4CH_2O$ groups has a glass point of −68 °C and does not swell in hydrocarbons; 86% of this copolymer comprises a macromolecular fraction having $\bar{M}_n$ = 1370600 and $\bar{M}_{wt}$ = 4085800 (M_{wt}/M_n = 3), whereas corresponding values for the unfractionated copolymer are 123700 and 3514500 (28.4).[92] The high polydispersity is evidently due to the presence of a considerable proportion of fractions of low molecular weight. For this copolymer the viscosity $[\eta] = 0.00488\bar{7}M_n$.[1,47]

Even with equimolecular proportions of the initial substituting reagents the resulting copolymers contain three types of units—two paired, NPR_2 and NPR'_2, and the mixed NPRR′—in quantities determined by (apart from the proportions of the initial reactants) the dimensions and the inductive properties of the new substituents. The presence in various combinations of three types of monomer units in the macromolecules of polyalkoxyphosphazen copolymers is responsible for their hyperelastic properties over a wide temperature range.

The low glass point of polyfluoroalkoxyphosphazens is due to the high thermodynamic flexibility of the main chain and the absence of side-group interactions. Introduction of bulky aromatic groups in the place of chlorine, however, raises the glass point, which is especially clearly shown[70] by the polyphosphazen copolymers $-[N{:}P(OCH_2CF_3)_{2-x}.(OC_6H_4C_6H_5\text{-}p)_x]-$. These copolymers are obtained by treating a solution of polydichlorophosphazen in benzene successively with a phenoxide and an alkoxide in oxolan, and are purified by reprecipitation from oxolan solution into water. In oxolan at 25 °C the copolymers have viscosities in the range $[\eta]$ = 1.06–2.20 dl g^{-1}, which fall with decrease in x; their molecular mass $\bar{M}_n = (0.9\text{–}3.3) \times 10^5$ (measured osmometrically in cyclohexanone). Fractionation showed the copolymers to be inhomogeneous with respect to composition: thus for a product having x = 0.15 this parameter is 0.32 for the fraction of high molecular weight, and 0.08 for that of low molecular weight. Heating the copolymers in air at 150 °C for 12 h lowers their viscosity $[\eta]$ by factors of 4–5. X-Ray examination shows the copolymers to be relatively disordered, with crystallites formed by the crystallisation of microblocks comprising $-N{:}P(OCH_2CF_3)_2-$ units, the presence of which is confirmed by the fluorine-19 nuclear magnetic resonance spectra[70].

A convenient method for the synthesis of polydialkoxyphosphazen copolymers is the transetherification of alkoxylated polymers with higher alcohols; alkoxides of the latter are used to obtain polyperfluoroalkoxyphosphazens[73,85]. Besides the alkoxide–phenoxide method an acceptor method is also available for the synthesis of polyalkoxyphosphazens[86,90,106,107]. Thus, when trifluoroethanol in oxolan at 60 °C is used to replace chlorine atoms in polydichlorophosphazen, the degree of substitution reaches 65% after 5 h, and a limiting value of 85% after 100 h; introduction of lithium chloride into the reaction mixture increases this to 90%. However, substitution is accompanied by side-reactions of polydichlorophosphazen with triethylamine and other processes, so that the heterounit character of the resulting polymer reaches 6.8%.[86] Nevertheless, the acceptor method of substitution in polydichlorophosphazen is more convenient for preparative purposes[50,106,107].

Table 5. Polydiaryloxyphosphazens $-[PN(OAr)_2]_n-$.

Ar	$[\eta]$, dl g^{-1}* initial polymer	$[\eta]$, dl g^{-1}* after heating**	T_{gl}, °C	M.p., °C	T_l, °C***	Ref.
C_6H_5	2.4	—	−1	160	400	[77]
m-ClC_6H_4	1.5	0.08	−35	—	380	[76]
p-ClC_6H_4	1.4	0.42	−12	—	400	[76]
p-ClC_6H_4	1.6	—	5	167	385	[77]
2,4-$Cl_2C_6H_3$	12.0	1.5	2	—	440	[76]
p-FC_6H_4	9.0	—	−14	—	385	[76]
p-$CH_3C_6H_4$	1.8	—	3	152	310	[77]
m-$CH_3C_6H_4$	1.8	—	−25	90	340	[77]
p-$C_2H_5C_6H_4$	3.2	—	−36	43	250	[77]
o-$CH_3OC_6H_4$	1.8****	—	6	125	330	[77]
β-$C_{10}H_7$	1.9*****	0.5	47	—	475	[76]
p-$C_6H_4C_6H_4$	1.2*****	0.7	43	—	390	[76]

* Measured in oxolan at 25 °C.
** At 255 °C for 8 h.
*** T_l = temperature of 10% loss in mass.
**** In chloroform.
***** In dimethylformamide.

Table 6. Polybisarylaminophosphazens $-[PN(NHAr)_2]_n-$.

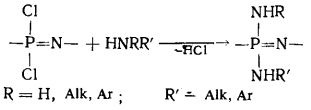
Ar	$[\eta]$ *dl g^{-1}*	T_{gl}, °C	T_{decomp}, °C**	Ref.
C_6H_5	1.4	105	—	[87]
C_6H_5	1.2	98	—	[88]
p-$CH_3C_6H_4$	1.3	97	250	[87]
p-$CH_3C_6H_4$	1.1	95	—	[88]
p-$CH_3OC_6H_4$	1.3	92	266	[87]
p-$CH_3OC_6H_4$	1.2	90	—	[88]
p-$C_2H_5C_6H_4$	0.7	61	243	[87]
m-$C_2H_5C_6H_5$	1.5	53	253	[87]
n-$C_4H_5C_6H_4$-p	0.9	92	266	[87]
p-ClC_6H_4	0.6***	85	265	[87]
p-ClC_6H_4	1.0***	70	—	[88]
p-ClC_6H_4	1.3***	80	253	[87]
p-FC_6H_4	0.7***	—	260	[87]
m-FC_6H_4	0.3***	80	249	[87]

* Measured in oxolan at 25 °C.
** From dynamic thermogravimetric analysis in air, ΔT = 20 deg min^{-1}.
*** In chloroform.

Several polyaryloxyphosphazens having identical side-groups have been synthesised and characterised[75-77]. These polymers are soluble in dimethylformamide and oxolan, have viscosities $[\eta]$ = 0.8–12 dl g^{-1} (Table 5), and are shown by X-ray examination to be only slightly ordered with glass points between −40 and +50 °C. Polydialkoxyphosphazens $\{[P(OR)_2{:}N]_2.P(OR)(OR'){:}N-\}_n$ with regularly alternating (every two phosphorus atoms) R′ groups are obtained by the action of alkoxides or phenoxides on linear polymerisation products of monoaryloxypentachlorocyclotriphosphazens $R'OP_3N_3Cl_5$.[12,133]

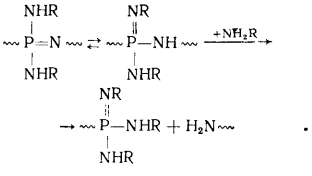
2. Polydiaminophosphazens

Polydiaminophosphazens are obtained by replacing chlorine atoms in polydichlorophosphazen with residues of primary or secondary amines:



Either the initial amine or a specially added tertiary amine can act as acceptor of the hydrogen chloride formed[87,88,94-96].

Polybisarylaminophosphazens have higher glass points (Table 6) than have polydiaryloxyphosphazens, as a consequence of the greater rigidity of chains due to hydrogen bonding in the former[87,88]; a similar pattern is observed on comparing corresponding polydialkoxyphosphazens[1,9] and polybisalkylaminophosphazens[94-96]. The latter differ from the former in possessing an ordered structure (Table 7), although their formation is accompanied by degradative processes, as is indicated by the considerably lower molecular mass in comparison with the initial polydichlorophosphazen or corresponding polydialkoxyphosphazens[96]. This may be due to the reaction [87]



When primary amines are used as substituting reagents, however, the molecular mass may be increased by partial cross-linking[96]

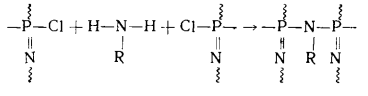


Table 7. Polybisalkylaminophosphazens $-[N{:}P(NHR)(NHR')]-$[96].

R	R′	M.p., °C	T_{gl}, °C	M_z***	[η], dl g^{-1} (solvent, t °C)
$NHCH_3$	$NHCH_3$	140	14	8.1	2.0 (water, 30°)
NHC_3H_7	NHC_3H_7	151	4	—	1.1 (trifluoroethanol, 30°)
NHC_4H_9	NHC_4H_9	139	8	—	2.5 (trifluoroethanol, 30°)
$NHCH_3$	$N(C_2H_5)_2$	174	8	23.0	1.4 (benzene, 30°)
NHC_2H_5	$N(C_2H_5)_2$	111	−11	27.4*	1.2 (benzene, 30°)
NHC_3H_7	$N(C_2H_5)_2$	—	−5	13.2**	1.2 (benzene, 30°)
NHC_4H_9	$N(C_2H_5)_2$	—	−6	15.5	1.4 (benzene, 30°)

* $\bar{M}_n = 1.55 \times 10^5$.
** $\bar{M}_n = 1.27 \times 10^5$.
[***M_z = molecular weight by ultracentrifugation (Ed. of Translation)].

Polyaminophosphazens are chemically stable. The use of alkyl esters of amino-acids[97,98], however, entails not only increase in the proportion of degradative processes in main chains and decrease in degree of substitution with bulky ligands but also diminished chemical stability of the polyphosphazens, which begin to decompose even at room temperature.

When sterically hindered nucleophiles, e.g. *p*-phenylazoaniline[99], derivatives of other colorants or steroids[100], are used for the preparation of polyphosphazens, at most one chlorine atom can be substituted at each phosphorus atom in polydichlorophosphazen, and the activity of the remaining chlorine atoms is sharply diminished even towards such highly active reagents as sodium trifluoroethoxide and methylamine[100].

An original method for synthesising polybistrifluoroethoxyphosphazen[101] consists in heating tristrifluoroethoxy-*N*-trimethylsilylphosphazen at 200 °C. Trifluoroethoxytrimethylsilane separates and a polymer of molecular mass 4000–10000 is formed.

3. Polyalkylphosphazens

Since alkylated cyclophosphazens cannot be polymerised, polyphosphazens containing organic groups attached by a carbon–phosphorus bond are obtained by the action of various organometallic compounds on polyhalogenophosphazens. Thus boiling polydichlorophosphazen in benzene with a double excess of phenyl-lithium gives a 22% yield of polydiphenylphosphazen[102]. Polydifluorophosphazen reacts more readily with phenyl-lithium, and also with diethyl- and dibutyl-magnesium[103], although in this case, too, only one halogen atom on each phosphorus atom is replaced preferentially. Thus an attempt to replace all the fluorine atoms in polydifluorophosphazen enabled only 80–90% substitution to be attained, with considerable degradation of macromolecules[103,104].

Table 8. Molecular-mass and physicochemical characteristics of polyphosphazens $-[PNR_2]_n-$.

R	$10^{-3}\bar{M}_n$	$10^{-3}\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	$10^4 A_2^*$, cal mole g^{-2}*		$\langle(S^2)^{1/2}_z\rangle$**, Å	ΔC_p, cal g^{-1} deg^{-1}	ρ_{25}, g cm^{-4}	Ref.
				osmometry	light scattering				
C_6H_5NH	0.87	11.6	13.4	−0.055	−0.072	548	0.048	1.289	[88]
p-$CH_3C_6H_4NH$	0.93	15.3	16.5	+0.007	+0.007	665	0.050	1.172	[88]
p-$OCH_3C_6H_4NH$	1.24	18.2	14.7	0	0	418	0.064	1.240	[88]
p-ClC_6H_4NH	0.55	7.6	13.9	−0.015	−0.033	479	0.032	1.440	[88]
C_6H_5O	1.3	6.1	4.7	+1.440	—	348	—	—	[77]
p-ClC_6H_5O	2.2	21.3	9.7	+1.600	—	638	—	—	[77]

* Second virial coefficient.
** Hydrodynamic radius.

IV. PROPERTIES OF POLYPHOSPHAZENS

Molecular-mass Characteristics

These characteristics of polyphosphazens have been the subject of lively discussion, primarily because of the unusually wide molecular-mass distribution noted by many workers[1,76-78,87,88,95,96]. Thus the polydispersity coefficient of polyaryloxyphosphazens may reach 30,[76] and amounts to 5–10 even for individual fractions; in most cases gas-absorption chromatography indicates a bimodal distribution for these polymers[70,78], the origin of which is still obscure. Nor has the reason been ascertained why radii of inertia of

macromolecules found from light scattering considerably exceed the calculated values: $\langle S^2\rangle^{\frac{1}{2}} = 546$ or 638 nm[76,77] for polydi-*p*-chlorophenoxyphosphazen, but 600–1300 nm[78] for the corresponding *m*-chlorophenoxy-derivative. The calculated value for phosphazen chains having $M = 10^6$ is $\langle S^2\rangle^{\frac{1}{2}} = 40$–50 nm. Such a substantial divergence is assumed[76,78] to be due to a wide molecular-mass distribution or a branched character of the macromolecules.

Similar anomalies are observed with polybisarylaminophosphazens (Table 8). The identical character of molecular-mass characteristics for polyphosphazens having different types of side-groups indicates that the distributions are "prescribed" during formation of the initial polydichlorophosphazen. This hypothesis is confirmed by results[114] showing a significant difference between the molecular-mass distributions of polyphosphazens prepared from polydichlorophosphazen and those obtained by the polymerisation of hexachlorocyclotriphosphazen in the mass and in solution.

Structure of Polyphosphazens

Little work has yet been done on structure, although definite progress has been noted in recent years. Thus two transition points have been observed[8,108–112] in certain partly crystalline polyphosphazens, the difference between which may reach 150–250 deg. The first T_1 corresponds to a transition from an ordered three-dimensional to a mesomorphous state. In polybischlorophenoxyphosphazens the latter is characterised by a pseudohexagonal structure with two-dimensional order in the packing of parallel oriented chains[108]. Study of polybistrifluoroethoxyphosphazen by optical microscopy, nuclear magnetic resonance, X-ray diffraction, and differential scanning calorimetry[109,110] has revealed spherulitic morphology remaining unchanged on passage through the first transition point, although this is accompanied by disruption of ordered orientation of macromolecular axes and a transition to structures with hexagonal packing. These transition temperatures and melting points are given for several polyphosphazens in Table 9.

Table 9. Transition and decomposition temperatures of polyphosphazens $-[PN(OR)_2]-$[8].

R	T_{gl}, °C	Transition temp., °C		T_{decomp}, °C**
		T_1^*	m.p.	
CF_3CH_2	−66	90	240	360
C_6H_5	6	160	390	380
m-ClC_6H_4	−24	66	370	380
p-ClC_6H_4	4	167	365	410
C_6H_5 + *p*-ClC_6H_4 (1 : 1)	5	77, 94	—	—

* T_1 = temperature of transition to liquid-crystalline state.
** From dynamic thermogravimetric analysis in air.

The mesomorphous transitions in polyphosphazens are characterised by considerable enthalpy changes, exceeding those for a transition into the isotropic melt by factors of 10 and > 50 in polybistrifluoroethoxyphosphazen and polydi-*p*-chlorophenoxyphosphazen respectively[109] (Table 10). This feature is more characteristic of liquid-crystalline systems of low molecular weight[113]. The discrepancies in transition points and melting points given by different workers (Tables 9 and 10) are apparently due to the dependence of these temperatures on the preliminary annealing conditions. Thus the former polymer exhibits a significant dependence of the transition point on the conditions of crystallisation, the temperature, and the duration of the anneal (Fig.1).[109] The highest value (T_1 = 91.5 °C) and the maximum heat of transition are achieved after the polymer has been preheated in the range 240–255 °C.[109]

Table 10. Transitions in polyphosphazens and other compounds[109]*.

Compound	T_1, °C	M.p., °C	ΔH, cal g^{-1}, at		$\Delta V(T_1)$	ΔV(m.p.)
			T_1	m.p.		
Polybistrifluoroethoxyphosphazen	92	240	8.6	0 8	5	6
Polydi-*p*-chlorophenoxyphosphazen	169	356	6.6	0	3.5	5.7
Polyethylene	—	141	—	68	—	15
p-Azoxyanisole	116	133	28.0	0 7	0.10	0.36

* ΔH = change in enthalpy; ΔV = volume change, %.

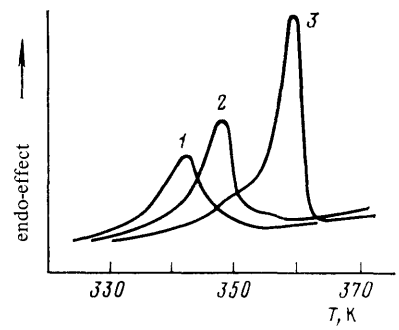


Figure 1. Effect of heat-treatment on the endotherms for the transition of polybistrifluoroethoxyphosphazen from the crystalline to the mesomorphous state: 1) specimen obtained from melt by moulding (T_1 = 79.5 °C); 2) as (1) after recrystallisation by cooling from 112 °C at 20 deg min^{-1} (80.5 °C); 3) specimen preheated at 240–255 °C (91.5 °C).

Dynamic mechanical tests on polybistrifluoroethoxyphosphazen have shown[76,112] a sharp decrease in modulus of elasticity at the transition point, at or slightly above which the polymer can already be moulded under pressure into strong flexible films. Despite considerable interest in the mesomorphous state of polyphosphazens, it is not yet clear what type of structure it possesses—whether smectic, nematic, or plastic crystalline.

Amorphous polyphosphazens can be assumed to have a globular structure in view of the great flexibility of the macromolecules[1] and by analogy with amorphous polysiloxanes. This hypothesis is consistent with the closely similar permeabilities of these two groups of polymers to water vapour and diffusion coefficients of the vapour in them[114, 115]. Mixtures of partly crystalline homopolymers differ from the corresponding phosphazen copolymers in having a single glass point and several transition points T_1, which indicates

compatibility of the amorphous phases and absence of such compatibility from crystalline regions[116].

Like polydichlorophosphazen[28] its isothiocyanato- and alkylamino-derivatives[117,118], in contrast to corresponding cyclic analogues, exhibit predominantly electronic conduction.

Chemical Properties

The chemical properties of polyphosphazens are determined in considerable measure by the nature of the side-groups. The completely substituted compounds containing inert aliphatic and aromatic groups attached to phosphorus atoms of the main chain directly through oxygen or nitrogen atoms resist the action of atmospheric moisture and weak acids and bases[1,8]. Thus polydiphenylphosphazen remains unchanged after being boiled in 1 *N* nitric acid and 1 *N* aqueous potassium hydroxide for 48 h.[102] Polymers containing residues of amino-acids in the side-chain, however, readily undergo spontaneous decomposition when stored under normal conditions[97].

Thermal Stability

Polyphosphazens containing organic substituents are considerably less stable than the original polydichlorophosphazen, which begins to depolymerise only above 350 °C,[1,8] a first-order reaction having activation energy 98 ± 8 kJ mole^{-1}.[119,126] The temperatures given in Tables 5, 6, and 9 for the start of decomposition of various polyphosphazens were obtained by dynamic thermogravimetric analysis. However, viscosimetric measurements indicate that macromolecules of most of the organically substituted polyphosphazens begin to break down over the range 100–200 °C.[78,119–121]

Polybisalkylaminophosphazens are thermally the most stable, like their cyclic analogues beginning to undergo deaminolysis above 100–150 °C.[1,8,122] Polydialkoxyphosphazens are somewhat more stable, although both polydiphenoxy- and polydi-*m*-chlorophenoxy-phosphazens[119,78] exhibit a decrease in molecular mass over the range 130–160 °C. In contrast to the results of dynamic thermogravimetric analysis (Table 9), polybistrifluoroethoxyphosphazen is relatively thermostable under conditions of isothermal heating and resembles most other polyperfluoroalkoxyphosphazens in decomposing under equilibrium and non-equilibrium conditions with the formation of cyclic homologues[120,121].

Experimental results at present available indicate that the thermal stability of polyphosphazens is determined by the factors—thermal stability of side-groups, presence of weak, defective chain units resulting from incomplete substitution and other causes, steric interactions of side-substituents facilitating breakdown of the main chain, and degradation governed by the influence of terminal groups.

The influence of the nature of side-groups on the thermal stability of polyphosphazens is illustrated by polybisalkylaminophosphazens (Table 6)[37,88,122]. The presence of defective units is apparently responsible for cases of regular increase in molecular mass of polydiaryloxyphosphazens at 130–170 °C.[78,119] This is indicated by the formation of a small quantity of 2-chloro-1,1,1-trifluoroethane in the degradation of polybistrifluoroethoxyphosphazen[120]. Instability due to steric interactions of bulky side-groups has been examined in detail by Allcock[1,127,128].

With small and thermally stable side-groups (e.g. trifluoroethoxy) and with a sufficiently high degree of substitution, however, terminal groups begin to play an important part in the thermal stability of polyphosphazens. Thus it was shown[123] for polydibutoxyphosphazens that, as the molecular mass decreases and the concentration of terminal P:O and P.OH groups increases, the rate of degradation in a vacuum (0.133 Pa) at 200 °C rises, while the character of the weight-loss curves changes owing to depolymerisation with formation of cyclic butoxyphosphazens (Fig. 2). At higher temperatures (220–250 °C) the molecular mass of the polymer has hardly any effect on the character of degradation: under these conditions instability of side-groups obviously becomes the dominant factor. As decomposition diminishes (residual pressure 266 Pa), dibutyl ether and tributyl phosphate appear among the volatile degradation products[123].

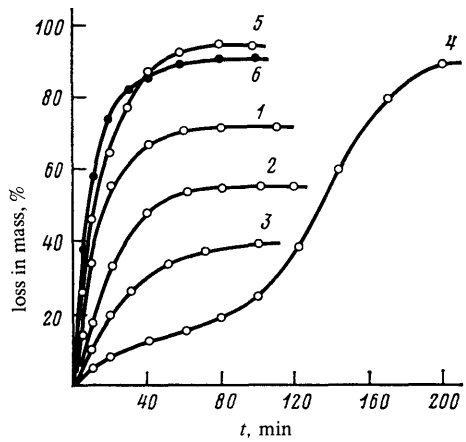
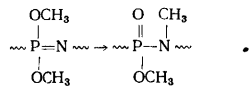


Figure 2. Thermal degradation of polydibutoxyphosphazens in a vacuum (0.133 Pa) at (°C) (molecular mass): 1) 200 (1340); 2) 200 (3100); 3) 200 (5400); 4) 200 (750000); 5) 220 (750000); 6) 250 (750000).

Establishment of the influence of the nature and concentration of terminal groups in polydialkoxyphosphazens on their thermal degradation has enabled coordinated polyphosphazens of chelate type to be obtained from analogous linear oligomers[124]. The thermal stability of polyphosphazens can be enhanced by the chemical blocking of terminal groups and also groups responsible for initiating the thermal breakdown of other weak bonds in macromolecules. Thus thiocarbonate derivatives of zinc and lead[129], oxides, hydroxides, and carbonates of alkali and alkaline-earth metals, quinolinol complexes of transition metals[130], a zinc derivative of mercaptobenzothiazole[131], and zinc hippurate[132] are used to stabilise polyphosphazens.

Among other thermal reactions of polyphosphazens mention must be made of the phosphazen–phosphazan rearrangement, which takes place in polydimethoxyphosphazen at 130 °C[125]:



After 6 h the degree of conversion into a polymeric phosphazan is 34.7%.

Vulcanisation of Polyphosphazens

Vulcanisation is acquiring increasing importance in view of the great practical value of these polymers. Traditionally, unsaturated groups are introduced into side-chains, and

vulcanisation is effected with peroxides[134,135]. In the case of polyaryloxyphosphazens, polymers containing unsaturated groups—mostly allyl[136,137] or alkenyl[90]—in the aryloxy-radicals are used. These polymers can be hardened also by heating with sulphur or by the action of ionising radiations[137,138,143].

In order to lower the temperature of the vulcanisation of polyphosphazens primary and secondary amino-groups[139] or hydroxyalkyl radicals[140] are introduced in their side-chains; such polymers can be cross-linked at moderate temperatures by the action of diazocyanates, polyanhydrides, and diepoxides. Polyphosphazens containing unsaturated bonds in side-chains can be vulcanised at room temperature by means of oligomeric siloxanes containing silicon–hydrogen bonds, the process being accomplished in the presence of catalysts containing platinum[141]. It has been suggested[73,142] that polyperfluoroalkoxyphosphazens could be cross-linked by treatment with alkoxides of perfluoroglycols.

V. APPLICATIONS

The main trends in the application of macromolecular polyphosphazens have been[6-10] the production of elastomers and hence articles able to withstand low temperatures and aggressive media, the preparation of non-flammable and incombustible materials, and biomedical uses. The most promising elastomers have been obtained from polyperfluoroalkoxyphosphazen copolymers, e.g. $\{(CF_3CH_2O)_x(H[CF_2]_4.CH_2O)_{2-x}PN\}$, and also polymers containing other perfluorinated alcohol residues[7,8,67,145].

Table 11. Fire resistance of polymers[7,148].

Polymer	O.i.	D_{sm}*
Polyethylene	17	150
Polystyrene	18	468
Polydimethylsiloxanes	26	385
Polycarbonates	27	660
Polyvinyl chloride	44	525
Polybistrifluoroethoxyphosphazen	67	—
Polydiaryloxyphosphazens $[PN(OC_6H_4R)_2]_x$		
R = H	33	343
R = *p*-Cl	44	455
R = *p*-Br	65	—
R = *p*-OCH_3	26	120
R = H, C_2H_5 (copolymer)	43**	40

* Obtained on testing in a smoke chamber.
** Copolymer filled with 50 mass % of aluminium hydroxide; the unfilled copolymer has O.i. = 28.

Elastomers are obtained by adding to the initial polyperfluoroalkoxyphosphazens 30–40 mass % of reinforcing fillers (carbon black, Aerosil, clay, aluminium hydroxide, etc.) and also vulcanising and stabilising agents. Those resulting from the vulcanisation of such mixtures have good low-temperature properties, modulus of elasticity at 100% elongation 3.5–10.5 MPa, tensile strength 7.0–14.0 MPa, and elongation at break 100–200%. They resist the action of oils, liquid fuels, and hydraulic fluids, and can operate at temperatures up to 175 °C for a long time[7,145]. Such elastomers are used to make flange seals, airtight and damping packing, glands, fuel hoses, and other components employed in aviation and other branches of technology[144,146,147].

Polyphosphazens have been widely used to obtain fire-resistant and non-flammable polymeric materials. Table 11 compares oxygen indices (O.i.) and specific optical densities of smoke D_{sm} for the combustion of several industrial polymers and polyphosphazens. The latter are either incombustible (O.i. > 30) or self-extinguishing (> 25). Polyphosphazens have the advantage over difficultly combustible or self-extinguishing organic polymers (polyvinyl chloride, polycarbonates) of forming less toxic products on combustion or thermal decomposition[149,150]. The presence of halogens in organic side-chains improves considerably the fire-resistance of polyphosphazens[7,148,149].

An interesting field of application of polydialkoxyphosphazen homopolymers and copolymers is the production of elastic and semi-rigid foams[149,151].

REFERENCES

1. H.R.Allcock, "Phosphorus–Nitrogen Compounds" (Translated into Russian), Mir, Moscow, 1976.
2. V.V.Kireev, G.S.Kolesnikov, and I.M.Raigorodskii, Uspekhi Khim., 1969, **38**, 1503 [Russ.Chem.Rev., 1969, **38**(8)].
3. C.Georghiu and M.Chirca, Rev.Chim.(Bucharest), 1978, **29**, 210.
4. H.Struszcyk, Polymery, 1978, No.23, 41.
5. M.Kajiwara, Sen'i Kako, 1978, **30**, 61.
6. J.A.Beckman, Rev.gén. Cauch.Plast., 1976, No.53, 98.
7. R.E.Singler, G.L.Hagnauer and N.S.Schneider, Polymer News, 1978, **5**, 9.
8. R.E.Singler, G.L.Hagnauer, and N.S.Schneider, Polymer Eng.Sci., 1975, **15**, 321.
9. H.R.Allcock, Chem.Brit., 1974, **10**, 118.
10. R.Calvert, Nature, 1977, **266**, 497.
11. H.Stokes, J.Amer.Chem., 1897, 782; see Ref.7.
12. BRD P.2745885 (1977); Chem.Abs., 1978, **89**, 25099.
13. Neth.P.7609263 (1977); Chem.Abs., 1977, **87**, 152733.
14. J.B.Thomson and J.W.Wittman, "Reynard Open-cell Fire-resistant Foams", Horizons Inc., Cleveland, NASA Contract NAS9-14717, April 1976 (No.76-27424); see Ref.7.
15. US P.411689 (1978); Chem.Abs., 1979, **93**, 26302.
16. N.L.Paddock and T.Searle, "Phosphonitrilic Halides and Their Derivatives", in "Inorganic Polymers" (Translated into Russian), Inostr.Lit., Moscow, 1961, p.180.
17. Canad.P.575069 (1961); Chem.Abs., 1962, **56**, 13809.
18. M.Biddlestine and R.A.Shaw, J.Chem.Soc., 1969, 178.
19. M.Biddlestine and R.A.Shaw, J.Chem.Soc., 1971, 2765.
20. M.Biddlestine and R.A.Shaw, Phosphorus, 1973, **3**, 95.
21. R.O.Colclough and G.J.Gee, Polymer Sci., C, 1969, 3639.
22. US P.3829554 (1974); Chem.Abs., 1974, **81**, 137398.
23. F.G.R.Gimblett, Polymer, 1960, 418.
24. J.O.Konecny and C.M.Douglas, J.Polymer Sci., 1959, **36**, 195.
25. J.O.Konecny, C.M.Douglas, and M.Y.Gray, J.Polymer Sci., 1960, **42**, 383.
26. H.R.Allcock and R.J.Best, Canad.J.Chem., 1964, **42**, 477.

27. H.Takeshi and S.Hajime, J.Chem.Soc.Japan, 1971, **74**, 1348.
28. M.Kajiwara and H.Saito, Polymer, 1977, **18**, 351.
29. J.Emsley and P.B.Udy, Polymer, 1972, **13**, 593.
30. H.R.Allcock, J.E.Gardner, and K.M.Smeltz, Macromolecules, 1975, **8**, 36.
31. US P.3517802 (1975).
32. US P.3937790 (1976).
33. BRD.P.2220800 (1973); Chem.Abs., 1973, **78**, 98262.
34. V.Sulkovski, Candidate's Thesis, Mendeleev Moscow Institute of Chemical Technology, 1977.
35. G.I.Mitropol'skaya and V.V.Kireev, USSR P.697529 (1978); Byull.Izobr., 1979, No.42, 72.
36. V.Sulkovski, V.V.Kireev, and V.V.Korshak, Vysokomol.Soed., 1976, **18B**, 220.
37. V.V.Kireev, V.V.Korshak, G.I.Mitropol'skaya, and V.Sulkovski, Vysokomol.Soed., 1979, **21A**, 100.
38. V.V.Korshak, I.A.Gribova, T.V.Artamonova, and A.N.Bushmarina, Vysokomol.Soed., 1960, **2**, 377.
39. R.Ratz and H.Schroeder, J.Amer.Chem.Soc., 1962, **8**, 552.
40. R.A.Shaw and M.Biddlestone, Chem.Comm., 1965, 205.
41. V.V.Kireev, V.V.Korshak, V.Sulkovski, I.P.Mulyashova, I.I.Zhuravleva, T.P.Sadkova, and G.M.Maiorova, Dokl.Akad.Nauk SSSR, 1978, **239**, 853.
42. H.R.Allcock and D.B.Patterson, Inorg.Chem., 1977, **16**, 197.
43. H.R.Allcock, J.L.Schmutz, and K.M.Kosydar, Macromolecules, 1978, **11**, 179.
44. G.I.Dergach, I.N.Zhmurova, A.V.Kirsanov, V.I.Shevchenko, and A.S.Shtepanek, "Fosfazosoedineniya" (Phosphazo-Compounds), Naukova Dumka, Kiev, 1965.
45. R.H.Boyd and Z.Kesner, J.Amer.Chem.Soc., 1977, **99**, 4248.
46. V.N.Prons, M.P.Grinblat, A.L.Klebanskii, and A.G.Nikolaev, Vysokomol.Soed., 1974, **16A**, 1620.
47. USSR P.271021 (1970); Byull.Izobr., 1970, No.17, 79.
48. V.N.Prons, N.P.Grinblat, A.L.Klebanskii, and A.G.Nikolaev, Zhur.Obshch.Khim., 1970, **40**, 2128.
49. V.G.Sartaniya, V.V.Kireev, and V.V.Korshak, Vysokomol.Soed., 1974, **16B**, 38.
50. V.G.Sartaniya, V.V.Kireev, and V.V.Korshak, Trudy Moskov.Khim.-tekh.Inst.Mendeleeva, 1973, **74**, 103.
51. V.N.Prons, N.P.Grinblat, and A.L.Klebanskii, Zhur.Obshch.Khim., 1971, **41**, 482.
52. USSR P.531821 (1976); Ref.Zhur.Khim., 1977, 14S284.
53. H.R.Allcock and G.J.Moore, Macromolecules, 1975, **8**, 377.
54. USSR P.417452 (1973); Byull.Izobr., 1974, No.8, 73.
55. I.B.Telkova, Candidate's Thesis, Mendeleev Moscow Institute of Chemical Technology, 1973.
56. I.B.Telkova, V.V.Kireev, and V.V.Korshak, Trudy Moskov.Khim.-tekh.Inst.Mendeleeva, 1973, **74**, 105.
57. BRD P.2712542 (1977); Chem.Abs., 1978, **88**, 7890.
58. US P.3443913 (1969).
59. J.R.McCallum and A.R.S.Vernick, J.Macromol.Sci. Chem., 1971, **5**, 102.
60. H.R.Allcock, R.L.Kugel, Konopski, and E.G.Storgh, Inorg.Chem., 1972, **11**, 1120.
61. Navy Res., 1972, **5**, 22.
62. R.E.Singler and G.Hagnauer, Army Res.Develop. News Magazine, 1973, No.1–2, 20.
63. S.H.Rose, K.A.Reynard, and R.W.Sicka, VII Int. Symp.Fluorine Chemistry, 1973.
64. H.R.Allcock, Amer.Chem.Soc., Polymer Prepr., 1977, **18**, 857.
65. US P.3515688 (1970).
66. S.H.Rose, Polymer Letters, 1968, **B6**, 837.
67. S.H.Rose and K.A.Reynard, Amer.Chem.Soc., Polymer Prepr., 1972, **13**, 778.
68. US P.3702833 (1971); Chem.Abs., 1972, **78**, 98764.
69. US P.3370020 (1968); Chem.Abs., 1970, **49**, 45665.
70. G.Allen and R.M.Mortimer, Polymer, 1972, **13**, 253.
71. US P.397284 (1976).
72. US P.3896058 (1975).
73. H.R.Allcock and G.Y.Moore, Macromolecules, 1972, **5**, 321.
74. USSR P.217638 (1968); Ref.Zhur.Khim., 1969, 8S364.
75. G.Allen, C.J.Lewis, and S.M.Todd, Polymer, 1970, **11**, 31.
76. G.Allen, C.J.Lewis, and S.M.Todd, Polymer, 1970, **11**, 44.
77. R.E.Singler, G.L.Hagnauer, N.S.Schneider, B.R.Laliberte, R.E.Sacher, and R.W.Matton, J.Polymer Sci., Polymer Chem., 1974, **12**, 433.
78. G.L.Hagnauer and B.R.Laliberte, J.Appl.Polymer Sci., 1976, **20**, 3073.
79. US P.3838073 (1974).
80. US P.3883451 (1974).
81. US P.3856712 (1973).
82. US P.3853794 (1974).
83. US P.3856713 (1975); Chem.Abs., 1975, **82**, 39703.
84. US P.3700629 (1973); Chem.Abs., 1973, **78**, 39542.
85. US P.3845167 (1974).
86. S.V.Vinogradova, D.R.Tur, V.V.Korshak, L.M.Gil'man, and N.N.Kazarova, Vysokomol.Soed., 1978, **20A**, 1491.
87. J.E.White, R.E.Singler, and S.A.Leone, J.Polymer Sci., Polymer Chem., 1975, **13**, 2531.
88. L.Busilini, M.Osellame, S.Lora, and G.Pezzine, Makromol.Chem., 1977, **17**, 277.
89. USSR P.467610 (1975); Byull.Izobr., 1977, No.33, 127.
90. Jap.P.4937821 (1974).
91. US P.3888800 (1975).
92. D.P.Tate, J.Polymer Sci., Polymer Symp., 1974, **C48**, 33.
93. H.R.Allcock, R.L.Kugel, and K.J.Valan, Inorg. Chem., 1966, **5**, 1709.
94. H.R.Allcock, R.L.Kugel, and K.J.Valan, Inorg. Chem., 1966, **5**, 1716.
95. H.R.Allcock and D.P.Mock, Chem.Comm., 1970, 685.
96. H.R.Allcock, W.J.Cook, and D.P.Mack, Inorg. Chem., 1972, **11**, 2584.
97. H.R.Allcock, T.J.Fuller, D.P.Mack, K.Matsumura, and K.M.Smeltz, Macromolecules, 1977, **10**, 824.
98. US P.3893980 (1975).
99. H.R.Allcock, D.Wright, and K.M.Kosydar, Macromolecules, 1978, **11**, 357.
100. H.R.Allcock, T.J.Fuller, K.Matsumura, and K.M.Smeltz, Amer.Chem.Soc., Polymer Prepr., 1978, **19**, 92.
101. E.Flindt and H.Rose, Z.anorg.Chem., 1977, **428**, 204.
102. J.R.McCallum and J.Tarner, J.Polymer Sci., 1968, **A-1**, 3163.

103. H.R.Allcock, D.B.Patterson, and T.L.Evans, J.Amer.Chem.Soc., 1977, **99**, 6095.
104. H.R.Allcock, C.T.W.Chu, T.L.Evans, D.B.Patterson, and R.Ritchi, J.Amer.Chem.Soc., Polymer Prepr., 1978, **19**, 858.
105. M.A.Andreeva, E.G.Bulycheva, E.L.Lyubavskaya, G.A.Slonimskii, V.V.Korshak, and S.V.Vinogradova, Vysokomol.Soed., 1979, **21A**, 48.
106. Jap.P.48-30160 (1970).
107. Jap.P.49-39820 (1970).
108. C.R.Desper and N.S.Schneider, Macromolecules, 1976, **9**, 424.
109. N.S.Schneider, C.R.Desper, and R.E.Singler, J.Appl.Polymer.Sci., 1976, **20**, 3087.
110. M.N.Alexander, C.R.Desper, R.E.Singler, and N.S.Schneider, Macromolecules, 1977, **10**, 721.
111. C.R.Desper, N.S.Schneider, and E.Higginbotham, J.Polymer Sci., Polymer Letters, 1977, **15**, 457.
112. T.M.Connelle and J.K.Gillham, J.Appl.Polymer Sci., 1976, **20**, 473.
113. S.P.Papkov and V.G.Kulichikhin, "Zhidkokristallicheskoe Sostoyanie Polimerov" (Liquid-crystalline State of Polymers), Khimiya, Moscow, 1977.
114. V.V.Kireev, T.S.Klenova, V.V.Korshak, L.V.Dubrovina, V.G.Sartaniya, N.V.Trostenyuk, and O.G.Fortunatov, Vysokomol.Soed., 1976, **18A**, 228.
115. A.V.Tobolsky and H.F.Mark, "Polymer Science and Materials", Wiley Interscience, New York, 1971.
116. R.E.Singler, G.L.Hagnauer, T.T.Beres, N.S.Schneider, and C.R.Desper, Amer.Chem.Soc., Polymer Prepr., 1978, **19**, 859.
117. M.Kajiwara and H.Saito, J.Macromol.Sci., 1977, **A11**, 1081.
118. T.Hayashi and H.Saito, Bull.Chem.Soc.Japan, 1977, **50**, 1023.
119. J.R.McCallum and J.Tanner, J.Macromol.Sci., 1970, **A4**, 481.
120. H.R.Allcock and W.J.Cook, Macromolecules, 1974, **7**, 284.
121. H.R.Allcock, G.Y.Moore, and W.J.Cook, Macromolecules, 1974, **7**, 571.
122. H.R.Allcock, C.J.Kolich, and W.G.Kossa, Inorg. Chem., 1977, **16**, 3362.
123. S.S.Titov, Candidate's Thesis, Mendeleev Moscow Institute of Chemical Technology, 1969.
124. USSR P.491669 (1975); Byull.Izobr., 1975, No.42, 68.
125. V.D.Mochel and T.C.Cheng, Macromolecules, 1978, **11**, 176.
126. J.R.McCallum and A.Vernik, J.Macromol.Sci., 1971, 5, 651.
127. H.R.Allcock, J.Macromol.Sci., Rev.Macromol.Chem., 1970, **C4**, 149.
128. H.R.Allcock, Inorg.Chem., 1966, **5**, 1320.
129. US P.3843596 (1974); Chem.Abs., 1975, **86**, 137882.
130. US P.386734 (1974); Chem.Abs., 1975, **83**, 11881.
131. US P.4017458 (1977).
132. US P.4051103 (1977); Chem.Abs., 1978, **88**, 24106.
133. US P.4108805 (1978).
134. US P.3702833 (1972); Chem.Abs., 1973, **78**, 98764.
135. US P.3888799 (1975).
136. USSR P.472560 (1976); Byull.Izobr., 1977, No.33, 54.
137. US P.4107146 (1978).
138. BRD P.2706711 (1976); Chem.Abs., 1977, **87**, 153198.
139. US P.3844983 (1974).
140. US P.3998820 (1975).
141. USSR P.566853 (1976); Byull.Izobr., 1977, No.28, 74.
142. US P.3732750 (1973).
143. G.S.Kyker and T.A.Antowiak, Rubber Chem.Tech., 1974, **47**, 32.
144. R.E.Singler, K.A.Reynard, R.W.Sicka, J.C.Vicic, and S.H.Rose, New Ind.Appl.Advan.Mater.Technol. Nat.Symp.Exhib., 1974, 129.
145. K.A.Reynard, A.H.Gerber, R.W.Sicka, J.V.Vicic, and S.H.Rose, US Govt.Rep.Announce, 1974, **74**, 110.
146. P.Touchet and P.E.Gatza, J.Elastomers Plast., 1977, No.9, 8.
147. D.P.Tate, Rubber World, 1975, **172**, 41.
148. E.J.Quinn and R.L.Dieck, J.Fire Flammability, 1976, **7**, 358.
149. J.E.Thomson and K.A.Reynard, J.Appl.Polymer Sci., 1977, **21**, 2575.
150. K.Sclata, I.H.Magill, and J.C.Alarie, J.Fire Flammability, 1978, **9**, 50.
151. K.A.Reynard, R.W.Sicka, and J.E.Thomson, "Polyaryloxyphosphazene Foams", AD-A 009425, 1974; see Ref.7.

Mendeleev Moscow Institute of
Chemical Technology