Accounts

Synthesis and Functionality of Cyclophosphazene-Based Polymers

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Linear poly(organophosphazene)s have been widely investigated, mainly to correlate the structure of inorganic –P=N– backbone bearing organic groups with their properties and functionalites. Our interests have been directed to relatively new types of polymers containing a cyclophosphazene unit in the side chains, main chains, or as central core and end groups. The phosphazene groups in these polymers can serve as modification sites of polymers, leading to new functionalized materials. The six or more reactive sites of cyclophosphazenes are suitable for the preparation of star-shaped polymers or hyperbranched polymers including dendrimers. Recent works related with polymeric self-assembly showed that some organocyclophosphazenes are useful motifs for the construction of supramolecules, reflecting the structural features of the cyclotri(phosphazene)s. In this review, we describe the synthesis and functionalities of polymers containing cyclotri(phosphazene)s.

Cyclic- and polyphosphazenes composed of alternating phosphorus and nitrogen atoms continue to attract the attention of chemists, not only from synthetic points of view, but also with respect to the wide spectrum of chemical and physical properties of their materials. The most widely studied material in this field is the linear polyphosphazenes with two organic groups attached to each phosphorus atoms in a long-chain backbone.[1] Although there are now several methods for the preparation of such poly(organophosphazene)s, most of them were prepared via a thermal ring-opening polymerization of 2,2,4,4,6,6-hexachloro-2λ^5,4λ^5, 6λ^5-cyclotri(phosphazene) (**1**) followed by substitution of chlorine atoms with organic groups. The properties of poly(organophosphazene)s vary from rubbery elastomers to thermoplastics, depending on the introduced organic groups. Several reviews of this type of linear polyphosphazenes are available.[2–4]

Our approach to cyclophosphazene-based polymers is significantly different from the usual approach to these poly(organophosphazene)s with –P=N– backbone, i.e., the incorporation of cyclophosphazene ring into polymers. The first class of such polymers is organic–inorganic polymers, wherein the phosphazene rings are attached to organic polymers as side groups or linked via exocyclic groups to form linear or cross-linked polymers.[5] The polymers with pendant or skeletal cyclophosphazene units may provide a new type of polymers, since the properties and functionalities of polymers can easily be modified by organic groups as well as linear poly(organophosphazene)s. The cyclophosphazenes with six or more reactive sites are also useful to prepare star-shaped polymers, hyperbranched polymers, and dendrimers.[6–10] Such approaches represent a great potential for the preparation of new functional polymers.

The second class derived from cyclophosphazene is a polymeric self-assembly which is constructed by means of coordination bonding, hydrogen bonding, or other weak intermolecular interactions. Design of supramolecular architectures with potentially useful properties for relevant scientific and technological applications is of great interest in organizing solid-state chemistry.[11,12] The formation of supramolecules derived from cyclotri(phosphazene)s is based on the their structural features: the ring of cyclotri(phosphazene) is approximately planar, which may be sufficiently flexible to permit deformation by incoming organic substituents, and some of the organic groups on the phosphazene can be located perpendicularly on the ring.[13–15] These might permit the selective and directional interactions of functional groups required for the formation of supramolecules.

In this paper, the synthesis and functionality of polymers and polymeric self-assembly containing cyclotri(phosphazene)s, a relatively new class of phosphazenes, are described.

Synthesis and Properties of Polymers Containing Cyclotri(phosphazene)s

Vinyl Polymers with Pendant and Terminal Cyclophosphazene Units. A number of substituted cyclophosphazenes have been prepared by the nucleophilic replacement of P–Cl

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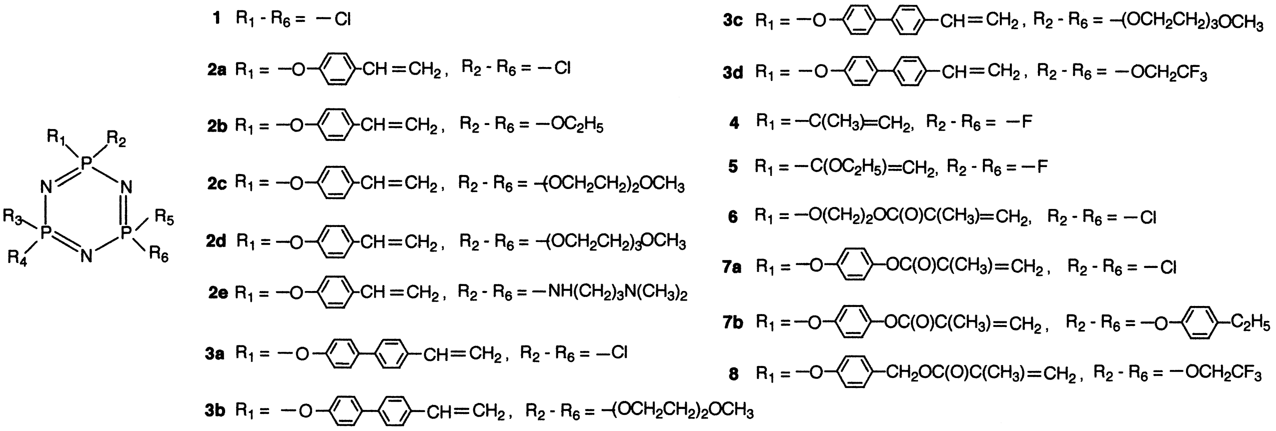


Chart 1. Polymerizable monomers (**2b**–**8**) with cyclotri(phosphazene)s.

group in cyclophosphazene (**1**) by organic moieties. In this reaction, the stoichiometric control is important to obtain a desired degree of substitution. In the progressive substitution of $-N=P(Cl)_2-$, two different reaction schemes are involved: geminal and non-geminal replacements where *cis* and *trans* isomers may be formed. The electronic and steric effects are major factors to determine regio- and stereoselectivity. Solvent effects and the reaction temperature have also been recognized as being important for the control of stereo- and regioselectivity. A typical example has been reported by Song et al.,[16] who showed that, in the substitution of **1** with sodium salt of polyethylene glycol derivatives, a non-geminal *cis*-2,4,6 trimeric phosphazene is formed at −60 °C. The regio- and stereochemical control in substitution reactions of cyclophosphazenes has been extensively studied.[17,18]

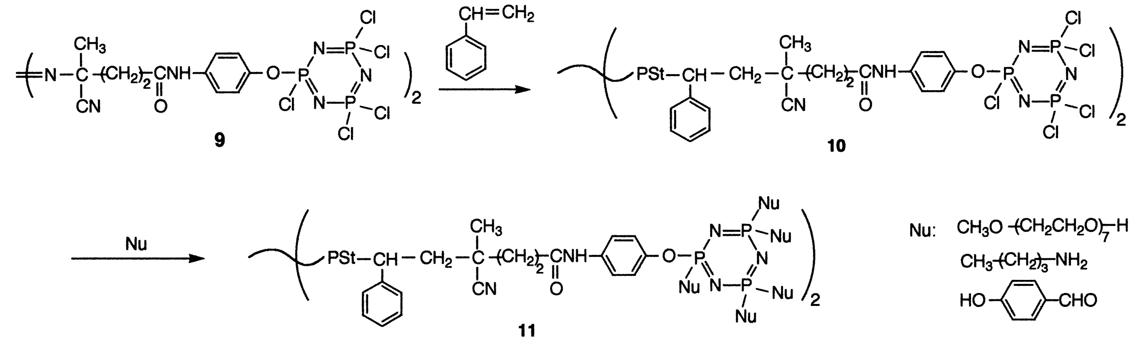
From an experimental point of view, the preparation of vinyl monomers with cyclophosphazenes is quite straightforward (Chart 1). For example, the monomer **2a** was synthesized in a moderate yield by the reaction of 4-vinylphenol and **1** in the presence of triethylamine.[19a] The radical polymerizations of vinyloxy-, 2-propenyl, 3- and 4-(α-methylethenylphenyl)-, methacryloyl-, and styryl derivatives with halocyclophosphazenes have been reported.[19–27] Except for 2-propenyl derivative, the homopolymerization of these monomers leads to moderate or high molecular weight polymers which are soluble in common solvents. The kinetic study of **3a** indicates that the polymerization proceeds by a normal radical mechanism and that the pentachlorocyclophosphazene moiety does not significantly affect on the polymerization processes. The reactivity parameters of the monomers estimated from copolymerization with styrene or methyl methacrylate are demonstrated to be influenced by the polarity effects of the phosphazenes.[23–25]

The monomers with pentachlorocyclotri(phosphazene) units could be easily modified by introducing organic groups, which make them suitable for many applications. These monomers with pendant organophosphazenes also underwent a facile polymerization with radical initiators to give the corresponding multi-armed polymers. For the polymerization of **3c**, the polymerization was significantly affected by the solvent properties, especially the hydrogen bond accepting abilities.[23] The degree of polymerization (DP_n) of poly(**3c**) obtained in ethanol was roughly 2 times larger than that in 1,2-dichloroethane. The low and high intrinsic viscosity of poly(**3c**) in ethanol and in 1,2-dichloroethane, respectively, suggested that a growing polymer chain in ethanol is liable to form a coiled conformation, whereas the polymers exist as a relatively extended structure in 1,2-dichloroethane, indicating that the acceleration of propagation and the suppression of termination are operative in the former solvent. The dependence of molecular weights on the solvent properties could be interpreted by the conformational change of the growing polymer chains. For the polymerization of vinyl monomer with pendant 2,2,4,4,6-pentakis(2,2,2-trifluoroethoxy)cyclotri(phosphazene) (**8**), the polymerization competes with depolymerization.[21]

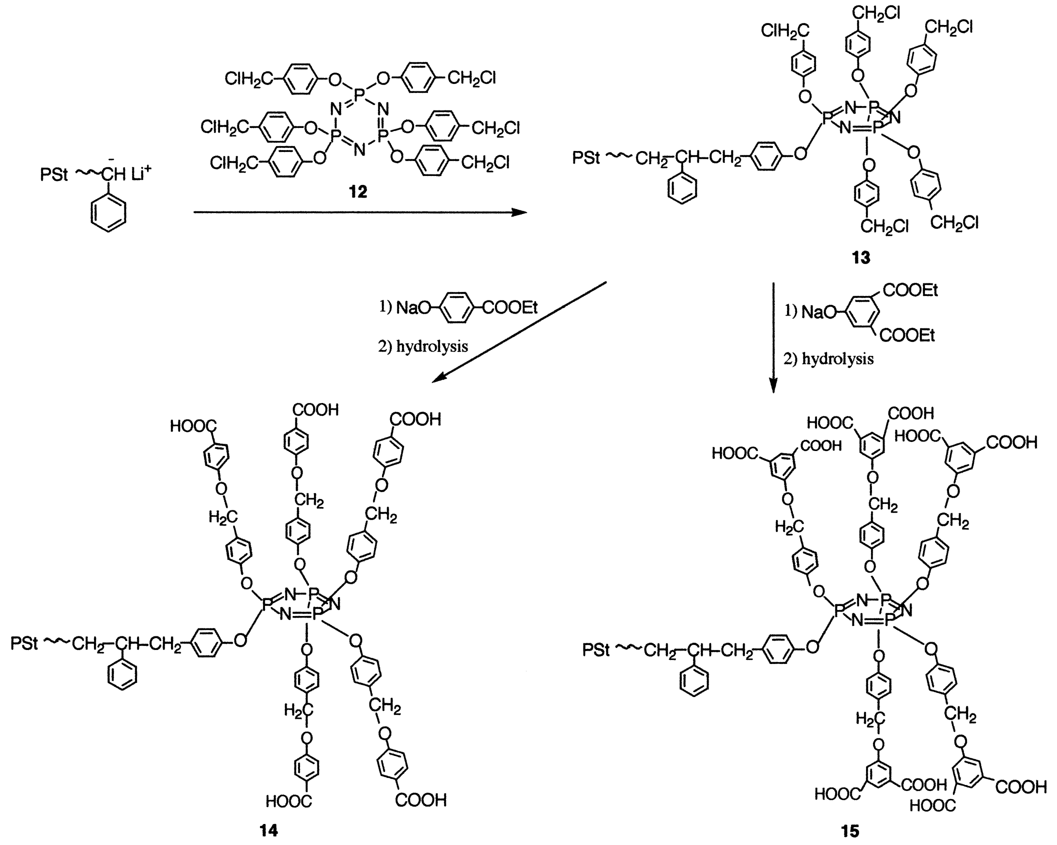
Thus, the polymerization was significantly affected by the organic groups introduced on the side phosphazene units. It should be noted here that the complete substitution of P–Cl group in the vinyl polymers with nucleophiles was rather difficult and a few percent of P–Cl groups often remained without suffering any displacement.

Telechelic polymers with cyclophosphazene moiety at the polymer end have been prepared by radical and anion polymerizations.[28] For the radical polymerization of styrene, the polystyrene radicals are well-known to be terminated predominantly by the recombination process, implying that the polymer ends have structure arising from the initiator. The polymerization of styrene with azo initiator containing pentachlorocyclotri(phosphazene) (**9**), in fact, gave polymers with phosphazene units at both ends (**10**).[23] Various functional groups such as oligo(oxyethylene) units and aldehyde can be introduced into the terminal phosphazene group (Scheme 1). The coupling reaction of (polystyryl)lithium with **1** or $N_3P_3F_6$ gave polymers with terminal phosphazene units but unfavorable ring-opening reaction of these phosphazenes competes.

Telechelic polystyrenes with five chloromethyl groups at the polymer end (**13**) were prepared by the coupling reaction of (polystyryl)lithium with 2,2,4,4,6,6-hexakis(4-chloromethylphenoxy)-$2\lambda^5$, $4\lambda^5$,$6\lambda^5$-cyclotri(phosphazene) (**12**).[29] When [**12**]/[*s*-BuLi] = 9.3 was used, the polystyrene with cyclophosphazene carrying five chloromethyl groups at the polymer end was obtained in a high yield, which has narrow and predictable molecular weight ($M_w/M_n = 1.05$). Similar polystyrenes with two, four and six chloromethyl groups at an intended position in the polymer chains have been synthesized.[30] The chloromethyl group in the polymer chains has been frequently used as a



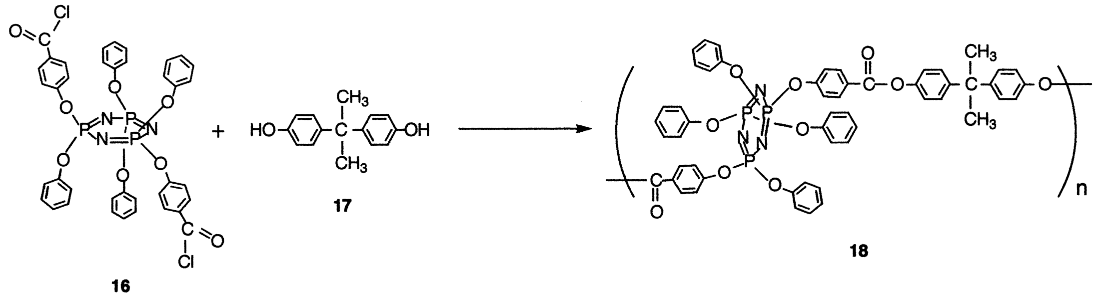
Scheme 1. Preparation of polystyrene with terminal phosphazene moiety.



Scheme 2. Preparation of polystyrene with 5 (**14**) and 10 (**15**) carboxyl groups at the polymer end.

key group to synthesize functional polymers.

The polystyrenes with 5 (**14**) and 10 carboxyl groups (**15**) at the polymer end were synthesized by hydrolysis of the corresponding ester functionalized structure (Scheme 2), prepared from the reaction of sodium salt of ethyl 4-hydroxybenzoate and diethyl 5-hydroxyisophthalate with the polymer (**13**).[30] Since the functional groups capable of forming a self-assembly on the rigid organic units often act as a powerful tool for the spontaneous formation of well controlled nanoscale architecture, these polymers might afford opportunities to improve and optimize functionalities compared to conventional linear polymers with randomly introduced functional groups. The polycarboxylic acid-terminated polystyrenes are expected to form a micelle-like and a reverse micelle-like structure in water and in some organic solvents. In DMSO-d_6, acetone-d_6, and THF-d_8 the peaks of the proton signals in the ^{1}H NMR spectra of **15** with M_n = 10000 were well resolved and the molecular weight of polystyrene units calculated from terminal aromatic ring protons was in agreement with the value of **13** determined by gel permeation chromatography (GPC). This indicates that **15** is in a monomeric form in these solvents. Contrary to this, for **15** in 2% DMSO-d_6-$CDCl_3$, both protons in benzyl and carboxyphenyl groups disappeared, while polystyrene units were observable, showing that phosphazene units at the polymer end are confined inside the aggregate. A similar result was obtained for **14**. The titration curves using DMSO-d_6 in ^{1}H NMR spectra showed that the disaggregation of **13** with M_n = 10000 and M_n = 5900 in $CDCl_3$ occurs at the presence of 5% and 10% (v/v) of DMSO-d_6, respectively. Thus, the stability of aggregation is significantly affected by the chain length of poly-



Scheme 3. Polyester **18** prepared from **16** and **17**.

styrene. Interestingly, for **15** with M_n = 5900, only a broad peak was observed in the region 6.50–8.95 ppm in D_2O–NaOD, suggesting that both carboxylatocyclophosphazene and polystyrene units were restricted outside and inside the aggregates, respectively. A similar but significant difference has been reported for the polystyrene-*dendr*-$(COOH)_{8-32}$ in D_2O at high pH, in which only polystyrene block is restricted in the aggregates.[31,32] The restriction of both the terminal group and polystyrene units for **15** might be due to the introduction of a polar group into the rigid and bulky phenoxyphosphazene moiety.

One of characteristic features of vinyl polymers with phosphazene units is the thermal properties. Among these polymers, poly(**3a**) containing biphenyl and phosphazene units is expected to exhibit the excellent thermal properties.[20] The thermogravimetric analysis showed that the decomposition of poly(**3a**) started at 280 °C and the maximum weight loss occurred at 425–510 °C, while 60% residue was observed at 800 °C. The polymer obtained from bulk polymerization showed that the decomposition in nitrogen started at 400 °C; 60% residue was observed at 800 °C. A qualitative test of flame retardance indicates that poly(**3a**) has a self-extinguishing property, indicating that the polymer is superior in heat and fire resistance. The formation of a high yield of residue in both air and nitrogen atmospheres may be explained by the presence of the thermally stable biphenyl unit and the high contents of phosphorus, chlorine, and nitrogen atoms in the polymers.

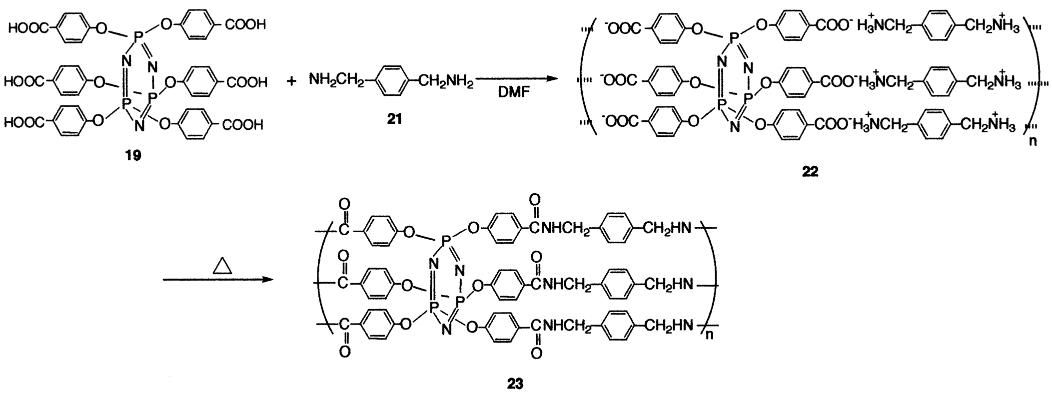
Polymers Composed of Cyclophosphazene Backbone. The polymers containing cyclotri(phosphazene) units in the main chains were commonly prepared by polycondensation of **1** with multifunctional substrates. Most of these studies deal with the thermal behavior of the polymers, e.g., maleimide-end-capped aromatic cyclotri(phosphazene),[33] poly(ether ketone)s,[34] polyuretanes,[35] and epoxy resins[36] containing cyclophosphazenes exhibited excellent fire- and heat-resistant properties. In general, the polycondensations may be complex due to the involvement of multiple displacements of Cl-atoms in the same phosphazene. We studied the influence of stereoisomers of bifunctional phosphazene monomers on the polycondensation. Here, it should be pointed out that, under controlled conditions, the reaction of polyamines and diols with **1** leads to the formation of various types of macrocyclic phosphazenes; spiro, ansa, or tribino derivatives were obtained, depending on the nature of the organic compounds.[6]

The polycondensation of acid chloride of *trans*-2,4-bis(carboxyphenoxy)-2,4,6,6-tetra (phenoxy)-$2\lambda^5,4\lambda^5,6\lambda^5$-cyclotri(phosphazene) (**16**) and bisphenol A (**17**) in the presence of the phase transfer reagent gave the polyester (**18**) with molecular weight of 22000 relative to standard polystyrene (Scheme 3).[37] In contrast to this, the polycondensation of **17** with a mixture of 7:3 *trans*-/*cis*-2,4-bis(carboxyphenoxy)-2,4,6,6-tetra(phenoxy)cyclotri(phosphazene) gave the polyester with a relatively low molecular weight of M_n = 14 000, and only oligomer was obtained when *cis*-isomer was used. Such a result indicates that *trans* form is important for effective growth of the polyester. In the copolycondensation of **17** with acid chlorides of **16** and terephthalic acid, the compositions of copolyesters (M_n = 13000–25000) were almost identical to the monomer feed ratios. The inherent viscosity of the copolyester with 5 mol% cyclotri(phosphazene) units was low compared to that of the polyester prepared from terephthalic acid and **17**. The homopolyester **18** exhibited a low glass transition temperature of 65 °C, and the copolymers had glass transition temperatures in the range 91–220 °C, depending on the contents of **16** units. These properties could be attributed to the involvement of the highly cranked cyclotri(phosphazene) units in the polyesters.

Thermogravimetric analysis showed that the homopolyester was stable up to 390 °C in a nitrogen atmosphere. The char yield of copolyester with 10 mol% of **16** unit was 36% at 600 °C, which was 7 times higher than that of the polyester without cyclotri(phosphazene) units. As expected, the qualitative test of flame retardation indicates that the polymers have self-extinguishing properties.

As will be described later, the complementary interactions between 2,2,4,4,6,6-hexakis(4-carboxyphenoxy)-$2\lambda^5,4\lambda^5,6\lambda^5$-cyclotri(phosphazene) (**19**) and 2,2,4,4,6,6-hexakis(4-pyridylmethoxy)-$2\lambda^5,4\lambda^5,6\lambda^5$-cyclotri(phosphazene) (**20**) provide a novel class of cylindrical self-assembly,[38] suggesting that the molecules could be components for the sort of tailoring of three-dimensional intermolecular architectures (Fig. 2). Such a cylindrical assembly was based on a unique geometry of hexaphenoxycyclotri(phosphazene) derivatives, in which the phenoxy groups are aligned approximately perpendicular to the nearly planar phosphazene ring.[13–15] Our interests lay in extending the processes to the preparation of covalently bonded polymers from self-assembled supramacromolecules with three-dimensional structure. The polymerization of assembly with a regular structure might be considered as another example of the template polymerization, where directional and specific interactions allow the preparation of polymers with a regular structure without undesired side reactions.

The salts composed of **19** and 1,4-phenylenebis(methyleneamine) (**21**) would be expected to take a similar cylindrical structure and to give three-dimensional polyamides when the



Scheme 4. Polyamide **23** prepared from "template" polycondensation.

salts are heated (Scheme 4).[39] The needle crystals of salt (**22**) were obtained by mixing a solution of **19** and **21** in DMF. Elemental analysis, FT-IR, ^{1}H NMR, and X-ray studies of **22** showed the formation of the salt composed of 1:3 **19**–**21**, suggesting that all of carboxyl group in **19** interact with amino groups in **21** to give salts with a cylindrical structure. Such salts with a defined stoichiometry were not obtained when *p*,*p*′-diaminodiphenylmethane, bis(*p*-aminophenyl)sulfone, *p*-phenylenediamine, and bis(*p*-aminophenyl) ether, indicating that the rigid, flat, and symmetrical diamines are essential for the formation of well-defined salts.

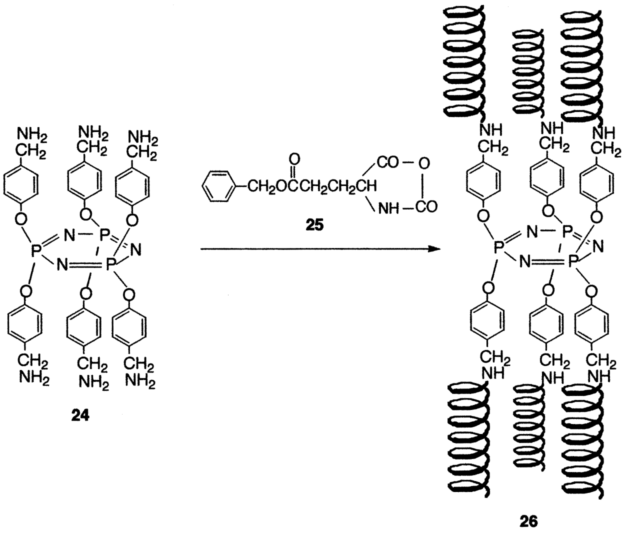
The polycondensation of salt **22** at 240 °C gave a polyamide (**23**) but some -COOH groups remained unreacted due to the elimination of **21**. This unfavorable decomposition, however, could be avoided by the addition of a small amount of **21** in a sealed tube. Spectroscopic data of the polymer suggest the formation of cylindrical polyamide with a regular structure. The polyamides were insoluble in organic solvents such as phenol, formic acid, *m*-cresol, and H_2SO_4.

The onset temperature of decomposition was somewhat low compared to that for the linear polyamide prepared from terephthaloyl chloride with *p*-xylylenediamine, probably due to the ring stress. However, the char yields of **23** at 800 °C were 3 times higher than those of linear polyamides, reflecting the involvement of flame-retardant properties of the cyclophosphazene group.

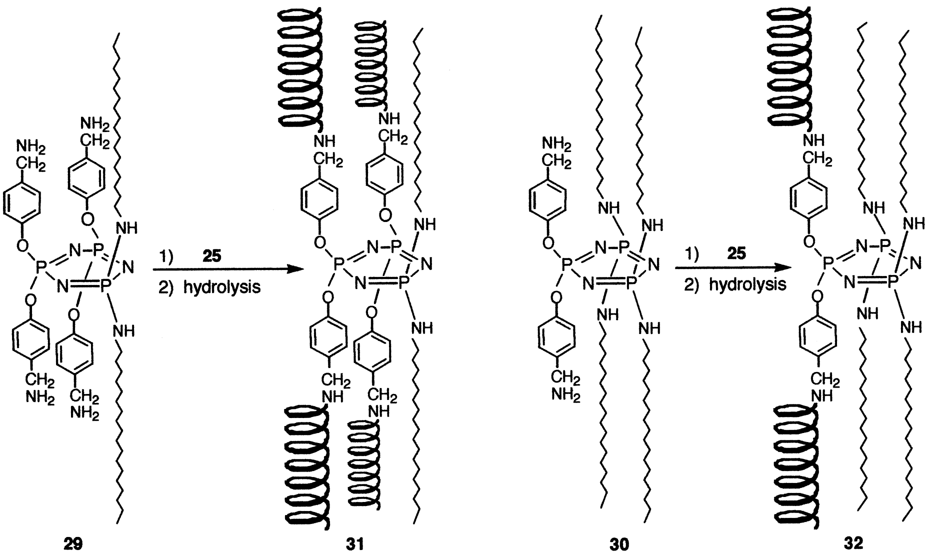
Polymers with Phosphazene Core. Cyclophosphazene is suitable as a core or a building block for generating well-defined functionalized macromolecules with a highly branched architecture. In the reaction of hexamethylenediamine with **1**, the 8th generation dendrimer has been synthesized, although unavoidable cross-linking reactions were operative and incompletely substituted side products increased with increasing the generation.[8] Majoral and his co-workers[6,7] prepared phosphorus containing dendrimers using hexapodand $N_3P_3(OC_6H_4CHO\text{-}4)_6$ core. The dendrimers prepared have inorganic P=N–P fragments, which are useful units for controlling branch assembly and introducing various reactive sites on the surface. The dendritic macromolecule composed of chiral ferrocenyl ligands and cyclophosphazene core has been prepared as a homogeneous asymmetric catalyst.[40] Cyclophosphazenes bearing alkyl halide act as multi initiator for the atom transfer radical polymerization (ATRP) of styrene, acrylates, and methacrylates.[9] The polymerization gave hexa-armed polymers with narrow molecular weight distributions. Such a star-shaped polymer has also been reported by Chang et al.[10]

The functionalities on the basis of helical structure of poly(amino acid) derivatives are of great interest from biological points of view, and hence applications in various fields have been demonstrated.[41] However, such a mimic function of peptides is not always as good as one expects for such synthetic polymers, probably due to the lack of organized ternary structure of the polymers employed as functional materials. A well-defined three-dimensional structure might be the fundamental prerequisite for proteins to manifest their biological functions.

The polymerization of *N*-carboxy amino acid anhydride (NCA) with a primary amine is well-established to proceed by a mechanism involving the attack of the amino group at the C_5 carbonyl group of the NCA, giving rise to well-ordered polymer chains. 2,2,4,4,6,6-Hexakis(4-aminomethylphenoxy)-$2\lambda^5,4\lambda^5,6\lambda^5$-cyclotri(phosphazene) (**24**) has, in principle, the same ability to initiate the polymerization of *N*-carboxy anhydride of γ-benzyl-L-glutamate (**25**) (Scheme 5).[42] In fact, ^{1}H NMR spectra of [**25**]/[**24**] = 10 showed that the peak at 3.8 ppm assignable to benzyl protons of the initiator disappeared



Scheme 5. Star-shaped poly(γ-benzyl-L-glutamate) **26** on the phosphazene core.



Scheme 6. Amphiphilic poly(glutamic acid)s attached to the phosphazene core.

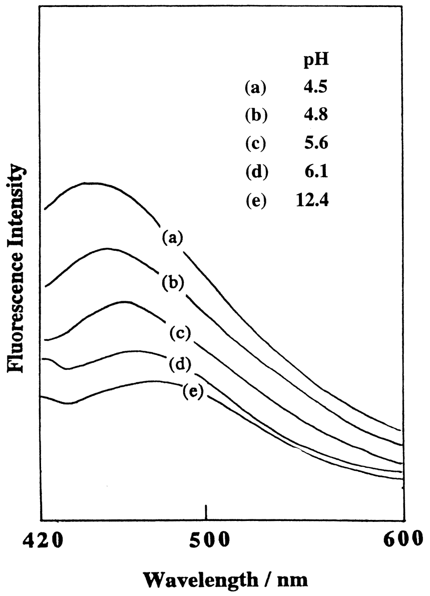


Fig. 1. Fluorescence spectra of ANS in the presence of **31**. [**31**] = 1.0×10^{-5} M, [ANS] = 8.2×10^{-7} M. λ_{ex} = 350 nm.

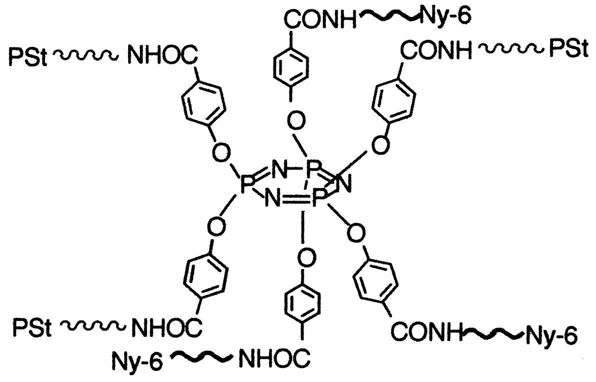


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Chart 2. Miktoarm polymer with central phosphazene core.

immediately when **25** was added to a solution of **24** in $CDCl_3$. For the polymerization at [**25**]/[**24**] = 30–300, the molecular weights of polymers determined by GPC were in agreement with the calculated values, and the molecular weight distribution of these polymers (**26**), was remarkably narrow (M_w/M_n = 1.05–1.30). Furthermore, IR spectra of **26** with M_n = 5400, for which the degree of polymerization of each chain ($DP_n/6$) would be expected to be $DP_n/6$ = 3–4 if the simultaneous propagation occurs at six reactive sites, exhibited peaks at 1660 and 1631 (amide I) and 1538 and 1526 (amide II) cm^{-1}, suggesting that the chains take β-form and random structure but not α-helical structure. These results suggest that all of amino group in **24** initiate the polymerization of **25** without delay and that the lengths of polymer chains attached to the phosphazene core are well controlled.

The relationship between the degree of polymerization and the conformation of the polymers has been studied in detail by Shoji et al.,[43] who showed that for a conventional poly(γ-benzyl-L-glutamate), polymers with DP_n = 16 and 10 take α-helical structure and β-sheet form, respectively. IR and CD spectra of **26** with M_n = 1.4×10^4 ($DP_n/6$ = 9.8) cast from $CHCl_3$ showed peaks at 1653 and 1550 cm^{-1} and a negative peak at 226 nm, respectively, indicating that the hexa-armed polyglutamates take a right handed α-helical structure, in a manner similar to conventional glutamates. This result suggests that the star-shaped polyglutamate is liable to take a helix structure. Consistent with this, the helix contents of polyglutamate with relatively high molecular weights were significantly higher than those of the linear polymers. This behavior might be due to the interactions of polymer chains. A similar result has been reported for the polyglutamates on the dendrimers.[44]

In the helical structure, the intramolecular hydrogen bonds confer a rigidity to the polyglutamate so that the chain behaves like a rigid rod. As described earlier, the phenoxy groups are aligned approximately perpendicular to the nearly planar phosphazene ring.[13–15] If this geometrical arrangement holds for

26, it seems reasonable to assume that the rigid polyglutamate chains form 3α-helix bundle structures on both sides of the phosphazene ring.

For the polymerization of *N*-carboxy anhydride of β-benzyl-L-aspartate (**27**) with 2,2,4,4,6,6-hexakis(4-aminophenoxy)-2λ^5,4λ^5,6λ^5-cyclotri(phosphazene) (**28**), the hexa-armed star poly(β-benzyl-L-aspartate)s, which take mainly a left-handed α-helical structure, could be obtained only at a high ratio of [**27**]/[**28**] and at high conversion, due to the relatively low reactivity of amino group in **28** in the initiation process.[45]

Recently, we prepared amphiphilic star polymers comprised of stearylamino arms and polyglutamic acid arms from the polymerization of **25** initiated by 4,4,6,6-tetrakis(4-aminomethylphenoxy)-2,2-bis(stearylamino)-(**29**) and 6,6-bis(4-aminomethylphenoxy)-2,2,4,4-tetrakis(stearylamino)-2λ^5,4λ^5,6λ^5-cyclotri(phosphazene)s (**30**) as initiator and subsequent hydrolysis of resulting polymers (Scheme 6).[46]

The pH dependence of the helix content of polymers (**31**) consisting of four poly(glutamic acid)s ($DP_n/4 = 38$) and two alkyl chains attached to the phosphazene core showed that, upon a pH decrease, the helix content increases first rapidly in the pH range from ~6.5 to ~5.4 and then slowly in the pH range from ~5.4 to ~4.0. The helix content at pH = 5.0 was 28%, which was roughly three times higher than that of hexa-armed poly(glutamic acid). Similar increases of helix contents were observed for amphiphilic star-shaped polymers comprised of four poly(glutamic acid) arms with relatively short chains (**31**, $DP_n/4 = 22$) and two stearylamino arms or comprised of two poly(glutamic acid) arms and four stearylamino arms (**32**, $DP_n/2 = 32$). As shown in Fig. 1, the fluorescence of 8-anilinonaphthalene-1-sulfonic acid (ANS) in the presence of **31**, which has been extensively employed in describing the hydrophobic character of macromolecules, shifted from 490 nm at pH = 12.4 to 450 nm at pH = 4.5, accompanied by the enhancement of the intensity. The results suggest that the polymers with helical structure formed in the low pH region assemble to form hydrophobic sites. Such a assembly based on additional hydrophobic interactions might be responsible for the enhancement of the stability of helical structure.

The cyclotri(phosphazene), **19**, can be used as a core for the miktoarm stars (Chart 2). The polymers (**33**) consisting of polystyrene and nylon 6 branches[47] were prepared by two steps: the partial attachment of polystyrene with terminal NH_2 group (PSt-NH_2) to the acid chloride of the core and the subsequent ring-opening polymerization of ε-caprolactam (ε-CL) with carboxyl group formed by hydrolysis of the remaining acid chlorides. The increase in molecular weights by the polymerization of ε-CL and the ratio of polystyrene to nylon 6 units attached to the phosphazene core, determined by GPC and ^{1}H NMR spectra, are essentially consistent with the values calculated from the PSt-NH_2, initial ratio of [ε-CL]/[COOH], and conversion. These polymers **33** act as an excellent compatibilizer for poly(oxy-1,4-phenylene)-nylon-6 blends, as will be described later.

Polymeric Self-Assembly Materials Based on Cyclotriphosphazenes

Supramolecules (supramolecular structures) are formed through the spontaneous association of molecular subunits by noncovalent interactions such as hydrogen bonding, coordination bonding, or other weak intermolecular interactions into structurally well-defined aggregates.[11] The constituent molecules capable of selective and directional interactions giving rise to the assembly, however, are rather limited and the development of new building blocks is highly desirable.

The combination of the unique structure of phenoxycyclophosphazene[13–15] and the hydrogen bonding, a most powerful organizing force, might allow the construction of new rod-shaped supramolecular materials. Recent works have shown that the combination of carboxyl and pyridyl groups is a useful tool to form three-dimensional networks and mesogenic supramolecules.[48] If the carboxyl and pyridyl groups of **19** and **20** take a similar conformation to 2,2,4,4,6,6-hexa(4-phenoxy)-2λ^5,4λ^5,6λ^5-cyclotri(phosphazene), the complementary hydrogen bonding between them would be expected to form a cylindrical structure.[38] The supramolecular assembly (**34**) was obtained as prismatic crystals by allowing a solution containing **19** and **20** in equimolar ratio in DMF to stand for 6–10 h at room temperature. The single crystal X-ray diffraction analysis of **34** showed that the hydrogen bonding between pyridyl and carboxyl groups occurs in both sides on the phosphazene ring to give a rod (*tsuzumi*) structure, where the organic substituents in **19** and **20** are alternatively positioned above, and below the plane of the ring (Fig. 2). The X-ray analysis also showed that the phenoxy group in **34** stacked with pyridyl groups in neighboring rods. The hydrogen bonded $–OC_5H_5N\cdots HOOC–$ distances are 2.69, 2.66, 2.61, 2.82, 2.72, and 2.66 Å, which are considerably shorter than the sums of the van der Waal's radii, 3.20 Å, indicative of the formation of strong hydrogen bonding. Interestingly, in this *tsuzumi* structure, one of the $–OCH_2–$ moieties in the repeating units takes a disordered conformation. This implies that the flexible $–OCH_2–$ groups might act as an elbow joint which adjusts the pyridyl group so as to fit a suitable position required for the formation of *tsuzumi* structure. It appears that for **19** the intramolecular hydrogen bondings of carboxyl groups located on both sides of the phosphazene ring may make it possible to place carboxyl groups at a fixed position on the phosphazene ring. When **19** was added to **20**, these carboxyl groups might prefer to form hydrogen bonding with pyridine units rather than self-association. In **34**, the absence of single and double hydrogen bondings between **19** and **20** suggests that these incomplete hydrogen bondings break and the redisposition occurs until triple hydrogen bonding is formed.

On the basis of the above finding, the formation of new supramolecules from the combination of **20** and terephthalic acid, naphthalene-1,4-dicarboxylic acid, and anthracene-1,4-dicarboxylic acid in DMF were examined.[49,50] Characterization of the structure of these assemblies was proved to be possible with elemental analysis, FT-IR, ^{1}H NMR, and X-ray studies. The stoichiometry of the assemblies was **20**–dicarboxylic acids = 1:3. The spectroscopic data suggest that all pyridyl groups in **20** form hydrogen bonds with dicarboxylic acids to constitute supramolecular assemblies. The X-ray diffraction pattern showing sharp peaks was very similar to that of **34**. These results suggest that the assemblies, **35**, **36**, and **37** also take a rod structure composed of an alternating sequence of one **20** and three aromatic dicarboxylic acids (Chart 3).

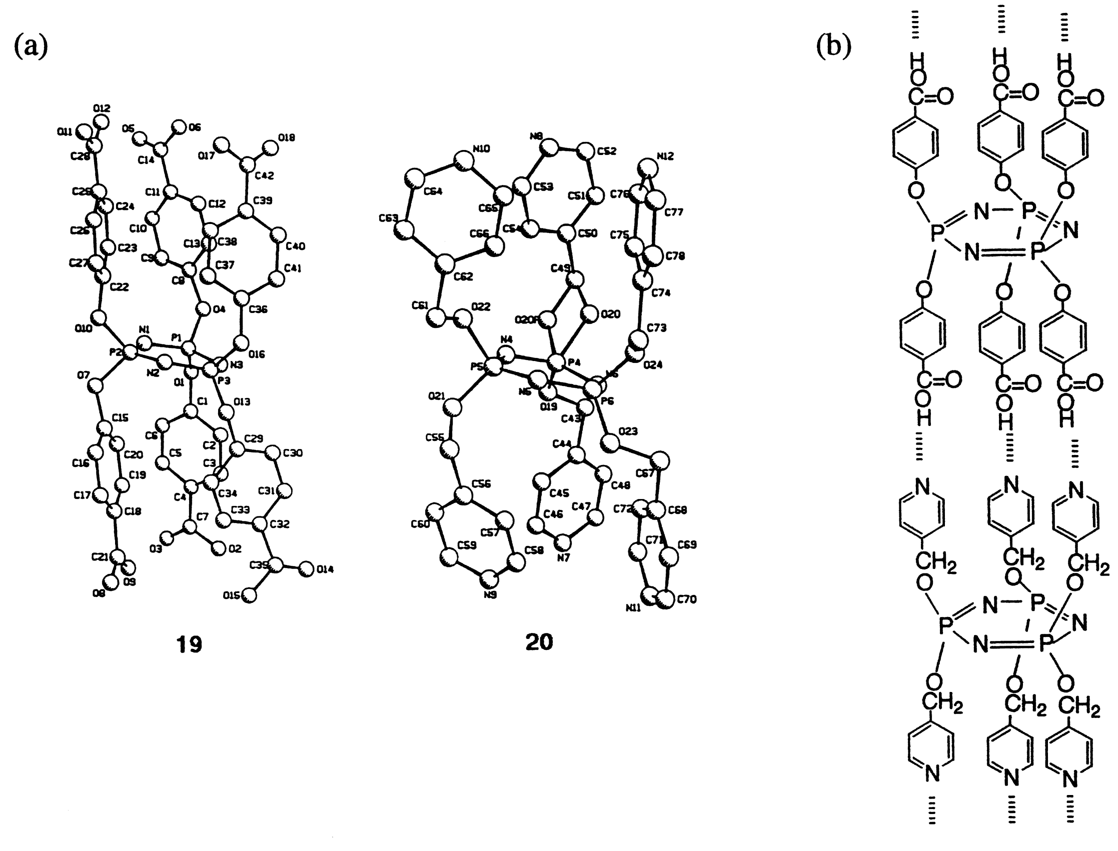


Fig. 2. (a) ORTEP drawings of **19** and **20**. Thermal ellipsoids are at the 50% probability level and hydrogen atoms were omitted for clarity. (b) Self-assembly of **34**.

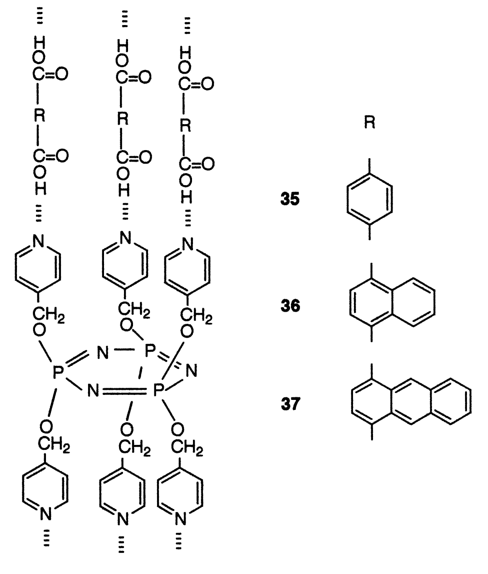
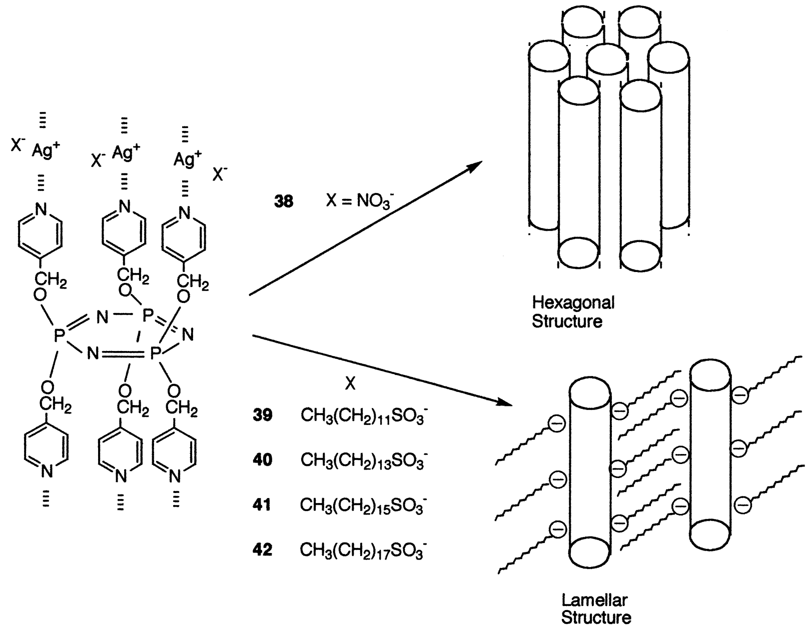


Chart 3. Supramolecules based on cyclotri(phosphazene)s.

From the fluorescence spectra and X-ray analysis of **36**, the assemblies can be presumed to be laterally packed into a hexagonal arrangement with the space of 13.3 Å, where the naphthalene rings are placed to avoid steric congestion. This implies that there is a possibility to develop substantial voids along the assemblies in the crystal of **36**. In fact, when iodine was mixed with a suspension of **36** in water, its white color changed to blue-black as time went by, and no noticeable discoloration was observed over one week, indicating that iodine molecules are trapped strongly in **36**. On the other hand, such a behavior was not observed for the assembly **35**. From FT-Raman spectroscopy, the iodine in **36** was found to exist as polyiodine linear I_5^- ion. These results show that the crystal of **36** has a tunnel-like void capable of including iodine. Furthermore, ^{1}H NMR studies of the assembly **37** obtained from **20** and bulky anthracene-1,4-dicarboxylic acid showed the inclusion of DMF molecules used as a solvent. The number of the DMF molecules trapped was estimated to be 1.1–1.2 per repeating unit of assembly, suggesting that the use of bulky component is effective for the formation of assembly with larger voids. The removal of DMF and the insertion of alternative compounds without significant destruction of the assembly, however, were unsuccessful at present. It is an interesting challenge to construct the supramolecular solids capable of reversible binding of guests.

Coordination bondings have emerged as an alternative tool for the construction of supramolecular species with well-defined shapes and geometries.[51,52] The self-assembling of **20** and $AgNO_3$ in DMSO gives a white rod-shaped coordination polymer **38** (Scheme 7).[53] The polymer structure originates from the unique molecular structure of **20** and the tendency of



Scheme 7. Rod-shaped supramolecules.

Ag^+ for linear coordination. FT-IR spectra, X-ray absorption fine structure spectra, and X-ray diffraction analysis showed that the rod-shaped coordination polymers **38** are laterally arranged to form a regular hexagonal structure. Thus, the linking of silver ions with **20** has created a new organometallic supramolecule. Interestingly, such a self-assembly was not obtained for the **20**–$AgBF_4$ system, suggesting that NO_3^- ions play an important role in the packing as counter anions to the polymers.

As research of coordination polymers based on cyclophosphazenes has developed, attempts to prepare hairy-rod polymers, rodlike polymers with flexible side chains, have been made. The most interesting property of these materials is their ability to form layered structures in crystals and liquid crystals when the alkyl side chains reach a critical length. Recently, this type of polymer has been demonstrated for the combination of 4,4′-bipyridine and silver alkanesulfonates, i.e., the rod-shaped coordination polymers with long alkyl chains take a lamellar structure.[54] As expected, the coordination polymers **39**–**42** with hairy-rod structure composed of **20**–silver alkanesulfonates (C_{12}, C_{14}, C_{16}, and C_{18}) = 1:3 were obtained (Scheme 7).[55] The coordination polymers **39**–**42** are stable indefinitely in air, and are insoluble in water and in common organic solvents. The hairy-rod polymers **40**, **41**, and **42** are organized in a lamellar structure, where the alkyl chains of neighboring polymers, which tilted with respect to the polymer backbone by ca. 40°, are interdigitated each other. On the other hand, the polymer **39** did not distinctly form the lamellar structure due to the disorder packing of alkyl chains. Thus, cyclotri(phosphazene)s are a useful motif to construct unique rod-shaped supramolecules.

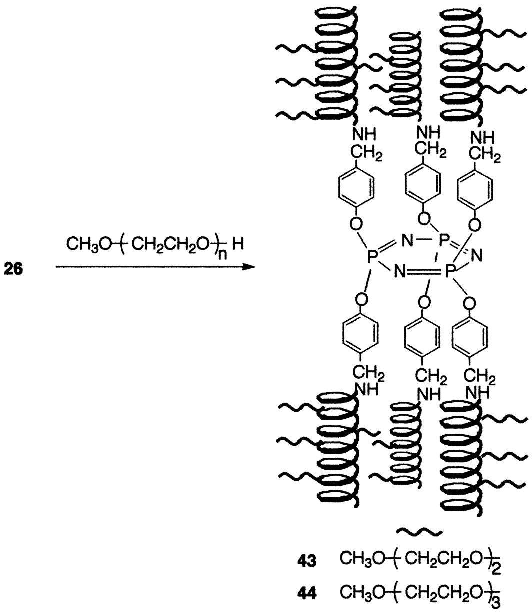
Functionality of Polymers Containing Cyclophosphazenes

Cyclic phosphazenes have attracted much interest since unique properties and functionalities are attainable through the introduction of organic groups into a P–Cl group. Although the synthesis of polymers containing cyclophosphazenes was rather recently achieved, several efforts have been made to use these polymers for specific applications.

Enantioselective Membranes. The development of membranes with high functionality is a subject on which future nanoscience in various fields depends.[56] If the hexa-armed star poly(amino acid) derivatives form 3α-helix bundle structures on both sides of a nearly planar phosphazene ring, new developments or improvements of functionalities based on α-helical structure would be expected, especially in the field of optical resolutions. Ogata et al.[57,58] have shown that the polyglutamates with amphiphilic side chains consisting of oligo(oxyethylene) and long alkyl chains can act as an effective membrane for resolving optical isomers. They demonstrated the importance of the formation of ordered α-helical structure for such a resolution. For the permeation of substrates across the membrane, the partition and diffusion factors are important for the membrane separation. The introduction of hydrophilic and flexible oligo(oxyethylene) units into hexa-armed polyglutamates (**26**) by transesterification might lead to an efficient permeation of amino acids across these membranes.

The polyglutamates with 57% (**43**, α-helix content = 82%) and 54% (**44**, α-helix content = 83%) of di- (DEG) and triethylene glycol monomethyl ethers (TEG) units as side arms, respectively, were used as enantioselective membranes (Scheme 8).[42] The helix contents of these polymers were not affected by the transesterification. Since the polymers obtained did not offer a self-standing membrane, teflon (diameter, 15 mm; porosity, 0.1 mm) was used as a supporting material for the permeation experiments. The membrane was prepared by dipping the teflon into a solution of the **44** (0.5–1 wt%) in $CHCl_3$. Then the membrane was sandwiched between donor containing D,L-amino acids and acceptor cells.

As shown in Fig. 3, the membrane **44** prepared from polyglutamates permeates only D-isomer for tryptophan (Trp), and the complete optical resolution held for over 200 h.[42] The ad-



Scheme 8. Star-shaped polyglutamates with oligo(oxyethylene) chains as enantioselective membrane.

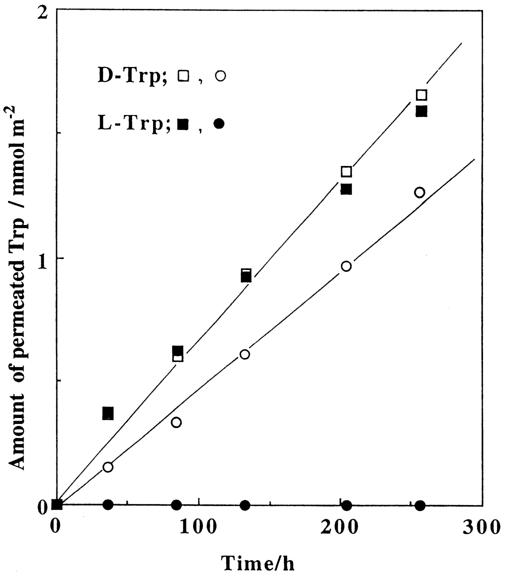


Fig. 3. Permeation behavior of D- (○, □) and L-Trp (●, ■) across the membrane **44** (○, ●) and the conventional linear polyglutamate membrane (□, ■).

dition of antibacterial reagent, NaN_3, did not exert any significant influence on the amount of permeate and the resolution. When the conventional polyglutamate with TEG units that was prepared from the polymerization of **25** with propylamine was used as a control experiment, the resolution of racemate of Trp was not observed. For the permeation of tyrosine (Tyr) and phenylalanine (Phe) through membrane **44**, the D-isomer permeated predominantly, and the enantioselectivities were 60% ee and 30% ee, respectively. For the polyglutamates with more than $DP_n/6 = 20$, the chain length did not affect the enantioselectivity significantly. However, the optical resolution of Phe was improved by changing from TEG to DEG units, i.e., for the enantioselectivity by **43** as high a value as 64% ee was attained.

It seems likely that the α-helical structure is essential for the chiral recognition of amino acids and that oxyethylene chains are concerned mainly in adsorption and transportation of the substrate. The absence of functionality of conventional polyglutamate with TEG units suggests that the additional factor, the assembly of the recognition sites, is required to attain a high enantioselectivity. A similar argument has been demonstrated for the polyglutamates carrying amphiphilic side chains, which have ability to form ordered structure, liquid crystals, at ambient temperatures.[57,58]

If the rigid polyglutamate chains with oxyethylene units form 3α-helix bundle structures on both sides of phosphazene ring, it appears that a relatively narrow channel along the α-helical structure is formed by the side-to-side interaction of the oxyethylene chains around hexa-armed polyglutamates, which makes possible effective molecular recognition of racemates in the vicinity of α-helical polyglutamate backbone. The increase in the enantioselectivity of Phe for **44** seems to relate with the size of channel, i.e., in such a narrow channel Phe with relatively small molecular size could interact efficiently with recognition site of α-helical polymer backbone. This is consistent with the observation reported previously.[57,58] It is worth noting that the structural change from linear to star-shaped polymers utilizing structural features of cyclotri(phosphazene) ring improves the functionality of molecular recognition.

Ag^+ Ion-Selective Polymers. A number of ionophores based on size-fitting concept including crown ethers have been prepared to achieve selective extraction and transport of a metal ion with high efficiency.[59] Although cyclophosphazenes can interact in several ways with metals, the most versatile method appears to be attaching suitable side groups containing donor atoms to the phosphorus atom of the ring.[60] Monomers (**2b**, **2c**, **2d**, **3b**, and **3c**) and their polymers are a kind of octopus (macro)molecules and are expected to display considerable discrimination abilities toward metal ions.[61]

The extractability of the monomeric ligands toward metal picrates such as Na^+, K^+, Cs^+ Ca^{2+}, and Cu^{2+} ions increased with increasing the length of oxyethylene arms. As expected, the extractability of polymer ligands enhanced compared to those of corresponding monomers. Interestingly, all of the ligands with $-(CH_2CH_2O)_nCH_3$ (n = 1–3) display high extractabilities (> 90%) toward Ag^+ ions, and even **2b** with ethoxy group extracts Ag^+ ion with a moderate efficiency (26%). The extraction equilibrium constant (log (Keq)) and the stoichiometry (n) determined were as follows: log(Keq) = 5.1 and n = 1 for **2b** and log (Keq) = 6.8 and n = 1 for poly(**2b**). ^{31}P and ^1H NMR spectra of the mixture of Ag^+ ions and poly(**2b**) suggest that Ag^+ ion lies above the cyclophosphazene units to form 1:1 Ag^+–cyclophosphazene units in the polymer chain.

The Ag^+ ion transports with monomers and polymers across $CHCl_3$ membrane were examined in the conventional U-type cell, where the source phase I is a solution of metal picrate in water, phase II is a solution of ligands in chloroform, and the receiving water is phase III. The rate of transport of Ag^+ ion mediated with **2b** was 23 times higher than that of K^+ ion. The selectivity of Ag^+ ion could be improved by controlling the hydrophobic and hydrophilic properties and localization of **2b** units in the copolymers. In fact, the poly(**2b**-co-MMA) with 38.4 mol% of **2b**, for example, can transport 75 times as many Ag^+ ions as K^+ ions. The high Ag^+ selectivity of the copolymer can hold even in the competitive transport of the mixture of Ag^+ and K^+ ions. Thus, the poly(**2b**-co-MMA) could extract and transport Ag^+ ions selectively, indicating that the cyclophosphazene is an excellent host molecule for Ag^+ ions.

Ionic Conductivity. Ionically conducting polymer electrolytes are the topic of considerable current research both for academic interests and for applications to electrochemical display devices, sensors, power sources, and high-energy-density batteries.[62] The ionic conductivity (σ) is known to be given simply by

$$\sigma = ne\mu$$

where n, e, and μ are the total number of carrier ions, the elementary electric charge, and the carrier mobility, respectively. This implies that two basic requirements are needed for an effective solid polymer electrolytes: a number of donor atoms capable of complexing metal ions and high flexibility to provide a passage for the transport of metal ions, which can be estimated by the glass transition temperature of polymers. In such polymers, ionic conductivity occurs via random walk of ions from one transient coordination site to another, facilitated by the segmental motions of the polymers. Hence, most of polymer electrolytes have been prepared taking into account the flexibility of the backbone, e.g., the linear polyphosphazens carrying $-(OCH_2CH_2)_2OCH_3$ units display as a highly ionic conductive polyelectrolyte, ($\sigma = 5 \times 10^{-5}$ S cm^{-1} at 20 °C for $LiN(CF_3SO_2)_2$ complexes), reflecting the flexibility of the backbone.[63]

The polymers poly(**2c**), poly(**2d**), and poly(**3c**)[19a,64c] have various features as a polymeric electrolyte host: (i) the introduction of many short oxyethylene chains into a phosphazene ring of polystyrene derivatives brings about a low glass transition temperature; (ii) the rigid and sterically large groups, such as benzene and phosphazene rings, impart a greater free volume around oxyethylene chains; and (iii) the formation of complex with a small solvated ion radius is possible. If the oxyethylene chains form a continuous conducting phase around the backbone, carrier ions could move in the phase independent of the nature of the polymer backbone and a high conductivity would be expected.

The introduction of oligo(oxyethylene) units into cyclophosphazene units brought a favorable effect on the glass transition temperatures of polymers. The T_g values of these polymers (-65–-60 °C) increase monotonically with increasing in the concentration of the $LiClO_4$. These behaviors can be attributed to the restriction of segmental motion caused by the polymer-salt interaction. In Fig. 4 is shown the temperature dependence of the ionic conductivity of poly(**2d**)–$LiClO_4$ complexes. For all of the complexes, the plots of log σ vs $1/T$ are curved, indicating an ion transport in the amorphous phase, which is prerequisite to achieve a high ionic conductivity. Such a type of ion transport has been described by the Vogel–Tamman–Fulcher (VTF) equation. The VTF plots of the complexes exhibit straight lines when the standard temperature is defined as T_g-50 °C. This implies that the ion transport is controlled by the segmental motion of oxyethylene chains. The maximum conductivity of 1.8×10^{-5} S cm^{-1} at 30 °C has been achieved for the poly(**2d**)–Li^+ salt complex of $[Li^+]/O = 0.05$. A similar value was obtained for polybiphenyl derivatives (poly(**3c**))–Li^+ complexes. The observed values were 10–10^4 times higher than those of most of the complexes based on polyacrylates and poly(styrene-*alter*-maleic anhydride) and comparable to those of highly flexible polyphosphazene-alkali metal salt complexes. Such a high conductivity indicates that the flexibilities of the backbone are not the critical factor required to achieve high conductivities and each ion transport is mediated by the segmental motion of side chains without being significantly affected by the mobility of the main chain. In addition, one of characteristic features of these polyelectrolytes is that the temperature dependence of conductivity is rather small compared to that of comb-shaped polymer–Li^+ salt complexes reported in the literature.

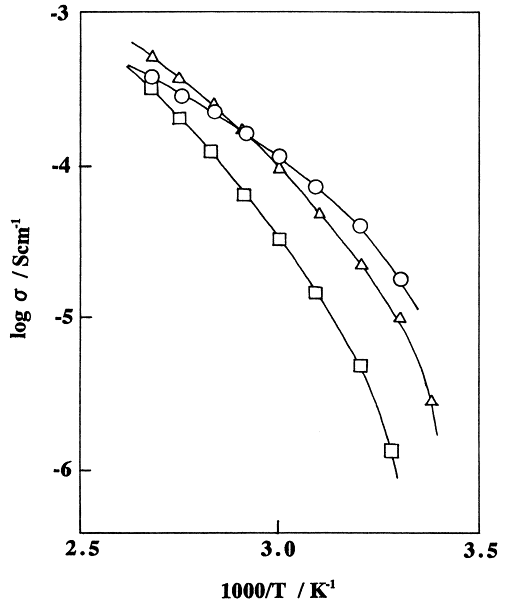
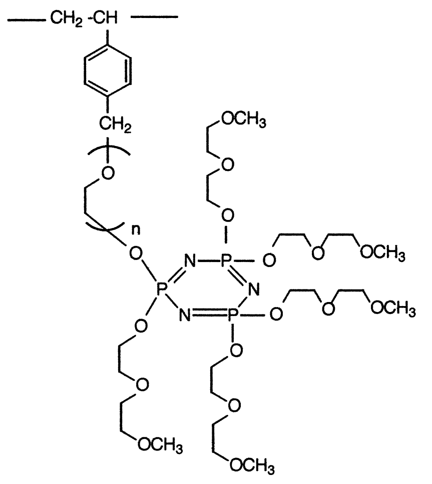


Fig. 4. Temperature dependence of ionic conductivity for poly(**2b**)–$LiClO_4$ complexes. $[Li^+]/[O] = 0.05$ (○), 0.075 (△), 0.1 (□).

The conductivity values of Li^+ salt complexes of polystyrenes with a spacer (poly(**45**), $-CH_2OCH_2CH_2)-$; poly(**46**), $-CH_2(OCH_2CH_2)_2-$) between the polymer backbone and (methoxyethoxyethoxy)cyclotri(phosphazene) moiety have been studied (Chart 4).[64a] The maximum conductivity at 60 °C increased in the order poly(**46**) > poly(**2d**) = poly(**3c**) > poly(**2c**) = poly(**45**) > poly(**3b**). From the relationship between the polymer structure and conductivity, it appears that the ease of the formation of continuous oxyethylene phase around backbone is a key for fast ion transport, independent of the rigidity of the polymer backbone. In consistent with this argument, the complexes of rigid polynorbornene backbone carrying oligo(oxyethylene)cyclophosphazene with $LiN(SO_2CF_3)_2$ were reported to have conductivities above 10^{-5} S cm^{-1} at 25 °C.[65]

The complex formed might be related structurally to the complex Li^+-octopus molecule, which is known to occur faster and more completely than that of crown ethers.[59] This implies that the Li^+ ion coordinated with oxygen atoms in the oli-



poly(45) n = 1

poly(46) n = 2

Chart 4. Ionically conductive polystyrene derivatives with flexible spacer.

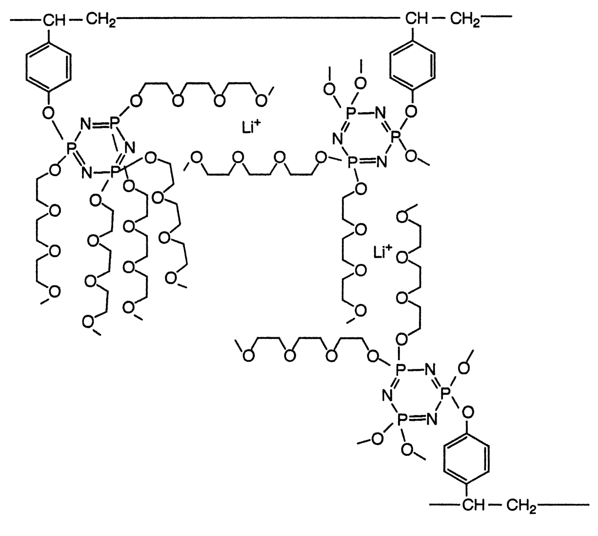


Fig. 5. Schematic representation of poly(**2b**)–Li$^+$ complexes.

go(oxyethylene) chains on a phosphazene ring forms moves with difficulty (a tight complex), whereas the complex formed by the side chains on neighboring monomer units salt interactions seems to be relatively loose and the Li$^+$ ion moves with ease (Fig. 5). The polymer with long oxyethylene chains appears to facilitate the formation of a loose complex, since the chains can easily come near one another, although this interchain salt interaction adversely effects on the segmental mobility. The conductivities for the multi-armed polystyrene–Li$^+$ complex systems might be governed by both the mobility of continuous oxyethylene chains and the stability of the complex.

The additions of low molecular weights of linear and cyclic polyethers into polymeric electrolytes have been demonstrated to be one of the effective methods to improve the conductivity.[66] These additives could contribute to the increase in carrier ions due to effective cation solvation and the decrease of microviscosity of polymer matrix, although the additives adversely effect the mechanical properties of the polymer electrolyte film.

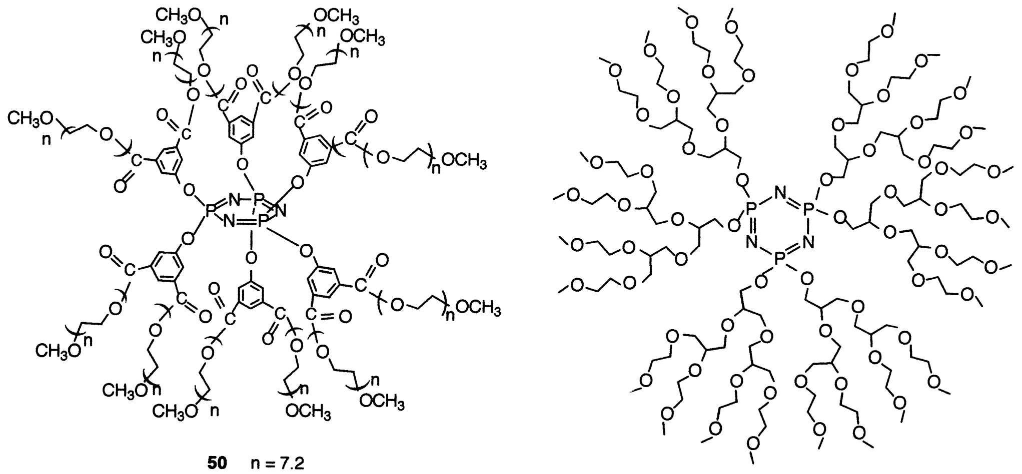
The addition of 18-crwon 6-ether (**47**) and 12-crwon 4-ether (**48**) to the poly(**2d**)–Li$^+$ system did not affect the extents of T_g elevation, whereas the increase in T_g values is considerably suppressed when 1,4,8,11-tetrakis(2-methoxyethyl)-1,4,8,11-tetraazacyclotetradecane(**49**) is used.[67] For **47**, the conductivity of the complex with Li$^+$/O = 0.03 increased slightly from $\sigma = 1.8 \times 10^{-4}$ S cm^{-1} to $\sigma = 2.7 \times 10^{-4}$ S cm^{-1} at 30 °C, and, for **48**, the increase in the conductivity was a factor of 2.5 compared to the poly(**5**)–$LiClO_4$ complex with the same Li$^+$/O ratio. The addition of **49** was more effective to improve the conductivity; the conductivities of the complexes with Li$^+$/O = 0.04 and 0.05 have been raised to 10^{-4} S cm^{-1} at 30 °C and 10^{-3} S cm^{-1} at 90 °C, respectively, suggesting that effective ion separation by **49** occurs and a large number of carrier ions is available.

From the behaviors of T_g elevation for the poly(**2d**)–$LiClO_4$-additive systems, it appears that Li$^+$ ions move out from the cavity of **47** or **48** and prefer to bind with oxyethylene chains of poly(**2d**), whereas most of Li$^+$ ions have been trapped in the cavity of **49**. This implies that Li$^+$ ions could not appreciably contribute to the conduction, so the anions might be mainly responsible for conduction. Such anions are considered to be loosely associated to the dipoles of the polymer and fast transport might be possible in tune with the high segmental motion.

Branches in polymers play an important role in determining properties like their viscosity and density, and the ionic conductivity of these polymers has also been studied. For example, the hyperbranched poly(ether ester) was synthesized by the polycondensation of AB_2 monomers prepared from the reaction of methyl 3,5-dihydroxybenzoate with di-, tri-, or hexaethylene glycol derivatives.[68] As expected, the polymers were amorphous and the glass transition temperatures decreased with increasing of oxyethylene units. The conductivity of hyperbranched polymer linked with $-(CH_2CH_2O)_6-Li^+$ salt complexes was $\sigma = 7 \times 10^{-5}$ S cm^{-1} at 60 °C.

For the Li$^+$ salt complexes with star-shaped polyelectrolytes based on cyclophosphazene core, the conductivities depend on the number and length of oxyethylene units ($-(CH_2CH_2O)n-CH_3$ (**50**, n = 7.2 and **51**, n = 11.8) (Chart 5). The Tg elevation of the polymer–Li$^+$ complexes was significantly suppressed compared to that of linear counterparts.[69] The maximum conductivity of 4×10^{-5} S cm^{-1} at 30 °C was observed for the **51**–Li$^+$ salt complexes. The observed values are somewhat higher than those of the polystyrenes carrying pendant oligo(oxyethylene)cyclophosphazene–Li$^+$ salt system.[19a] This improvement is ascribed to the high segmental mobility of oxyethylene chains, as judged from the extent of T_g elevation.

Hyperbranched poly(oxyethylene) attached to cyclotri(phosphazene) core (**52**) was also used as ion transport assistance in the poly[bis(methoxyethoxyethoxy)phosphazene] (MEEP)–Li$^+$ system.[70] The addition of **52** to the MEEP–$LiSO_3CF_3$ system improved the conductivity, suggesting that the hyperbranched cyclophosphazenes contribute to decreasing the degree of ionic crosslinking between metal ion and oxyethylene chains in MEEP.



50 n = 7.2

51 n = 11.8

52

Chart 5. Star-shaped ion-conductive polymers (**50** and **51**) and ion transport assistance (**52**).

Compatibilizers. Block and graft copolymers have been of interest as compatibilizing agents for immiscible blends. For the compatibilizing process, the interpenetration of segments of copolymers and blend components is necessary to achieve a strong mechanical adhesion caused by the reduction of the surface tension due to the presence of the copolymers. Of even more interest, from the practical point of view, is the effect of the hyperbranched and star-shaped polymers on the immiscible polymer blends. However, only a few examples of blends with these materials are known. The heteroarm block copolymers with phosphazene core as a compatibilizer were examined for the immiscible blend of poly(oxy-1,4-phenylene) (PPO) and nylon-6.[47]

For binary blends of PPO and miktoarm star with about four PSt arms and two nylon-6 arms (**33**), T_g values of PPO were shifted to lower temperatures and the T_g decreased with increasing the amount of **33**. Only a single T_g was observed for all binary blends, indicating the miscibility of the two polymers. The behavior of the degree of lowering of T_g indicates that the high polystyrene units/nylon 6 ratio and long polystyrene chains are required for the achievement of sufficient miscibility.

For a ternary blend of PPO/nylon-6/**33**, only one T_g was observed, corresponding to the PPO/PS phase. Scanning electron microscopy experiments showed that the fracture is smooth and domains were smaller in the blends containing **33**. In particular, the ternary blend of PPO/nylon-6/**33** with 45/45/10 exhibited finer dispersion of PPO with an average size of 0.3 μm. Reflecting this, ternary blends were found to have higher modulus, strength and elongation than binary PPO/miktoarm blend. These improvements were attributed to the increased adhesion at the PPO/nylon-6 interface due to the presence of polystyrene-containing copolymer on the phosphazene core.

Conclusion

Relatively new types of polymers and polymeric self-assemblies containing cyclophosphazenes have been described. These polymers might offer another dimension to the already well-known field of poly(organophosphazene)s composed of –P=N– backbone. The general synthetic strategies presented here could be extended to other monomers by virtue of the facile introduction of functional groups into the cyclophosphazene ring and might provide a route to potential modification of properties of the traditional polymers. One of the important aspects of cyclotri(phosphazene)s is their unique conformation, which brings about the development of functionality as observed for the permeation of amino acids or the construction of rod-shaped self-assembly. The cyclophosphazene units could contribute to the preparation of well-defined molecular objects and devices.

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