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Effects of Organic Side Group Structures on the Properties of Poly(organophosphazenes)[1]

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ABSTRACT: Methods are reported for the synthesis of three new classes of poly(organophosphazenes) via the substitution reactions of poly(dichlorophosphazene). The first class consists of single-substituent polymers with aromatic rings separated from the main chain by methyleneoxy-spacer groups. The second and third classes comprise mixed-substituent polymers that contain aryloxy and aryl ester or aryl Schiff's base side groups. The variations in glass transition temperature with changes in side groups are discussed and are compared with the values for various alkoxy and alkoxy ether side group systems. The absence of liquid crystallinity for most of the derivatives was ascribed to the restricted rotational freedom of the side groups and, for the mixed-substituent polymers, to a lack of stereoregularity.

Since the initial discovery of the poly(organophosphazene) system,[4-6] it has been clear that these polymers provide an excellent means for exploring the effects of changes in side group structure on the physical properties of macromolecules that possess inherently flexible polymer chains.[7-15] This feature is a consequence of the substitutive method of synthesis[4-6,15] that allows a wide variety of different organic or organometallic side groups to be attached to the polymer chain.

In a number of papers published in recent years we and others have explored the influence of the shape, size, and flexibility of organic side groups on the solid-state physical properties of high molecular weight poly(organophosphazenes).[4-12] The overall pattern emerging for this system is one in which the polyphosphazene backbone has a high inherent flexibility that can give rise to low glass transition temperatures (-60 to -100 °C) and, in the absence of extensive microcrystallinity, to the appearance of elastomeric properties. Indeed, this characteristic underlies most of the current technological uses for polyphosphazenes.[16-18]

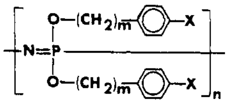
Given the inherent skeletal flexibility, the side groups play a critical role in determining the physical property variations among the many different poly(organophosphazenes) now known. Side group rigidity raises the glass transition temperature, an effect that is quite marked when aryloxy or arylamino side groups are linked directly to the chain. Thus, for single-substituent polymers, the measured glass transition temperatures (in parentheses) for polymers $(NPR_2)_n$ increase with changes in the side group in the order: R = F (-96 °C),[19] OC_2H_5 (-84 °C),[5] $OCH_2CH_2OCH_2CH_2OCH_3$ (-84 °C),[20] OCH_3 (-74 °C),[5] Cl (-63 °C),[4,5,9] $OCH_2CH_2OCH_3$ (-75 °C),[20] OC_6H_5 (-8 °C),[5] NHC_6H_5 (+91 °C).[6]

These effects can be ascribed mainly to steric hindrance between side groups on the same chain or between side groups and skeletal atoms as the skeleton attempts to undergo conformational changes under thermal- or stress-induced activation. Additional restrictions are evident when the side units or skeletal nitrogen atoms bear ionic sites,[21] when transition metals are present in the side group units and can coordinate to two different side unit structures,[22] or when planar side groups can "stack" to form quasi-crystalline arrays.[12] On the other hand, flexible side groups, such as OCH_2CH_3, $OCH_2CH_2OCH_3$, or $OCH_2CH_2OCH_2CH_2OCH_3$, have a minimal effect on the reorientational freedom of the backbone.

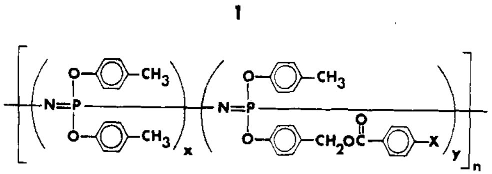
Certain polyphosphazenes with trifluoroethoxy or aryloxy side groups have been shown to exist in a mesogenic or quasi-crystalline state between a transition temperature $T(1)$ and the true melting temperature (T_m). This phenomenon was first reported by Allen and co-workers[23] and has been studied in some detail by Schneider, Singler, Desper, Beres and their co-workers.[24,25]

Given these facts, two questions are of special interest. First, what is the influence of side groups that consist of rigid organic side units separated from the main chain by flexible spacer groups? And second, what influence on the solid-state properties results from the presence of two or more different but bulky substituent groups arrayed randomly or sequentially along the same chain? These questions are relevant not only to the design of low-temperature elastomers and glassy materials but also to the prospective synthesis of liquid crystalline polymers.

In this paper we describe three new classes of polyphosphazenes that contain bulky, aromatic side groups. The first (species 1) contains aryl side units separated from the skeleton by alkyleneoxy spacer groups. The second (2) contains two different types of aryloxy substituent groups, including one in which a second aryl ring is connected to the first through a flexible, alkylene ester linkage.[26] The third class (3)[26] consists of mixed-substituent polymers bearing both *p*-methylphenoxy and rigid, aromatic, Schiff's base side groups. In addition, comparisons are made with polyphosphazenes that bear highly flexible alkoxy ether side groups (4) or alkoxy groups with alkyl units of increasing chain length (5).



1



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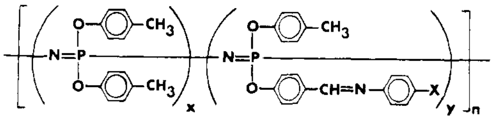

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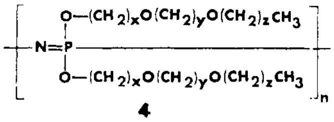
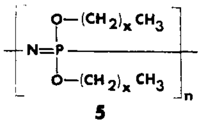


$$\left[N{=}P\left(O(CH_2)_xO(CH_2)_yO(CH_2)_zCH_3\right)_2\right]_n$$

4



$$\left[N{=}P\left(O(CH_2)_xCH_3\right)_2\right]_n$$

5

It should be noted that the synthesis of new polyphosphazenes usually requires exploratory chemistry to be carried out first at the small molecule level.[27] This

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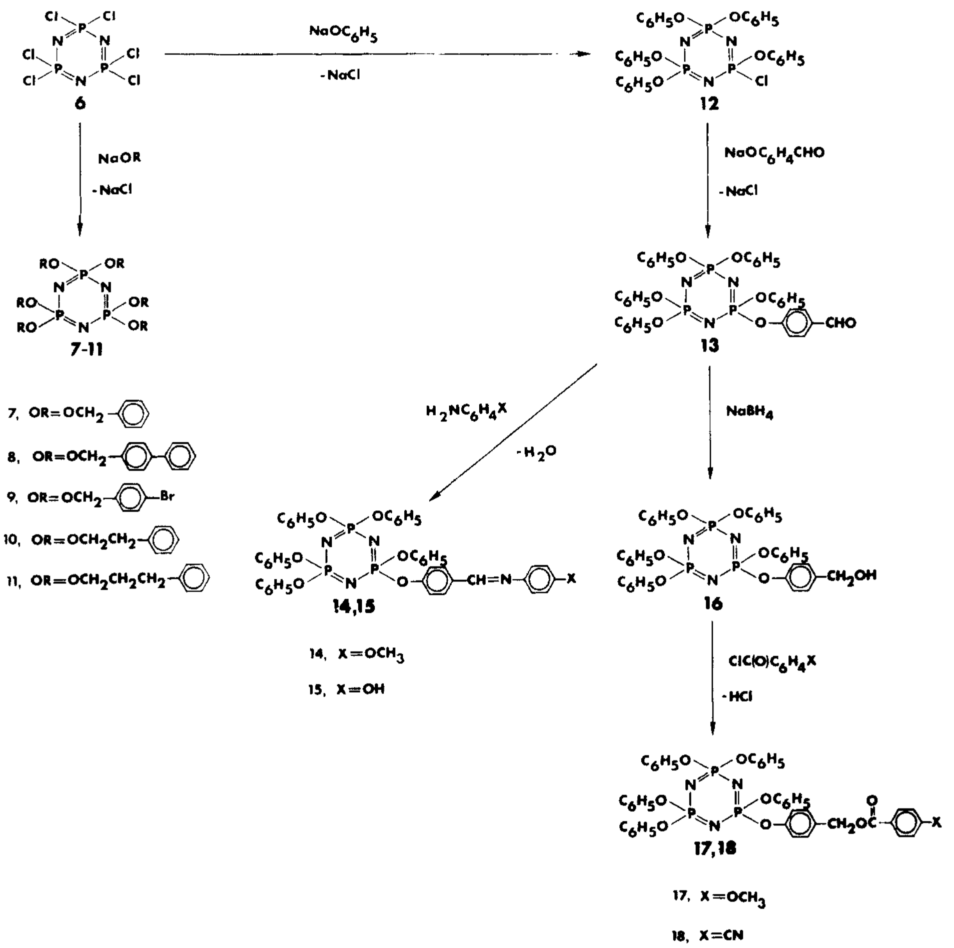
Scheme I



principle was followed in the present work, with the cyclic trimeric analogues of 1–3 being synthesized and characterized first.

Results and Discussion

Cyclic Trimeric Model Systems. The small-molecule model reactions were carried out with the use of hexachlorocyclotriphosphazene (**6**) as a substrate for substitution by $NaOCH_2C_6H_5$, $NaOCH_2C_6H_4C_6H_5$-*p*, $NaOCH_2C_6H_4Br$-*p*, $NaOCH_2CH_2C_6H_5$, and $NaOCH_2CH_2CH_2C_6H_5$ to give species **7–11** (Scheme I). Species **7–9** are white, crystalline solids. Compounds **10** and **11** were oils at room temperature. Compound **10** underwent no detectable O → N alkyl group migration at 176 °C in a sealed, evacuated tube during 22 h. This contrasts with the reported behavior of **7**.[28]

In addition, trimer **6** was treated with 5 equiv of sodium phenoxide to yield **12**, which formed the starting point for two alternative trial synthetic pathways. First, treatment of **12** with *p*-formylphenoxide yielded **13**, which formed the Schiff's base compounds **14** and **15** when treated with *p*-methoxy- or *p*-hydroxyaniline. Alternatively, **13** was reduced to the primary alcohol, **16**, by treatment with sodium borohydride, and **16** was then allowed to react with *p*-methoxy- or *p*-cyanobenzoyl chloride to yield the esters, **17** and **18**.

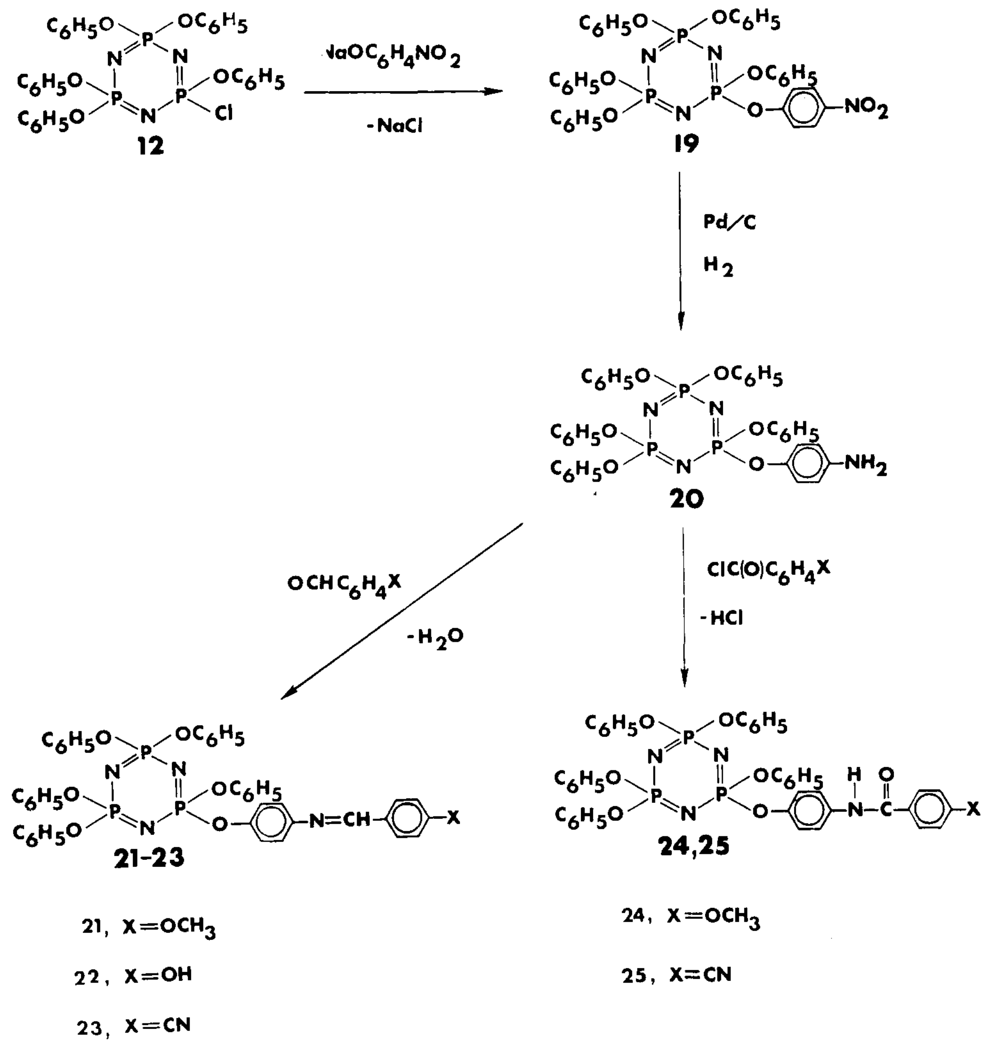
In the second route (Scheme II), species **12** was treated with *p*-nitrophenoxide to give **19**, which was reduced to the amine, **20**, by hydrogen over palladium. Compound **20** then formed the Schiff's base derivatives, **21–23**, when treated with *p*-methoxy-, *p*-hydroxy-, or *p*-cyanobenzaldehyde. Amine **20** also reacted with *p*-methoxy- or *p*-cyanobenzoyl chloride to give the amides, **24** and **25**. Although these synthesis via the nitroaryloxy derivative, **19**, were accomplished readily at this small molecule level, serious difficulties were encountered when attempts were made to transpose this chemistry to the macromolecular level (see later). Hence, only those syntheses based on **7–11**, **14**, **15**, **17**, and **18** could be adapted to the high polymeric system.

The cyclic trimeric compounds were characterized by a combination of elemental analyses, mass spectrometry, ^{31}P NMR, and ^{1}H NMR spectroscopy (Tables II and III). Thus, cyclic trimers **7–11** absorbed strongly in the infrared region at 1100–1300 cm^{-1}, which provided confirmation for the presence of the six-membered phosphazene ring. Absorptions characteristic of methylene groups and aryl rings were also detected. All five compounds yielded a single resonance at $\sim$+18.5 ppm in the ^{31}P NMR spectra.

The structures of trimers **13–25** were verified by the following information. Again, the retention of the cyclic trimeric ring was indicated by the presence of a strong infrared absorption at 1100–1300 cm^{-1}. The carbonyl groups in **13**, which were detected at 1710 cm^{-1}, and the primary amine groups in **20** at 3150–3350 cm^{-1}, disappeared following Schiff's base formation. This was accompanied by the appearance of C=N stretching modes in the 1600–1630 cm^{-1} region. Formation of the amides, **24** and **25**, was accompanied by the appearance of an amide carbonyl stretching absorption at 1650–1660 cm^{-1}. For the esters, **17** and **18**, the carbonyl absorption appeared at 1720 cm^{-1}.

The ^{31}P NMR spectra for **13–25** contained single, sharp resonances between +8 and +11 ppm (the structural differences appear to be so far from the skeletal phosphorus atoms that a separate chemical shift is not detected for

Scheme II



the unit that bears the unique substituent). The Schiff's base products gave a ^1H NMR singlet near 8.4 ppm, with an absence of the aldehydic proton resonance found in **14** and **15**. In esters **17** and **18** the methylene protons at 5.3 ppm were shifted from the 2.8 ppm value in alcohol **16**.

With the practicality of these synthetic routes confirmed at the small molecule level, an attempt was then made to apply the same chemistry to the high polymeric analogues.

Synthesis of High Polymers. The synthetic pathways are outlined in Scheme III. Poly(dichlorophosphazene) (**26**), prepared by the thermal polymerization of the cyclic trimer (**6**), was allowed to react with the sodium salts of benzyl alcohol, 4-biphenylmethanol, 4-bromobenzyl alcohol, phenethyl alcohol, and 3-phenyl-1-propanol, to give the poly(organophosphazenes) **27**–**31**.

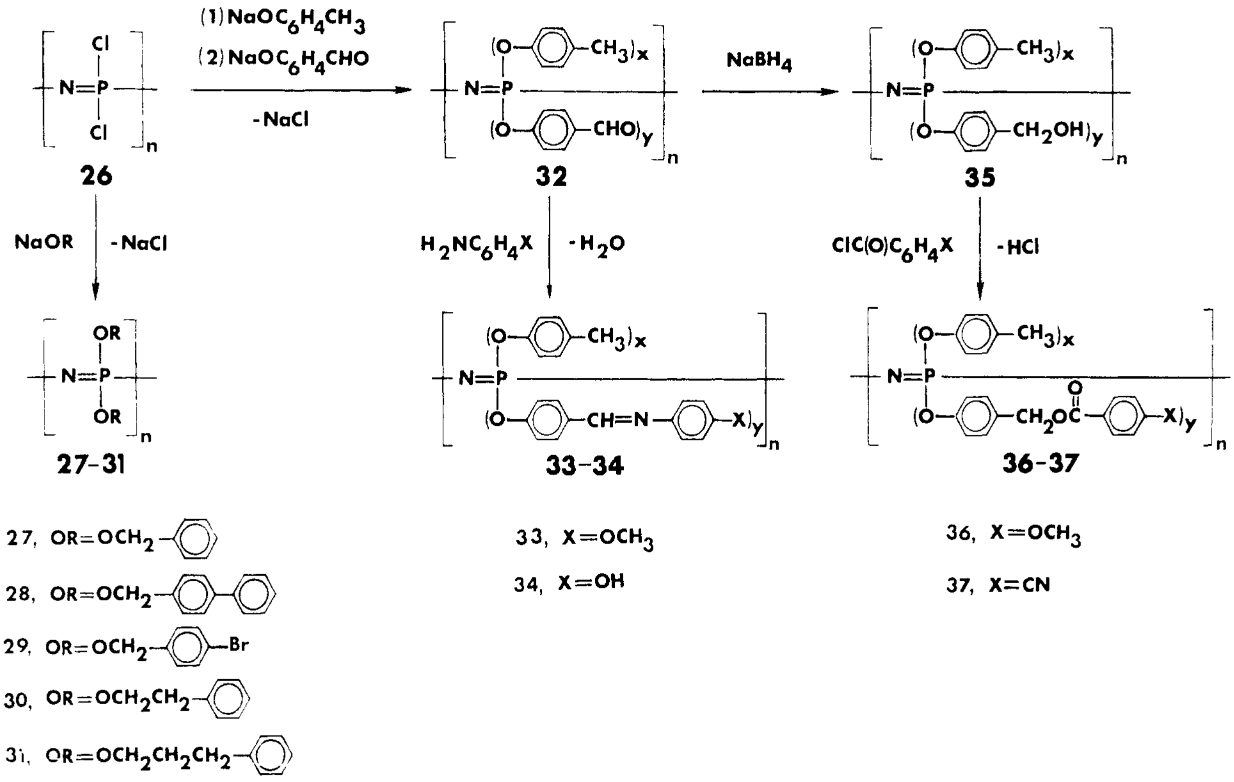
As anticipated from the small-molecule reactions, polymers **30** and **31** could be prepared only by the use of mild (room temperature) reaction conditions. At higher temperatures, or if $(n\text{-Bu})_4NBr$ was added as an accelerator, the polymers underwent decomposition during substitution. The related polymer, $[NP(OCH_2CH_3)_2]_n$, behaves similarly. A side group O → N alkyl migration, followed by chain cleavage, could explain this behavior. Polymer **28** was unstable above 170 °C even after isolation and purification. Polymers **27** and **29**–**31** are colorless, flexible, film-forming materials. Compound **28** is a glass or microcrystalline material at room temperature.

Macromolecules **33**, **34**, **36**, and **37** (Scheme III) were prepared by processes similar to those explored at the small-molecule level. Specifically, poly(dichlorophosphazene) was treated sequentially with the sodium salts of *p*-methylphenol and *p*-hydroxybenzaldehyde to yield the mixed-substituent polymer **32**. A sequential mode of substitution was employed in order to allow the *p*-methylphenoxy units to replace only one chlorine atom per phosphorus in the initial stages. This nongeminal replacement pattern results mainly from steric hindrance by aryloxy groups. Thus, the procedure reduced the possibility that two *p*-formylphenoxy groups would be present on the same phosphorus atom. In this precursor polymer, the *p*-methylphenoxy groups constituted 67% and the *p*-formylphenoxy groups 33% of the total side groups present. Hence, the structure shown in **32** is an oversimplification, since roughly 30% of the repeating units bear two *p*-methylphenoxy side groups.

Treatment of **32** with *p*-methoxyaniline or *p*-hydroxyaniline yielded the Schiff's base derivatives, **33** and **34**. These proved to be sensitive to moisture. Hence, some *p*-formylphenoxy groups were always present after exposure of the polymers to water. Reduction of **32** with sodium borohydride generated the primary alcohol derivative, **35**, and this was converted to the esters **36** and **37** by treatment with *p*-methoxy- or *p*-cyanobenzoyl chloride in THF/triethylamine media.

It should be noted that the alternative route to Schiff's base or to side group amido polymers, analogous to **21**–**23** or **24** and **25**, proved to be unsatisfactory because of the difficulty experienced in the reduction of the high polymeric analogue of **19** to the macromolecular counterpart of **20**.

Scheme III



Polymer **54** (Table I) has been reported previously,[4,5] and the phenylphenoxy derivative, **55**, was prepared in a similar manner by the reaction of sodium 4-phenylphenoxide with poly(dichlorophosphazene).[30]

The compositions and structures of polymers **27–31**, **33**, **34**, **36**, and **37** were derived from a combination of elemental microanalytical data, gel permeation chromatography, differential scanning calorimetry, and ^{31}P NMR spectroscopy. These data are summarized in Table IV. All the polymers were soluble in organic media and were, therefore, uncross-linked.

For polymers **27–31**, the infrared spectra contained an intense absorption between 1200 and 1300 cm^{-1}, which is characteristic of a high polymeric phosphazene skeleton. The normal absorptions for methylene and aryl groups were also detected. The ^{31}P NMR spectra contained a single, sharp resonance at $\sim$-7.0 ppm (or $\sim$-8.0 ppm for **30** and **31**). The elemental analyses were compatible with structures **27–31**.

Polymers **32–37** also yielded a strong skeletal infrared absorption between 1200 and 1250 cm^{-1}. The disappearance of the characteristic carbonyl absorption at 1700 cm^{-1} when **32** was converted to **33–35** was compatible with the loss of the aldehydic function. In addition, the concurrent appearance of the C=N peak at 1620–1630 cm^{-1} in **33** and **34** confirmed the Schiff's base structures. The appearance of a carbonyl bond at 1720 cm^{-1} in **36** and **37** was compatible with the formation of the esters.

The ^{31}P NMR spectra of **32** and **35** contained only a single peak at $\sim$-20 ppm. The different para substituents are presumably too far from the phosphorus center to influence the ^{31}P NMR shift. Hence, phosphorus atoms that bear only *p*-methylphenoxy groups were indistinguishable from those that bear the two different substituents. Similarly, conversion of **32** to **33** or **34**, or of **35** to **36** or **37**, brought about no change in the phosphorus spectrum. The ^{1}H NMR spectra provided evidence for the presence of "imine" protons at 8.5 ppm in the linkage group of **33** and **34** and for the absence of or much decreased intensity of the aldehydic proton resonance at 9.9 ppm.

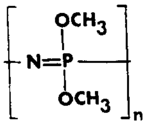
The alkoxyphosphazene high polymers **38–40** were prepared as described previously,[4,5] and **41–49** were synthesized by the same method—by the reaction of the appropriate sodium alkoxide with poly(dichlorophosphazene). The alkoxy ether substituted high polymers, **50–53**, were prepared by the method described previously.[21,29] Compounds **50** and **51** have been reported earlier. Polymers **52** and **53** are new. Characterization of these species was by means of ^{31}P NMR, infrared spectroscopy, microanalysis, and gel permeation chromatography.

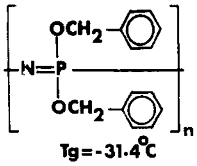
Thermal Analysis Data. The glass transition temperature (T_g) of a polymer is believed to be a measure of the reorientational freedom of the macromolecular chain. High T_g values are associated with rigid polymers; low T_g's are found in highly flexible polymers. However, highly flexible polymer chains can generate high T_g values if the reorientational freedom of the chain is restricted by steric or polar interference by rigid side groups. For multiatomic side groups, the shape of the torsional "cone angle" and the rigidity of the constituent atomic groupings have an important influence on the flexibility of the polymer chain.

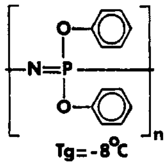
T_g values for polymers **27–31**, together with those of some related compounds, are shown in Table I. Two influences should be noted. First, an important role is played by the methylene groups that separate the phenyl rings from the oxygen atoms and the skeleton. Second, the presence of a second aryl ring at the para position of an aryloxy- or arylmethyleneoxy unit exerts an additional influence.

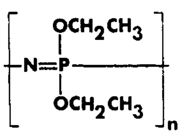
The T_g for **27** was found to be 23.4 °C lower than that of $[NP(OC_6H_5)_2]_n$ (**54**). This is a clear indication that the methylene spacer group in **27** reduces the intramolecular steric hindrance that is characteristic of **54**[8] by improving the reorientational freedom of the side group structure. The side groups in **27** are, therefore, capable of more facile "avoidance" motions as the backbone changes conformation under thermal- or stress-induced activation. The interposition of a second methylene spacer group, as in **30**,

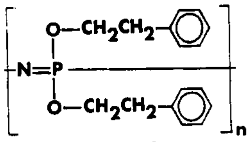
Table I
Variation in Glass Transition Temperature (T_g) with Polyphosphazene Side Group Structure

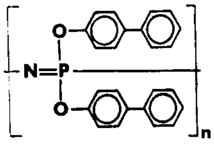

Tg=-74°C
38

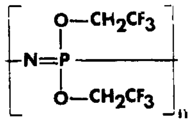

Tg=-31·4°C
27

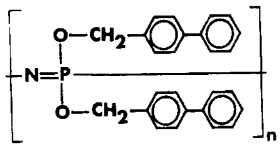

Tg=-8°C
54

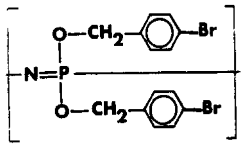

Tg=-84°C
39

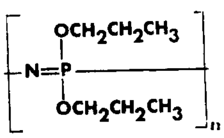

Tg=-32·7°C
30


Tg=+93°C
55


Tg=-66°C
40


Tg = +44 to +60°C
28


Tg =-0·8°C
29


Tg=-100°C
41

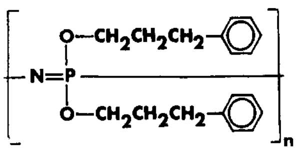
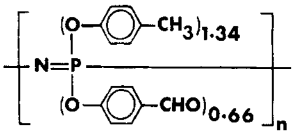
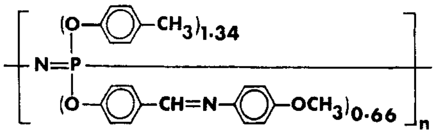
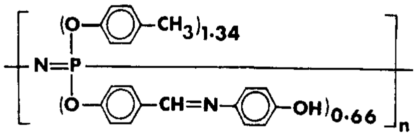
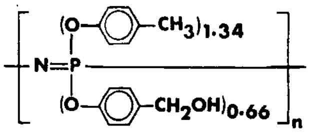

Tg=-47°C
31

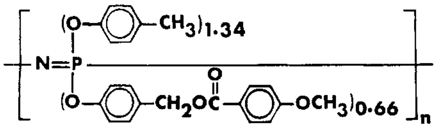
Table II
Variation in Glass Transition Temperature (T_g) with Polyphosphazene Side Group Structure

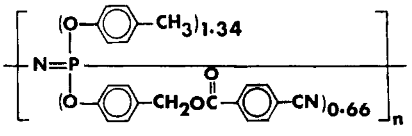

Tg=+11°C
32


Tg=+81°C
33


Tg=+25°C
34


Tg=+42°C
35


Tg=+46°C
36

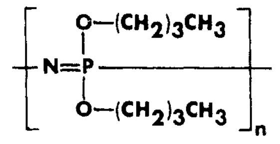

Tg=+75°C
37

has hardly any additional influence on the T_g. The presence of a third methylene group, in 31, lowers the T_g by a further 15 °C.

The role of phenyl groups in the side unit is illustrated by a comparison between 38 (Table I) and 27, between 39 and 30, and between 41 and 31. Replacement of a hy-

Table III

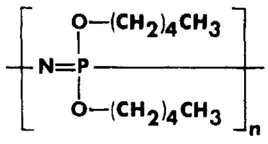
Variation in Glass Transition Temperature (T_g) with Polyphosphazene Side Group Structure



$$\left[N{=}P(O{-}(CH_2)_3CH_3)_2\right]_n$$

Tg = -105°C

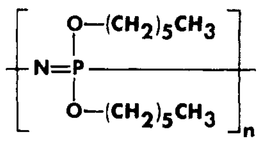
42



$$\left[N{=}P(O{-}(CH_2)_4CH_3)_2\right]_n$$

Tg = -104°C

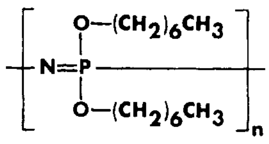
43



$$\left[N{=}P(O{-}(CH_2)_5CH_3)_2\right]_n$$

Tg = -104°C

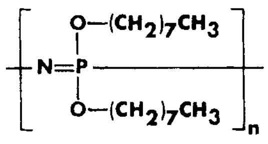
44



$$\left[N{=}P(O{-}(CH_2)_6CH_3)_2\right]_n$$

Tg = -94°C

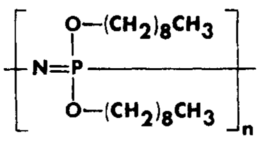
45



$$\left[N{=}P(O{-}(CH_2)_7CH_3)_2\right]_n$$

Tg = -84°C

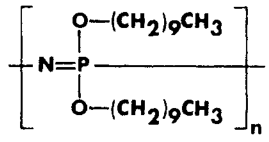
46



$$\left[N{=}P(O{-}(CH_2)_8CH_3)_2\right]_n$$

Tg = -56°C

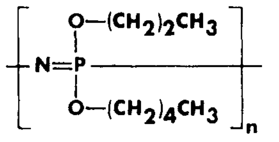
47



$$\left[N{=}P(O{-}(CH_2)_9CH_3)_2\right]_n$$

Tg = -44°C

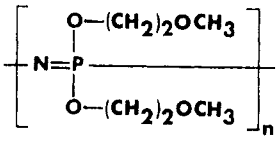
48



$$\left[N{=}\overset{O-(CH_2)_2CH_3}{\underset{O-(CH_2)_4CH_3}{P}}\right]_n$$

Tg = -100°C

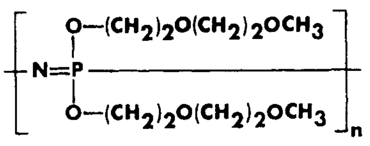
49



$$\left[N{=}P(O{-}(CH_2)_2OCH_3)_2\right]_n$$

Tg = -75°C

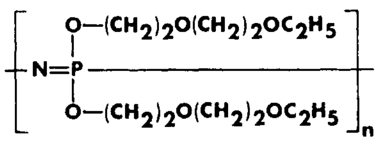
50



$$\left[N{=}P(O{-}(CH_2)_2O(CH_2)_2OCH_3)_2\right]_n$$

Tg = -84°C

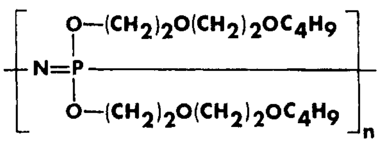
51



$$\left[N{=}P(O{-}(CH_2)_2O(CH_2)_2OC_2H_5)_2\right]_n$$

Tg = -78°C

52



$$\left[N{=}P(O{-}(CH_2)_2O(CH_2)_2OC_4H_9)_2\right]_n$$

Tg = -84°C

53

drogen atom in $[NP(OCH_3)_2]_n$ (**38**) by a phenyl group raises the T_g by nearly 43 °C. This must reflect the enhanced steric hindrance associated with the rigid phenyl group. A similar increase in T_g (51.3 °C) occurs when polymer **39** is compared with **30** and when **41** is compared with **31**.

A biphenyl unit has an additional influence on the T_g. For example, a comparison of **27** with **28** illustrates that the second phenyl group raises the T_g by 75–90 °C, presumably by further increasing steric hindrance and possibly by liquid crystalline type side group stacking behavior. A similar effect can be discerned when the T_g value for **54** is compared with that of **55**.[30]

Even a bromine atom attached to the aryl ring raises the T_g by a significant amount. For example, the T_g is raised by over 30 °C when the para hydrogen atoms in **27** are replaced by bromine (**29**). A similar effect has been detected when $[NP(OC_6H_4Br\text{-}p)]_n$ is compared to $[NP(OC_6H_5)_2]_n$.[31] This may be a consequence of dipole–dipole interactions of the type mainly responsible for the increase in T_g when the three β-hydrogen atoms in **39** are replaced by fluorine (**40**).

The variations in glass transition temperature with side group changes are less dramatic for the mixed substituent polymers **32**–**37**, as shown in Table II. The existence of only one glass transition in each DSC scan suggests that extensive blocks of single substituent or mixed substituent units are not present. Replacement of the *p*-formyl group in **32** by a primary alcohol group (**35**) brings about a modest rise in T_g of 31 °C. This may reflect an increase in hydrogen bonding. Introduction of the aryl Schiff's base residues in **33** and **34** results in a 14–70 °C rise in T_g. The Schiff's base units are rigid and would be expected to severely restrict the conformational reorientation of the backbone. The introduction of aryl ester units, as in **36** and **37**, brings about a 30–64 °C rise in T_g compared to **32**. Presumably the ester units generate a smaller effects because they are more flexible than the Schiff's base units.

These results illustrate the ways in which different types of aryl side groups alter the flexibility of a polyphosphazene chain and, thus, change the T_g over a wide temperature range.

This must be viewed against a background of the behavior of polyphosphazenes that bear nonaromatic side group residues, such as alkoxy or alkoxy ether units. The variations in glass transition temperatures for various alkoxy derivatives are illustrated in Tables I–III and Figure 1.

First, it must be stressed that simple alkoxy side groups, such as methoxy or ethoxy, exert a minimal effect on the reorientational freedom of the backbone (T_g's of −74 and −84 °C, respectively[4,6]). The question that must then be addressed is this: "What influence on the T_g results from the introduction of progressively longer chain alkoxy groups, for example, over the range $-OCH_3$, $-OCH_2CH_3$, $-OCH_2CH_2CH_3$, ..., $-O(CH_2)_9CH_3$? The answer is illus-

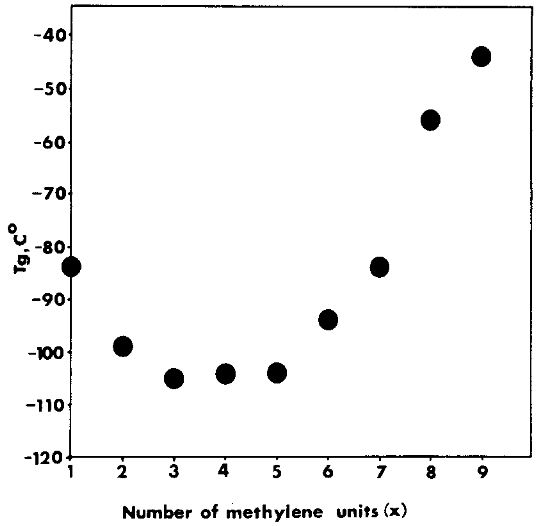


Figure 1. Variation of glass transition temperature (T_g) as a function of the number of methylene units in polymers of formula $[NP(O(CH_2)_xCH_3)]_n$.

trated in Tables I–III and in Figure 1. Increasing alkyl group chain length first lowers the T_g from −74 °C for $[NP(OCH_3)_2]_n$ to −105 °C for $[NP(O(CH_2)_3CH_3)_2]_n$ (**42**). The T_g remains virtually unaffected as the side chain is lengthened further to $-O(CH_2)_5CH_3$. It then rises steeply as additional methylene residues are added until it reaches −44 °C for side groups of type $-O(CH_2)_9CH_3$. The random, mixed-substituent polymer **49**, with $O(CH_2)_2CH_3$ and $O(CH_2)_4CH_3$ side groups, has a T_g at −100 °C. Thus, disruption of molecular symmetry does not improve the reorientational freedom of the system, and T_g's in the range of −100 to −105 °C may represent the lower limit to be expected from the polyphosphazene system.

Presumably, within the range of $-OCH_3$ through $-O(CH_2)_5CH_3$, the backbone bonds can maintain their maximum torsional freedom. Indeed, the lengthening of side groups within this range appears to remove what few restrictions already existed. The T_g values of −104 to −105 °C are among the lowest known for any polymer. As the side groups are lengthened beyond this point, mutual side group orientation probably increases until the side chains impose more and more linear hydrocarbon character on the system. It appears that the oxygen atoms play a major role in allowing the full flexibility of the chain to become manifest. This effect is diluted as the hydrocarbon chain is increased in length beyond $-O(CH_2)_5CH_3$.

It might be expected, then, that polyphosphazenes with alkyl ether alkoxy side groups should have especially low glass transition temperatures. This is, in fact, the case, although the values found for species with $-OCH_2CH_2OCH_3$ (−75 °C),[20] $-O(CH_2CH_2O)_2CH_3$ (−84 °C),[29] $-O(CH_2CH_2O)_2C_2H_5$ (−78 °C), $-O(CH_2CH_2O)_2C_4H_9$ (−84 °C), $-O(CH_2CH_2O)_7CH_3$ (−67 °C),[20] $-O(CH_2CH_2O)_{12}CH_3$ (−63 °C),[20] and $-O(CH_2CH_2O)_{17}CH_3$ (−59 °C)[20] do not reach the levels found for $-O(CH_2)_{3-5}CH_3$, even though more oxygen "swivel groups" are present. Weak side group dipolar interactions probably reduce the flexibility of the ether-type systems within this temperature range.

Microcrystallinity and Liquid Crystalline Character. The mixed-substituent aryloxy phosphazene polymers **32**–**37** did not undergo any detectable transitions when heated above their T_g. The lack of microcrystalline or liquid crystalline order can be attributed to two factors. First, the method of synthesis generates an overall atactic structure. Although the initial introduction of aryloxy groups appears to take place in a nongeminal fashion (i.e. with only one chlorine atom replaced per phosphorus), there is no evidence that adjacent aryloxy groups have a preferred cis or trans orientation to each other. Moreover, the fact that 30% of the repeating units bear two *p*-methylphenoxy groups, and that these repeating units are probably distributed randomly along the chain, reduces the degree of molecular order even further. Thus, the structural requirements needed for crystallization are absent.

Second, in the absence of an organized, repetitive structure, it is still possible for liquid crystalline order to be established if the side groups can organize themselves in parallel arrays, independently of the chain orientation. This requires that the rigid mesogenic side units are separated from the main chain by flexible spacer groups that allow the orientation of the mesogenic units to be uncoupled from those of the supporting skeletal repeating units. We conclude that, in polymers **32**–**37**, the spacer group (the oxygen atom) is not sufficiently flexible to allow the development of side group liquid crystalline order.

By contrast, the single substituent polymers **27**, **31**, **40**, **54**, and **55** are microcrystalline and showed no thermotropic liquid crystalline character as evidenced by the results from DSC scans and optical microscopy. Approximate T_m values are, for **27**, <210 °C, and for **31**, 218 °C. Polymer **28** is also microcrystalline and may be liquid crystalline within the temperature range of 40–170 °C, although the polymer apparently underwent molecular changes during the first heating cycle. However, an oxygen atom alone as a spacer unit, in **55**, apparently does not allow sufficient flexibility to permit side group stacking.

Experimental Section

Materials. Hexachlorocyclotriphosphazene, $(NPCl_2)_3$, kindly supplied by Ethyl Corp. and the Firestone Tire and Rubber Co., was purified by two fractional sublimations at 0.05 Torr. Benzyl alcohol (99+%, Gold Label, Aldrich) was used as received. Phenethyl alcohol (99+%, Gold Label, Aldrich), 3-phenyl-1-propanol (Aldrich), propanol, butanol, heptanol, and octanol (Fisher), pentanol (Mallinkrodt), hexanol, nonanol, decanol, 2-(2-butoxy)ethanol, and 2-(2-ethoxy)ethanol (Aldrich) were dried over 3-Å molecular sieves before use. 4-Biphenylmethanol and 4-bromobenzyl alcohol were commercial products obtained from Aldrich and were purified by two vacuum sublimations (0.05 Torr) before use. Sodium hydride (60% dispersion in mineral oil, Aldrich) was washed with dry THF (2 × 100 mL) to remove the mineral oil, dried under vacuum, and stored in a drybox under an atmosphere of dry nitrogen. Tetra-*n*-butylammonium bromide was dried by an azeotropic distillation of benzene. 4-Aminophenol and 4-hydroxybenzaldehyde (Aldrich) were sublimed before use. Absolute ethanol (Pharmco) was dried over 3-Å molecular sieves. 4-Cyanobenzoic acid, 4-aminobenzonitrile, *p*-anisaldehyde, 4-nitrophenol, *p*-anisidine, 4-cyanobenzaldehyde, and *p*-anisoyl chloride were used as received. Tetrahydrofuran (THF) and 1,4-dioxane (Curtin-Matheson) were distilled into the reaction flask under an atmosphere of dry argon from a sodium–benzophenone ketyl drying agent. All reactions were performed under an atmosphere of dry argon by using standard Schlenk techniques.

Equipment. ^1H NMR spectra were recorded on a Varian EM360 spectrometer operating at 60 MHz or a Bruker WP-200 or a JEOL FX 90Q spectrometer. ^{31}P NMR spectra were recorded on a Varian CFT-20 spectrometer operating at 32 MHz in the Fourier transform mode or on a JEOL FX 90Q instrument. The data were processed by use of the integral computer of the spectrometer. Infrared (Nujol mull) spectra were recorded on a Perkin-Elmer 283B grating spectrometer. Electron-impact mass spectral results were obtained by using an AEI MS950 spectrometer, and the data were tabulated by a linked computer. Elemental analyses were performed by Galbraith Laboratories. Samples were dried under vacuum before analysis. Glass transition temperatures were recorded on a Perkin-Elmer or Du Pont 1090/910 different scanning calorimeter instrument. The heating

Table IV
Cyclotriphosphazene Characterization Data

compound	yield,[a] %	mp, °C	mass spectral data found	mass spectral data calcd	elemental anal. found	elemental anal. calcd
$[NP(OCH_2C_6H_5)_2]_3$ (**7**)	76	50.5–52	777	777	C, 65.17 H, 5.32 N, 5.46	C, 64.86 H, 5.44 N, 5.40
$[NP(OCH_2C_6H_4C_6H_5)_2]_3$ (**8**)	52	219	*b*	1233	C, 75.69 H, 5.52 N, 3.41	C, 75.90 H, 5.39 N, 3.40
$[NP(OCH_2C_6H_4Br)_2]_3$ (**9**)	46	140	1076[c]	1245	C, 40.60 H, 2.68 N, 3.28	C, 40.32 H, 2.90 N, 3.36
$[NP(O(CH_2)_2C_6H_5)_2]_3$ (**10**)	57	oil	861	861	C, 66.62 H, 6.13 N, 4.97	C, 66.89 H, 6.32 N, 4.88
$[NP(O(CH_2)_3C_6H_5)_2]_3$ (**11**)	69	oil	945	945	C, 68.68 H, 6.53[d] N, 4.33[d]	C, 68.56 H, 7.03 N, 4.44
$N_3P_3(OC_6H_5)_5(OC_6H_4CHO)$ (**13**)	83	71–72	721	721	C, 61.77 H, 4.25 N, 5.68	C, 61.58 H, 4.16 N, 5.82
$N_3P_3(OC_6H_5)_5(OC_6H_4CH{=}NC_6H_4OCH_3)$ (**14**)	91		826.1887	826.1887[e]	*f*	
$N_3P_3(OC_6H_5)_5(OC_6H_4CH{=}NC_6H_4OH)$ (**15**)	87		821.1746	812.1718[e]	*f*	
$N_3P_3(OC_6H_5)_5(OC_6H_4CH_2OH)$ (**16**)	94	71–80	723	723	C, 61.17 H, 4.76 N, 5.50	C, 61.41 H, 4.43 N, 5.81
$N_3P_3(OC_6H_5)_5(OC_6H_4CH_2OCC_6H_4OCH_3)$ (**17**)	91		857.1811	857.1821[e]	*f*	
$N_3P_3(OC_6H_5)_5(OC_6H_4CH_2OCC_6H_4CN)$ (**18**)	90		852.1611	852.1668[e]	*f*	
$N_3P_3(OC_6H_5)_5(OC_6H_4NO_2)$ (**19**)	64	78	738	738	C, 58.59 H, 3.87 N, 7.61	C, 58.53 H, 3.92 N, 7.58
$N_3P_3(OC_6H_5)_5(OC_6H_4NH_2)$ (**20**)	82	102	708	708	C, 60.87 H, 4.21 N, 7.83	C, 61.01 H, 4.37 N, 7.90
$N_3P_3(OC_6H_5)_5(OC_6H_4N{=}CHC_6H_4)CH_3$ (**21**)	91		826.1887	826.1875[e]	*f*	
$N_3P_3(OC_6H_5)_5(OC_6H_4N{=}CHC_6H_4OH)$ (**22**)	88		812.1746	812.1718[e]	*f*	
$N_3P_3(OC_6H_5)_5(OC_6H_4N{=}CHC_6H_4CN)$ (**23**)	92		821.1697	812.1722[e]	*f*	
$N_3P_3(OC_6H_5)_5(OC_6H_4NHCOC_6H_4OCH_3)$ (**24**)	84		842.1797	842.1824[e]	*f*	
$N_3P_3(OC_6H_5)_5(OC_6H_4NHCOC_6H_4CN)$ (**25**)	86		837.1664	837.1671[e]	*f*	

[a] All yields were after recrystallization (or chromatography for **8d** and **8e**). [b] Compound **8b** was involatile; therefore, no mass spectral ions were observed. [c] A parent ion was not observed for compound **9c**. The highest mass ion observed was the parent minus $-OCH_2C_6H_4Br$ fragment. [d] Average values from duplicate analyses. [e] High resolution mass spectrometry. [f] The extreme hydrolytic sensitivity of these derivatives prevented reliable elemental analysis from being obtained.

rate was 20 °C/min. Sample sizes varied from 5 to 20 mg.

Synthesis of 7–9. These reactions were carried out in a similar manner. The following procedure is typical. Sodium 4-biphenylmethoxide (2 equiv per P–Cl) was prepared by adding, via a double-tipped syringe needle, 4-biphenylmethanol (7.15 g, 0.0388 mol) in THF (50 mL) to NaH (0.83 g, 0.0346 mol) in THF (50 mL). A solution of $(NPCl_2)_3$ (1.0 g, 2.87 mmol) in THF (15 mL) was added dropwise over 15 min to the solution containing the sodium arylalkoxide. After this time the solution was heated to reflux for 48 h. The solution was then allowed to cool to room temperature, and the solvent was removed under reduced pressure. The products were isolated by use of the following procedures. For **7**, the crude product was purified by chromatography with the use of silica gel as a support and methylene chloride as the eluent, followed by recrystallization from toluene/hexane. For **8**, the crude product was washed with methanol (500 mL), and aqueous HCl (ca. 0.05%, 500 mL), distilled/deionized water (500 mL), and methanol (500 mL). The product was purified further by recrystallization from boiling toluene. For **9**, the crude product was washed with ethanol (95%, 500 mL), aqueous HCl (ca. 0.05%, 500 mL), distilled/deionized water (500 mL), ethanol (95%, 500 mL), and the hexane (500 mL). The product was purified further by recrystallization from toluene/hexane. Characterization data are listed in Tables IV and V. Species **7** and **10** were identical with samples prepared previously by the use of a similar synthetic procedure.[32,33]

Synthesis of 10 and 11. These compounds were prepared by use of the synthetic procedure reported above, with the following modifications. A solution of $(NPCl_2)_3$ (2.0 g, 5.74 mmol) in 1,4-dioxane (25 mL) was added dropwise over 15 min to the solution containing the sodium arylalkoxide (2 equiv per P–Cl). The reaction mixture was then stirred at room temperature for 24 h. If the solution was heated at reflux or if n-Bu_4NBr was added to accelerate P-Cl substitution, the phosphazene species were found to decompose. [The ^{31}P NMR spectrum of the reaction mixture contained a very broad (ca. 2.5 ppm) resonance centered at ca. +17.0 ppm. Products **10** and **11** would be expected to give rise to a sharp singlet at ca. +18.0 ppm, by analogy with the spectra observed for **7–9** (see Table V). The solvent was then removed under reduced pressure, and the crude products were purified by high-pressure liquid chromatography (HPLC) with the use of silica gel (Prep Pak-500, Waters Associates) as a support and methylene chloride as an eluent. The products **10** and **11** were recovered as oils. Characterization data are listed in Tables IV and V.

Effects of Heat on 10. Cyclophosphazene **10** (1.0 g, 1.16 mmol), purified as described previously, was stirred with $(n$-$Bu)_4NBr$ (1.0 g) in THF (50 mL) at reflux for 24 h. After this time, the ^{31}P NMR spectrum of the reaction mixture was compatible with unchanged **10**, and no decomposition or rearrangement to a phosphazane was detected. Alternatively, **10** (1.0 g, 1.16 mmol) was heated alone at 176 °C in a sealed, evacuated (~0.05 torr) polymerization tube for 22 h. Although the contents became slightly discolored, the ^{31}P NMR spectrum of the material was consistent with the presence of >99% unchanged **10**. However, if the reaction mixture containing **10** and excess $NaOCH_2CH_2C_6H_5/HOCH_2CH_2C_6H_5$ was heated to reflux for 48 h, complete decomposition of **10** was detected (by ^{31}P NMR analysis).

Synthesis of $N_3P_3Cl(OPh)_5$ (12). Phenol (13.5 g, 0.144 mol) was dissolved in THF (75 mL), and this solution was added to sodium hydride (14 g, 0.35 mol, used as an oil dispersion) suspended in THF (75 mL). When the reaction was complete, additional THF (200 mL) was added, and the reaction mixture

Table V
Cyclotriphosphazene NMR Data

compd	^{31}P NMR,[a] ppm	^{1}H NMR,[b] δ		coupling constant,[c] Hz
7	18.8	$-\mathrm{OC}H_2\mathrm{C_6H_5}$	4.96 (m)	
		$-\mathrm{OCH_2C_6}H_5$	7.30 (m)	
8	18.7	*d*		
9	18.3	$-\mathrm{OC}H_2\mathrm{C_6H_4}-$	4.81 (m)	
		$-\mathrm{OCH_2C_6}H_4-$	7.27 (d, d)	
10	17.9	$-\mathrm{OCH_2C}H_2\mathrm{C_6H_5}$	2.92 (t)	J_{HCCH} = 7.2
		$-\mathrm{OC}H_2\mathrm{CH_2C_6H_5}$	4.00 (m)	
		$-\mathrm{OCH_2CH_2C_6}H_5$	7.18 (m)	
11	18.2	$-\mathrm{OCH_2C}H_2\mathrm{CH_2C_6H_5}$	1.86 (m)	
		$-\mathrm{OCH_2CH_2C}H_2\mathrm{C_6H_5}$	2.60 (t)	J_{HCCH} = 7.7
		$-\mathrm{OC}H_2\mathrm{CH_2CH_2C_6H_5}$	3.83 (m)	
		$-\mathrm{OCH_2CH_2CH_2C_6}H_5$	7.11 (m)	
13	8.7	$-\mathrm{C}H\mathrm{O}$	9.9 (s)	
		$-\mathrm{C_6}H_4\mathrm{CHO}$	7.7 (d)	
14	11.9	$-\mathrm{C}H\mathrm{{=}N}$	8.5 (s)	
		$-\mathrm{OC}H_3$	3.8 (s)	
15	11.9	$-\mathrm{C}H\mathrm{{=}N}$	8.5 (s)	
16	8.6	$-\mathrm{C}H_2\mathrm{OH}$	4.6 (s)	
		$-\mathrm{O}H$	2.9 (s)	
17	11.6	$-\mathrm{C}H_2\mathrm{O}$	5.2 (s)	
18	8.6	$-\mathrm{C}H_2\mathrm{O}$	5.3 (s)	
19	9.7			
20	10.4			
21	10.2	$-\mathrm{C}H\mathrm{{=}N}$	8.4 (s)	
		$-\mathrm{OC}H_3$	3.8 (s)	
22	9.9	$-\mathrm{C}H\mathrm{{=}N}$	8.4 (s)	
23	9.5	$-\mathrm{C}H\mathrm{{=}N}$	8.6 (s)	
24	8.8	$-\mathrm{OC}H_3$	3.8 (s)	
25	8.6			

[a] All data recorded on solutions in THF, except for **8**, which was recorded in 1,4-dioxane at 80 °C. [b] All data recorded on solutions in $CDCl_3$. [c] Coupling constants that are not listed were unresolved. [d] ^{1}H NMR data could not be recorded for **8** as a result of its insolubility in organic media at room temperature.

was heated to 50 °C. The hot solution was filtered, and the warm filtrate was added dropwise to a cold (0 °C) solution of $(NPCl_2)_3$ (10 g, 0.028 mol) in THF (100 mL). The reaction mixture was stirred for 12 h at 25 °C. The solvent was removed by means of a rotary evaporator. Toluene (50 mL) was added to the residue, the solution was filtered, and the product was purified by means of high-pressure liquid chromatography. The product was recrystallized from heptane to yield $N_3P_3Cl(OPh)_5$ (mp 67 °C). Mass spectrometric measurements: *m/e* 635 calcd, 635 found. A ^{31}P NMR spectrum of the product consisted of an AB_2 pattern (ν_a = 22.1 ppm, ν_b = 6.90 ppm, J = 83.1 Hz).

Synthesis of $N_3P_3(OC_6H_5)_5(OC_6H_4NO_2\text{-}p)$ (19). 4-Nitrophenol (11.0 g, 0.078 mol) was dissolved in dioxane (50 mL), and this solution was added to sodium hydride (3.15 g, 0.078 mol, used as an oil dispersion) suspended in dioxane (50 mL). When the reaction was complete, the reaction mixture was heated to 50 °C, and $(n\text{-}Bu)_4NBr$ (1 g) was added as a rate accelerator. The hot solution was added dropwise to a solution of **13** (25 g, 0.039 mol). During this time the solution changed from bright orange to brown. The mixture was then cooled and filtered, and the filtrate was concentrated to a volume of 40 mL and added slowly to hexane (300 mL) to yield a precipitate of **19** (18 g, 62%). The white solid was recrystallized twice from ethanol. Characterization data are listed in Tables IV and V.

Synthesis of $N_3P_3(OC_6H_5)_5(OC_6H_4NH_2\text{-}p)$ (20). A 500-mL autoclave was charged with 40.0 g (0.054 mol) of (nitrophenoxy)pentaphenoxycyclotriphosphazene (**19**), THF (75 mL), and 0.1 g of Pd/C catalyst. The mixture was agitated vigorously under 50 psi of hydrogen pressure at 50 °C until no further pressure drop was evident. The reaction mixture was then filtered to remove the catalyst. The THF solvent was removed under reduced pressure to yield an oil, which solidified on standing. Crude **20** was recrystallized from ethanol. Characterization data are listed in Tables IV and V.

General Synthetic Route to Schiff Bases 14, 15, and 21–23. All cyclic trimeric Schiff base compounds of structures **14**, **15**, and **21–23** were prepared in the same manner. The following procedure is typical. The cyclic trimer **12** (0.76 g, 1.1 mmol) was dissolved in a THF/absolute ethanol solution (30 mL/10 mL). 4-Cyanobenzaldehyde (0.18 g, 1.4 mol) was added, and the mixture was stirred at 25 °C for 18 h. This solution was then concentrated to an oil under reduced pressure and dried in vacuo. The characterization data are listed in Tables IV and V.

General Synthetic Route to Amide Compounds 24 and 25. Both cyclic trimeric amide compounds were prepared in the same manner. The following procedure is typical. The cyclic trimer **20** (0.75 g, 1.1 mmol) was dissolved in THF (15 mL). Triethylamine (15 mL) was then added, followed by *p*-anisoyl chloride (0.21 g, 1.2 mmol). A white precipitate formed immediately. The mixture was stirred at 25 °C for 10 h, the precipitate was filtered off, and the filtrate was evaporated to an oil. Characterization data are listed in Table IV.

Synthesis of $N_3P_3(OC_6H_5)_5(OC_6H_4CHO)$ (13). 4-Hydroxybenzaldehyde (24.4 g, 0.20 mol) was dissolved in THF (50 mL), and this solution was added to sodium hydride (8.00 g, 0.20 mol, used as an oil dispersion) suspended in THF (50 mL). When the reaction was complete, the reaction mixture was heated to 50 °C, and $(n\text{-}Bu)_4NBr$ (1 g) was added to the reaction mixture as a rate accelerator. The hot solution was added dropwise to a solution of chloropentaphenoxycyclotriphosphazene (**6**) (15 g, 0.024 mol). The mixture was then cooled and filtered, and the filtrate was evaporated to dryness. The solid was recrystallized from a hexane/ethyl acetate solution. Characterization data are in Tables IV and V.

Synthesis of $N_3P_3(OC_6H_5)_5(OC_6H_4CH_2OH\text{-}p)$ (16). (4-Formyl-phenoxy)pentaphenoxycyclotriphosphazene (**13**) (4.0 g, 5.5 mmol) was dissolved in a THF/methanol solution (50 mL/25 mL). This solution was then cooled to 0 °C, and $NaBH_4$ (0.40 g, 8.3 mmol) was added. After the solution warmed to 25 °C, the reaction mixture was concentrated under reduced pressure and 2 N HCl (100 mL) was added. The white precipitate was washed with 2 N HCl, ethanol, and hexanes (150-mL each). Characterization data are listed in Tables IV and V.

General Synthetic Route to Esters 17 and 18. The following procedure is typical. The cyclic trimer **16** (0.75 g, 1.0 mmol) was dissolved in THF (25 mL). Triethylamine (15 mL) was then added, followed by *p*-anisoyl chloride (0.20 g, 1.2 mmol) which resulted in the immediate formation of a white precipitate. The mixture was stirred at 25 °C for 12 h. The mixture was filtered, and the filtrate was evaporated to an oil and dried in vacuo.

Characterization data are listed in Tables IV and V.

Preparation of Poly(dichlorophosphazene) (26). The polymer was prepared by the thermal, ring-opening polymerization of hexachlorocyclotriphosphazene (**6**).[4] Degassed, sealed Pyrex tubes containing **6** (ca. 150 g) were heated in a Freas Model 104 thermoregulated oven at 250 °C until the molten contents were almost immobile (ca. 12–24 h). The tubes were agitated during the polymerization so that a rocking motion was completed once every minute. The tubes were than allowed to cool to room temperature, and the residual cyclic species were removed by vacuum sublimation (0.05 Torr). Several polymerization tubes were filled, evacuated, and sealed at the same time with the use of trimer from one uniform batch. These tubes were stored in the dark and were polymerized as needed. Purified samples of **26** were stored in a drybox under an atmosphere of dry nitrogen.

Synthesis of 27–29. These reactions were all carried out in a similar manner. The following procedure is typical. Sodium benzyloxide (2 equiv per P–Cl) was prepared by addition, via a double-tipped syringe needle, of benzyl alcohol (29.3 g, 0.27 mol) in 1,4-dioxane (20 mL) to NaH (4.14 g, 0.17 mol) and $(n\text{-Bu})_4NBr$ (2.0 g) in 1,4-dioxane (200 mL). A sample of **26** (5.0 g, 43.1 mmol) was dissolved in warm 1,4-dioxane (400 mL) over 24 h with vigorous stirring and was then added dropwise over 1 h to the solution containing the sodium arylalkoxide. [Polymers **28** and **29** were prepared on a scale based on 1.0 or 1.5 g of **26**, respectively.] The reaction mixture was heated at ca. 100 °C for 9 h (15 h for **28**) and was then allowed to cool to room temperature. The solution was concentrated under reduced pressure and poured into ethanol (95%, 3.6 L) to precipitate the polymer. The crude material was purified further by reprecipitations from concentrated THF solution into aqueous HCl (ca. 0.05%, 3.6 L), distilled/deionized water (3.6 L), and hexanes (3.6 L). [For polymer **28**, the crude material, recovered after an initial precipitation into ethanol, was purified further by washing with distilled/deionized water (2.4 L) and hexanes (500 mL). This product was not purified by reprecipitation techniques due to its insolubility in organic media at room temperature.] All polymers were than subjected to Soxhlet extraction with methanol (3 days) and hexanes (3 days) to remove any residual salts and low molecular weight species. Characterization data are listed in Table VI.

Synthesis of 30 and 31. These compounds were prepared by use of the synthetic procedure reported above, with the following modifications. A solution of $(NPCl_2)_n$ (**26**) (2.0 g, 17.3 mmol) in warm 1,4-dioxane was added dropwise over 1 h to the solution containing the sodium arylalkoxide (2 equiv per P–Cl) at *room temperature*. After 2 h of stirring at room temperature, the ^{31}P NMR spectrum of the reaction mixture was consistent with replacement of 84% of the chlorine atoms in **26** by $-OCH_2CH_2C_6H_5$ units. After 24 h, **30** was formed in 100% yield. [Reaction for 72 h at room temperature was necessary to convert **26** quantitatively to **31**.] The reaction mixture was then stirred for an additional 48 h at room temperature (72 h for **13**). The phosphazene species were degraded when the solution containing **26** and $NaOCH_2CH_2C_6H_5$ was heated to reflux or when $(n\text{-Bu})_4NBr$ was added to accelerate the rate of P–Cl substitution. [The ^{31}P NMR spectrum of the reaction mixture contained a very broad (ca. 8 ppm) resonance centered at ca. +2.4 ppm.] Polymer **30**, when prepared at room temperature, gave rise to a sharp singlet at −8.2 ppm in the ^{31}P NMR spectrum (see Table VI). After this time, the polymers were isolated and purified in the same manner as described above for **27–29**. Characterization data for polymers **30** and **31** are listed in Table IV.

Synthesis of $[NP(OC_6H_4CH_3\text{-}p)_{1.34}(OC_6H_4CHO)_{0.66}]_n$ (32). Poly(dichlorophosphazene) (11.8 g, 102 mmol) dissolved in dioxane (1000 mL) was added slowly to a stirred solution of sodium *p*-methylphenoxide prepared from *p*-methylphenol (16.2 g, 150 mmol) and sodium hydride (6.0 g, 150 mmol) in dioxane (200 mL). The solution was stirred at reflux for 48 h, cooled to 35 °C, and treated dropwise with a solution of sodium 4-formylphenoxide prepared from 4-hydroxybenzaldehyde (30.0 g, 245 mmol) and sodium hydride (9.8 g, 250 mmol) in dioxane (200 mL). Tetrabutylammonium bromide (15 g) was added as a phase-transfer catalyst. This solution was boiled at reflux for 72 h. The polymer was purified by four reprecipitations from THF into water and one reprecipitation into hexane. It was then dried in vacuo. Characterization data are listed in Table VI.

Synthesis of Polymeric Schiff Bases 33 and 34. The following procedure is typical. Poly[(*p*-methylphenoxy)(4-formylphenoxy)phosphazene] (**32**) (2.0 g, 7.4 mmol) in THF (35 mL) was treated with *p*-anisidine (1.2 g, 9.8 mmol). The solution was stirred at 25 °C for 20 h, was concentrated under reduced pressure, and was precipitated into water. The polymer was further purified by two reprecipitations from THF into water and once into ethanol. It has then dried in vacuo. The characterization data are listed in Table VI. The Schiff base linkages were found to undergo some hydrolysis on precipitation into water or ethanol. Thus, only a minimum number of reprecipitations could be performed.

Synthesis of $[NP(OC_6H_4CH_3\text{-}p)_{1.34}(OC_6H_4CH_2OH\text{-}p)_{0.66}]_n$ (35). Poly[(*p*-methylphenoxy)(4-formylphenoxy)phosphazene] (**32**) (6.0 g, 0.022 mol) was dissolved in a THF/methanol solution (75 mL/25 mL) and cooled at 0 °C. Sodium borohydride (2.0 g, 0.053 mol) was added slowly, and this solution was stirred for 16 h. The polymer was then recovered by two precipitations into acidic water and was further purified by two more reprecipitations from THF into water. The white polymer was dried in vacuo. Characterization data are listed in Table VI.

Synthesis of Polymeric Esters 36 and 37. The following procedure is typical. Poly[(*p*-methylphenoxy)(*p*-(hydroxymethylene)phenoxy)phosphazene] (**35**) (0.80 g, 3.0 mmol) in a THF/Et_3N solution (20 mL/15 mL) was treated with 4-cyanobenzoyl chloride. A white precipitate formed immediately. The mixture was stirred for 20 h at 25 °C and filtered. The filtrate was concentrated under reduced pressure and then precipitated into water. The polymer was purified further by three reprecipitations from THF into water and once into hexane. It was then dried in vacuo. The characterization data are listed in Table VI.

Synthesis of 41–48. The following procedure is typical for all of the alkoxy and alkoxy ether derivatives. Sodium propoxide was prepared by the addition, via a double-tipped syringe needle, of 1-propanol (20 g, 518 mmol) to NaH (3.1 g, 77.3 mmol) in THF (100 mL). This mixture was then slowly added to a stirred solution of **26** (4 g, 34.5 mmol) in THF (400 mL). The partly substituted polymer precipitated initially but redissolved when the temperature was raised to 50 °C. After 24 h at this temperature the mixture was cooled to 25 °C, and the solvent was removed at reduced pressure. The polymer was isolated by precipitation into ethanol and by three precipitations from THF into water and twice from THF into ethanol. It was then dried in vacuo. Yield: 4.0 g, 71%. The ^{31}P NMR spectrum of the polymer consisted of a sharp singlet at −8.4 ppm. Characterization data for this and the related polymers are listed in Table VI.

Synthesis of $[NP(OCH_2CH_2OCH_2CH_2OCH_2CH_3)_2]_n$ (52). A solution of poly(dichlorophosphazene) (4 g, 34.5 mmol) in THF (300 mL) was added over a 0.5-h period to a stirred suspension of sodium 2-(2-ethoxyethoxy)ethoxide, prepared from sodium metal (4.76 g, 207 mmol) plus 2-(2-ethoxyethoxy)ethanol (34.99 g, 260 mmol) in THF (100 mL). The reaction mixture was heated for 24 h at refluxing temperature and was then cooled to room temperature. The polymer was recovered by precipitation into hexane and was purified by means of dialysis against water for 5 days. The solution was then filtered and poured out to air dry. Characterization data are listed in Table VI.

Synthesis of $[NP(OCH_2CH_2CH_3)_x(OCH_2CH_2CH_2CH_2CH_3)_y]_n$ (49). A solution of $(NPCl_2)_n$ (4 g, 34.5 mmol) in THF (300 mL) was added slowly to a stirred solution of sodium 1-pentoxide [prepared from NaH (2.76 g, 69 mmol) and 1-pentanol (16.22 g, 184 mmol) in THF (100 mL) at 50 °C. The mixture was stirred for 24 h and then cooled to room temperature. A solution of sodium 1-propoxide, prepared from NaH (5.52 g, 138 mmol) and 1-propanol (16.08 g, 268 mmol) in THF (100 mL), was added slowly to the mixture with constant stirring. On completion of addition the reaction mixture was heated at reflux for 48 h and then cooled to room temperature. The solution was concentrated, and the product was isolated by precipitation into ethanol, followed by precipitation from THF into water (three times) and ethanol (twice). It was further purified by Soxhlet extraction with ethanol for 96 h and was dried under vacuum. See Table VI for characterization data.

Synthesis of $[NP(OCH_2CH_2OCH_2CH_2OCH_2CH_2CH_2CH_3)_2]_n$ (53). A solution of sodium 2-(2-butoxyethoxy)ethoxide, prepared from NaH (8.28 g, 207 mmol) and 2-(2-butoxyethoxy)ethanol

Table VI
Poly(organophosphazene) Characterization and NMR Data

compound	yield,[a] %	elemental anal. found	elemental anal. calcd	^{31}P NMR,[b] ppm	mol wt (av, GPC)[d]	T_g, °C
$[NP(OCH_2C_6H_5)_2]_n$ (**27**)	72	C, 64.17[c] H, 5.19 N, 5.45 Cl, 0.023	C, 64.86 H, 5.44 N, 5.40 Cl, 0	−7.0	1.5×10^6	−31.4
$[NP(OCH_2C_6H_4C_6H_5)_2]_n$ (**28**)	86	C, 73.96[c] H, 5.10 N, 3.60 Cl, 0.18	C, 75.90 H, 5.39 N, 3.40 Cl, 0	−7.2		
$[NP(OCH_2C_6H_4Br)_2]_n$ (**29**)	74	C, 40.42[c] H, 2.89 N, 3.45	C, 40.32 H, 2.90 N, 3.36	−6.9	1.6×10^6	−0.8
$[NP(O(CH_2)_2C_6H_5)_2]_n$ (**30**)	65	C, 65.98[c] H, 6.58 N, 4.79 Cl, 0.12	C, 66.89 H, 6.32 N, 4.88 Cl, 0	−8.2	1.4×10^6	−32.7
$[NP(O(CH_2)_3C_6H_5)_2]_n$ (**31**)	58	C, 68.75 H, 6.78 N, 4.32 Cl, 0.063	C, 68.56 H, 7.03 N, 4.44 Cl, 0	−7.8	1.7×10^6	−47.0
$[NP(OC_6H_4CH_3)_x(OC_6H_4CHO)_y]_n$[e] (**32**)	g	C, 61.84 H, 5.18 N, 5.31	C, 62.64 H, 4.73 N, 5.22	−20.0	8×10^5	11
$[NP(OC_6H_4CH_3)_x(OC_6H_4CH{=}NC_6H_4OCH_3)_y]_n$[f] (**33**)	g	C, 64.26 H, 5.00 N, 6.60	C, 64.98 H, 5.02 N, 6.44	−19.5	1×10^6	81
$[NP(OC_6H_4CH_3)_x(OC_6H_4CH{=}NC_6H_4OH)_y]_n$[f] (**34**)	g	C, 63.35 H, 4.79 N, 6.75	C, 63.69 H, 4.75 N, 6.46	−19.7	1×10^6	75
$[NP(OC_6H_4CH_3)_x(OC_6H_4CH_2OH)_y]_n$[e] (**35**)	g	C, 61.47 H, 5.45 N, 5.20	C, 62.31 H, 5.19 N, 5.19	−19.4	8×10^5	25
$[NP(OC_6H_4CH_3)_x(OC_6H_4CH_2OOCC_6H_4OCH_3)_y]_n$[e] (**36**)	g	C, 54.97 H, 6.33 N, 3.28	C, 54.31 H, 6.52 N, 3.36	−20.1	1×10^6	46
$[NP(OC_6H_4CH_3)_x(OC_6H_4CH_2OOCC_6H_4CN)_y]_n$[e] (**37**)	g	C, 61.62 H, 4.84 N, 5.53	C, 61.38 H, 4.38 N, 5.99	−20.2	1×10^6	42
$[NP(OCH_2CH_2CH_3)_2]_n$ (**41**)	71	C, 43.34 H, 8.57 N, 8.24 Cl, 0.07	C, 44.16 H, 8.24 N, 8.58 Cl, 0	−8.4	1.5×10^6	−100
$[NP(O(CH_2)_3CH_3)_2]_n$ (**42**)	70	C, 49.40 H, 9.23 N, 7.14 Cl, 0.05	C, 50.24 H, 9.48 N, 7.32 Cl, 0	−8.4	3.3×10^6	−105
$[NP(O(CH_2)_4CH_3)_2]_n$ (**43**)	68	C, 53.08 H, 9.54 N, 6.69 Cl, 0.02	C, 54.77 H, 10.11 N, 6.38 Cl, 0	−8.4	1.1×10^6	−104
$[NP(O(CH_2)_5CH_3)_2]_n$ (**44**)	71	C, 57.95 H, 9.81 N, 5.24 Cl, 0.22	C, 58.27 H, 10.59 N, 5.66 Cl, 0	−8.4	1.5×10^6	−104
$[NP(O(CH_2)_6CH_3)_2]n$ (**45**)		C, 60.52 H, 10.94 N, 4.87 Cl, 3.2×10^{-3}	C, 61.05 H, 10.98 N, 5.08 Cl, 0	−8.4	6.7×10^5	−94
$[NP(O(CH_2)_7CH_3)_2]n$ (**46**)	70	C, 62.15 H, 10.34 N, 4.69 Cl, 0.2	C, 63.32 H, 11.29 N, 4.6 Cl, 0	−8.4	5×10^5	−84
$[NP(O(CH_2)_8CH_3)_2]_n$ (**47**)	70	C, 64.90 H, 11.17 N, 4.31 Cl, 0.02	C, 65.21 H, 11.55 N, 4.22 Cl, 0	−8.4	1.9×10^6	−56
$[NP(O(CH_2)_9CH_3)_2]_n$ (**48**)		C, 64.03 H, 10.83 N, 4.07 Cl, 0.89	C, 66.81 H, 11.77 N, 3.89 Cl, 0	−8.4	3×10^5	−44
$[NP(O(CH_2)_2O(CH_2)O(C_2H_5)_2)_2]_n$ (**52**)		C, 44.8 H, 8.08 N, 4.69 Cl, 0.05	C, 46.29 H, 8.42 N, 4.49 Cl, 0	−8.2	1.7×10^6	−78
$[NP(O(CH_2)_2O(CH_2)_2O(C_4H_9)_2)_2]_n$ (**53**)	66	C, 51.50 H, 9.25 N, 3.95 Cl, 0.02	C, 52.29 H, 9.32 N, 3.81 Cl, 0	−8.2	2.5×10^6	−84
$[NP(O(CH_2)_2CH_3)(O(CH_2)_4CH_3)]_n$ (**49**)	63	C, 51.46 H, 9.42 N, 7.01 Cl, 0.24	C, 50.24 H, 9.49 N, 7.32 Cl, 0	−8.2	1.4×10^5	−100

[a] All yields were after several reprecipitations (see Experimental Section) and Soxhlet extraction. [b] All data recorded for solutions in 1,4-dioxane. The spectrum of **9b** was recorded at 80 °C due to the insolubility of the material at room temperature. [c] Average values from two analyses. [d] The values shown represent gel permeation chromatography results from different synthesis reactions. The peaks corresponded to GPC average molecular weights based on comparisons with polystyrene standards (asterisk: insoluble in organic media). [e] The calculated analyses for these polymers were based on $x = 1.34$, $y = 0.66$. [f] The calculated analyses reflect the partial hydrolysis of the Schiff's base linkage during isolation and purification of the polymer and are based on the ratios of OC_6H_4CHO and $OC_6H_4CHNC_6H_4R$ units deduced from the NMR spectra. The ratios varied with different preparations but typically reflect a 40–50% reversion of Schiff's base to aldehydic units. [g] The overall yields of these polymers after purification were low and were typically less than 25%.

(38.08 g, 235 mmol) in THF (100 mL), was added dropwise to a stirred solution of $(NPCl_2)_n$ (4 g, 3.45×10^{-2} mol) in THF (350 mL) at room temperature. After the addition was complete, the reaction mixture was heated to 50 °C for 16 h and then cooled to room temperature. The polymer was recovered by precipitation into water, and this process was repeated twice, followed by precipitation from THF into methanol twice. The polymer was further purified by Soxhlet extraction with ethanol for 96 h and was dried under vacuum. Characterization data are listed in Table VI.

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Registry No. **6**, 940-71-6; **7**, 811-41-6; **8**, 111409-20-2; **9**, 111435-05-3; **10**, 42861-68-7; **11**, 111409-21-3; **12**, 5032-39-3; **13**, 101671-97-0; **14**, 111409-22-4; **15**, 111409-23-5; **16**, 101671-98-1; **17**, 111435-06-4; **18**, 111409-24-6; **19**, 85251-38-3; **20**, 86549-55-5; **21**, 111409-25-7; **22**, 111409-26-8; **23**, 111409-27-9; **24**, 111409-28-0; **25**, 111409-29-1; $NaOCH_2C_6H_5$, 20194-18-7; 4-$NaOCH_2C_6H_4C_6H_5$, 111409-30-4; 4-$NaOCH_2C_6H_4Br$, 111409-31-5; 4-$NaO(CH_2)_2C_6H_5$, 22096-25-9; 4-$NaO(CH_2)_3C_6H_5$, 111409-32-6; 4-$NaOC_6H_4CHO$, 22666-84-8; 4-$H_2NC_6H_4OCH_3$, 104-94-9; 4-$H_2NC_6H_4OH$, 123-30-8; 4-$ClCOC_6H_4OCH_3$, 100-07-2; 4-$ClCOC_6H_4CN$, 6068-72-0; 4-$NaOC_6H_4NO_2$, 824-78-2; 4-$OHCC_6H_4OCH_3$, 123-11-5; 4-HOC_6H_4CHO, 123-08-0; 4-$OHCC_6H_4CN$, 105-07-7.

References and Notes

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Miscibility of Poly(2-oxazolines) with Commodity Polymers

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ABSTRACT: Poly(*N*-acylethylenimines) (PMeOZO, PEtOZO, and PPrOZO) have been examined for miscibility with commodity polymers of poly(vinyl chloride) (PVC), polystyrene (PSt), polypropylene (PP), and poly(vinylidene fluoride) (PVF_2). The miscibility of polymer blends has been investigated by three methods: dynamic viscoelastic behaviors by rheovibron for all commodity polymer blends, differential scanning calorimetry, and wide-angle X-ray scattering, the latter two being for PMeOZO–PVF_2 blends. PMeOZO–PVC and PMeOZO–PVF_2 blends are miscible at the range of the PMeOZO fraction lower than 50 wt %. With the PMeOZO–PVF_2 blend system, miscibility is discussed for the amorphous and crystalline parts of PVF_2. PPrOZO is miscible with PSt when the PPrOZO is up to at least 25 wt %. Both PMeOZO–PP and PEtOZO–PP blends are not miscible.

Introduction

Polymer blends have recently received much attention with respect to development of new composite materials. In blending systems, miscibility (or compatibility) of polymers is very important since it affects the properties of the resulting polymer blend.[1-3] Accordingly, the usefulness of a polymer is increased when the polymer is made miscible (compatible) with other polymers. A recent report represents the studies of such direction; when *N*,*N*-dimethylacrylamide monomer unit is incorporated into

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