Poly[(aryloxy)carbophosphazenes]: Synthesis, Properties, and Thermal Transition Behavior

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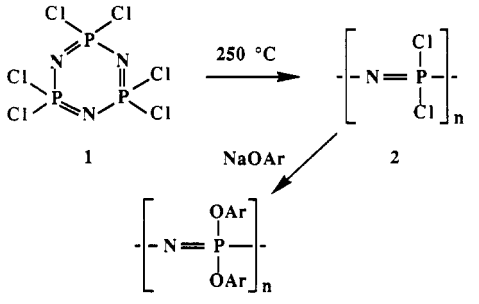
Received July 10, 1990; Revised Manuscript Received October 2, 1990

ABSTRACT: The cyclic carbophosphazene $N_3P_2CCl_5$ undergoes thermal ring-opening polymerization at 120 °C to yield the poly(chlorocarbophosphazene) $[N_3P_2CCl_5]_n$ as a hydrolytically sensitive elastomer. This polymer was allowed to react with a variety of aryloxide nucleophiles to afford a range of hydrolytically stable poly[(aryloxy)carbophosphazenes] $[N_3P_2C(OAr)_5]_n$. These macromolecules were characterized by ^{31}P, ^1H, and ^{13}C NMR spectroscopy, IR spectroscopy, elemental analysis, differential scanning calorimetry, gel permeation chromatography and, in one case, light scattering. Analogous, small-molecule model reactions, in which the cyclocarbophosphazene $N_3P_2CCl_5$ was allowed to react with the same aryloxide nucleophiles to yield the cyclic species $N_3P_2C(OAr)_5$, are also described. The glass transition temperatures of the poly[(aryloxy)carbophosphazenes] are 16–42 °C higher than those of their classical polyphosphazene analogues $[NP(OAr)_2]_n$. Possible reasons for the lower skeletal flexibility of poly(carbophosphazenes) compared to classical polyphosphazenes are discussed.

Introduction

The synthesis of new inorganic–organic macromolecules is an area of widespread current interest. This is a result of the need for new polymers that possess useful electrical, optical, thermal, or biomedical characteristics or that function as precursors to ceramic materials.[1]

The thermal ring-opening polymerization of cyclic phosphazenes such as **1** to yield macromolecules with backbones of alternating phosphorus and nitrogen atoms is well-known.[2] Furthermore, replacement of the halogen atoms in species such as **2** by organic or organometallic nucleophiles has provided access to a broad range of polymers with a variety of useful properties.[3]



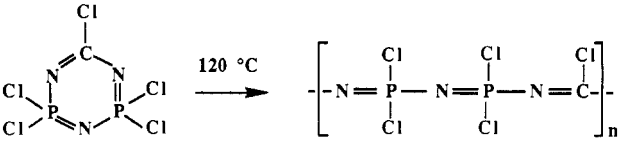
1 **2** **3-11**

We are currently studying the polymerization behavior of heterocyclic analogues of **1** that possess skeletal heteroatoms in addition to phosphorus and nitrogen. The polymerization of cyclic species of this type is of considerable interest as a route to new inorganic or inorganic–organic macromolecules. These polymers would be expected to possess properties that are different from those of classical polyphosphazenes because of the presence of heteroelements in the polymer main chain.

In this paper, we describe the thermal ring-opening polymerization of the cyclocarbophosphazene **12** to yield the hydrolytically sensitive polymer **13**, which is the first member of a new class of inorganic–organic macromolecules, the poly(carbophosphazenes).[4] We also report the replacement of the halogen atoms in **13** by a variety of aryloxy groups to yield a range of hydrolytically stable polymeric derivatives. The properties and thermal transition behavior of the resultant poly[(aryloxy)carbophosphazenes] are also discussed.

Results and Discussion

Synthesis and Ring-Opening Polymerization of $N_3P_2CCl_5$ 12. The synthesis of the cyclocarbophosphazene **12** was reported by Fluck, Schmid, and Haubold in



12 **13**

1975.[5] However, apart from the reaction of **12** with alkylamines to give hydrolytically stable amino derivatives,[6] no other studies of this compound have been reported. To our knowledge, no earlier attempts to polymerize this species have been carried out. We have studied the polymerization behavior of **12** as part of a program to synthesize heteroelement phosphazene polymers.

By analogy with the polymerization behavior of **1**, the initial attempts to thermally polymerize **12** employed temperatures of 200–250 °C. This yielded a complex mixture of products, which could not be characterized by ^{31}P NMR spectroscopy. At slightly lower temperatures (150–190 °C) the formation of an insoluble, cross-linked polymeric material took place. However, at temperatures below 150 °C, **12** underwent clean ring-opening polymerization to give **13**. The most convenient temperature for polymerization was found to be 120 °C, which yielded polymer **13** in high yield after approximately 4–6 h. The lower polymerization temperature of **12** compared to that of **1** (250 °C) probably reflects an increase in ring strain, which arises from the replacement of a skeletal phosphorus atom by the smaller carbon atom. This aspect of the polymerization will be discussed more fully in a forthcoming paper.[7]

Polymer **13** is a hydrolytically sensitive, adhesive, elastomeric material, which was studied by ^{31}P and ^{13}C NMR

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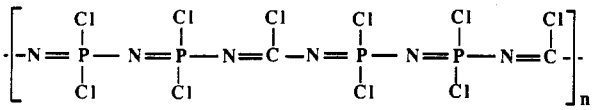
spectroscopy and differential scanning calorimetry. The ^{31}P NMR spectrum (THF) consisted of a singlet resonance at −3.7 ppm, which is significantly shifted to high field compared to that of **12** (δ = 36.5 ppm). A similar shift of the ^{31}P NMR resonance occurs in the formation of $[NPCl_2]_n$ **2** (δ = −18.4 ppm) from **1** $(NPCl_2)_3$ (δ = 19.9 ppm). The ^{13}C NMR ($CDCl_3$) spectrum showed a singlet resonance at 154.5 ppm that was assigned to the carbon atoms of the polymer backbone. The glass transition temperature of **13**, determined by differential scanning calorimetry, was −21 °C. This is significantly higher than the value for poly(dichlorophosphazene) **2** (T_g = −63 °C).[2b] The difference in T_g indicates that the backbone bonds of polymer **13** have significantly less torsional flexibility than those in polymer **2** (see below).

Interestingly, the detection of a single, singlet ^{31}P NMR resonance even at high field (146 MHz) suggests the presence of a single head-to-tail polymer microstructure (**14**). A head-to-head arrangement (**15**) would be expected to give rise to a more complex ^{31}P NMR spectrum.



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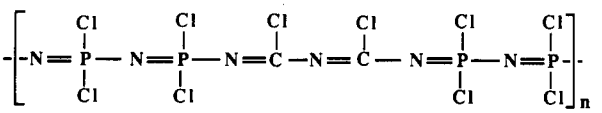
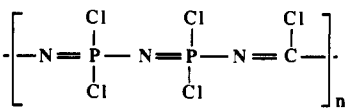


15

Synthesis and Properties of the Poly(aryloxycarbophosphazenes) 16–24. Poly(chlorocarbophosphazene) **13** functions as a reactive macromolecular intermediate in a manner analogous to that of poly(dichlorophosphazene) **2**. Thus, reaction of **13** (as a mixture with **12**) with a variety of aryloxide nucleophiles yielded the hydrolytically stable polymers **16–24** (Chart I). A range of aryloxy nucleophiles was investigated in order to provide a detailed comparison of the properties of the new polymers with those of their classical polyphosphazene counterparts.[8]



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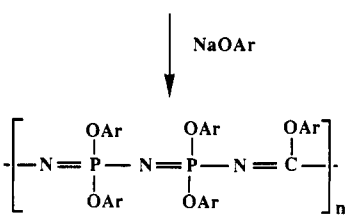
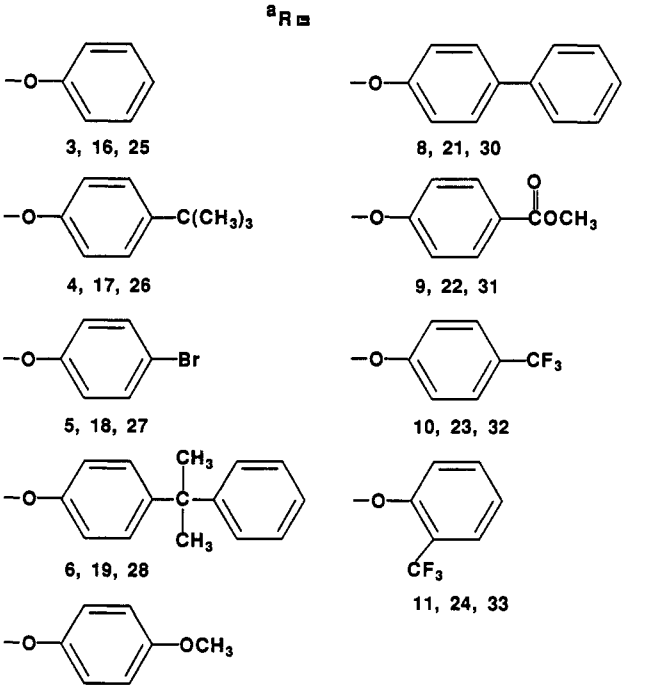


16-24

Both the cyclic and high polymeric chlorocarbophosphazenes **12** and **13** proved to be significantly more reactive toward nucleophilic substitution than did the corresponding classical phosphazenes **1** and **2**. For example, the preparation of poly[bis(*p*-*tert*-butylphenoxy)phosphazene] from **2** required 24 h in an autoclave at 150 °C, but the synthesis of the analogous poly(carbophosphazene) required only 24 h at room temperature.[9] The separation

Chart I

$-[-NPR_2-]-_n$ $-[-N_3P_2CR_5-]-_n$ $N_3P_2CR_5$



[a] The numbers under each substituent R refer to compounds $-[-NPR_2-]-_n$, $-[-N_3P_2CR_5-]_n$, and $N_3P_2CR_5$, respectively.

of the cyclic carbophosphazenes **25–33** from the analogous polymer was achieved by precipitation techniques.

Polymers **16–20** and **22–24** were isolated as white powders that were soluble in polar organic solvents such as THF and acetone. By contrast, polymer **21** was soluble only in hot THF. Similar solubility characteristics have been noted for the polyphosphazene analogue of **21**.[9] Polymers **16–24** were characterized by ^{31}P NMR, ^{13}C NMR, and ^1H NMR spectroscopy, elemental microanalysis, IR spectroscopy, gel permeation chromatography, and differential scanning calorimetry. These data are summarized in Tables I and II. In addition, the molecular weight of polymer **19** was determined by the absolute method of light scattering.

The ^{31}P NMR spectra of **16–24** contained a single, singlet resonance at ca. −10 ppm. A similar shift to higher field is also seen in the ^{31}P NMR spectrum when poly(dichlorophosphazene) **2** is allowed to react with aryloxide nucleophiles.[9] This provides additional evidence for the presence of a single head-to-tail polymer microstructure (see above). The ^1H and ^{13}C NMR spectra were also consistent with the assigned structures. Thus, low-field ^{13}C NMR resonances at ca. 160 ppm were assigned to the carbon atoms of the polymer backbone. Furthermore, two different ^{13}C resonances were detected for the ipso, ortho, meta, and, in some cases, para carbon atoms of the aryloxy side groups. The relative intensities of these two resonances (4:1) are consistent with four side groups per repeat unit bound to phosphorus and one to carbon. A representative ^{13}C NMR spectrum that illustrates these points is shown in Figure 1.

The infrared spectra of polymers **16–24** contained intense absorptions at 1250–1300 cm^{-1}. These are characteristic of P=N skeletal vibrations. In addition, absorptions detected at 1400–1480 cm^{-1} were assigned to backbone C=N vibrations. Elemental analyses of **16–24** were consistent with the assigned structures. They showed very small amounts of chlorine present (0–0.3%), which

Table I

$-[-N_3P_2CR_5-]-_n$	^{31}P,[a] ppm	^{13}C,[a] ppm	^{1}H,[a] ppm
16	−10.4	121.2 (*o*-PhOP), 122.6 (*o*-PhOC), 123.9 (*p*-PhOP), 124.1 (*p*-PhOC), 128.3 (*m*-PhOC), 129.0 (*m*-PhOP), 151.4 (ipso PhOP),153.2 (ipso PhOC), 159.8 (NCN), all s	6.9 (br s)
17	−9.9	31.4 (CH_3), 34.0 ($C(CH_3)$), 120.9 (*o*-PhOP), 123.9 (*o*-PhOC), 125.5 (*m*-PhOC), 126.2 (*m*-PhOP), 144.9 (*p*-Ph), 148.2 (ipso PhOP), 150.5 (ipso PhOC), 159.2 (NCN), all s	1.1 (s), 6.9 (br s)
18	−10.0	120.6 (*p*-Ph), 122.4, (*o*-PhOC), 123.7 (*o*-PhOP), 131.7 (*m*-PhOP), 132.2 (*m*-PhOC), 149.7 (ipso PhOP), 151.5 (ipso PhOC), 159.5 (NCN), all s	6.6 (br s)
19	−10.0	30.8 (CH_3), 42.2 ($C(CH_3)_2$), 120.8 (*o*-PhOC), 121.9 (*o*-PhOP), 125.4 (*p*-Ph′), 126.6 (*m*-PhOC), 127.2 (*m*-PhOP), 127.8 (*o,m*-Ph′), 145.8 (*p*-Ph), 149.2 (ipso PhOP), 150.6 (ipso Ph′), 151.0 (ipso PhOC), 159.7 (NCN), all s[b]	1.3 (s), 6.7 (d), 7.0 (br s)
20	−9.0	55.2 (OCH_3), 113.2 (*m*-PhOC), 113.8 (*m*-PhOP), 122.0 (*o*-PhOP), 123.2 (*o*-PhOC), 145.1 (ipso PhOP), 147.0 (ipso PhOC), 155.7 (*p*-PhOP), 155.9 (*p*-PhOC), 160.1 (NCN), all s	3.6 (s), 6.7 (m)
21	−9.2	*c*	7.3 (m)
22	−10.9	52.0 (CO_2CH_3), 120.1 (*o*-PhOP), 121.6 (*o*-PhOC), 126.6 (*p*-PhOP), 127.0 (*p*-PhOC), 130.3 (*m*-PhOC), 130.9 (*m*-PhOP), 153.9 (ipso PhOP), 155.6 (ipso PhOC), 159.3 (CNC), 165.8 (CO_2CH_3), all s	3.8 (s), 6.7 (m), 7.5 (m)
23	−10.8	122.7, 125.8, 128.7, 131.59 (q, CF_3), 124.3 (*o*-PhOP), 125.7 (*o*-PhOC), 129.9 (*m*-PhOC), 130.4 (*m*-PhOP), 131.2 (*p*-Ph), 156.5 (ipso PhOP), 158.3 (ipso PhOC), 168.1 (NCN)	6.5 (m), 7.2 (m)
24	−10.4	117.2 (6-PhOP), 118.3 (6-PhOC), 118.5, 122.0, 124.9, 127.5 (q, CF_3), 121.6 (4-Ph), 123.4 (5-PhOP), 124.5 (5-PhOC), 129.2 (3-PhOC), 129.8 (3-PhOP), 131.6, 131.9 (d, 2-Ph), 150.4 (ipso PhOP), 152.0 (ipso PhOC), 159.6 (NCN)	6.8 (m), 7.0 (m)

[a] ^{31}P values obtained in THF. ^{13}C and ^{1}H values obtained in $CDCl_3$. [b] Ph refers to the carbons in the phenyl ring closest to the polymer backbone; Ph′ refers to the carbons in the phenyl ring furthest from the polymer backbone. [c] The ^{13}C NMR spectrum of this compound could not be obtained due to insolubility.

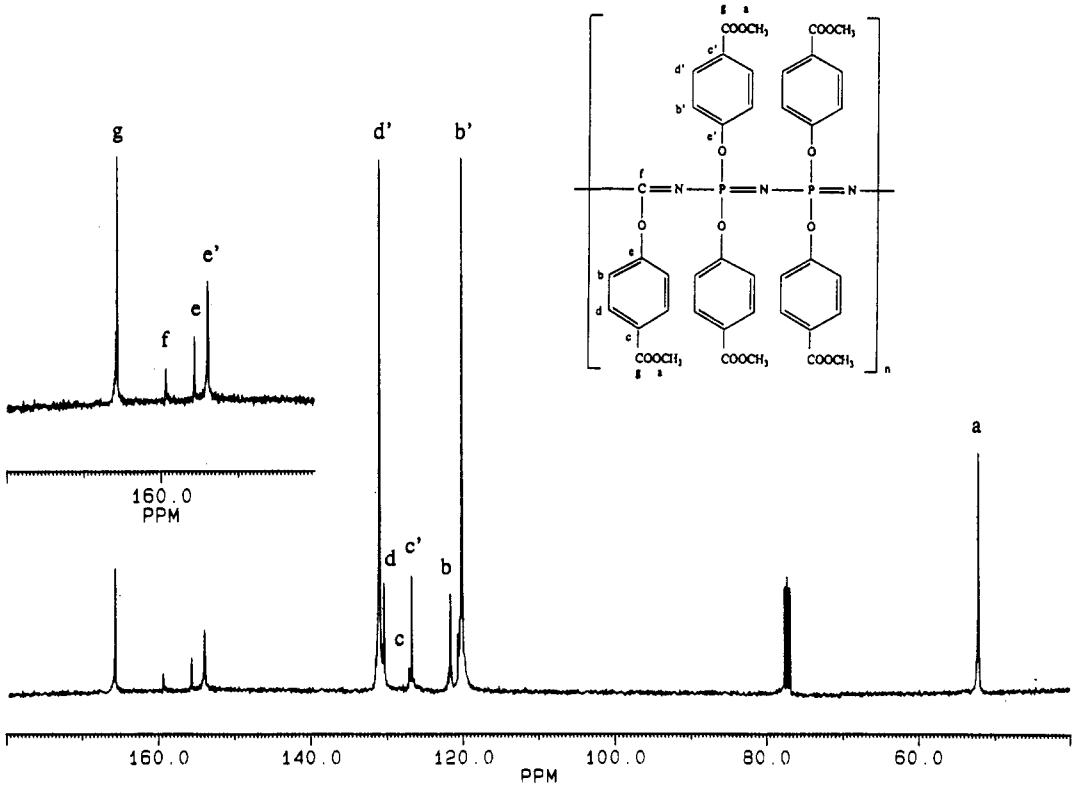


Figure 1. 90 MHz ^{13}C NMR spectrum of polymer **22** in $CDCl_3$.

indicated that virtually complete replacement of the halogen atoms in **13** had occurred. The weight-average molecular weight (M_w) of polymers **16–24** was estimated to be in the range of 1×10^5 by gel permeation chromatography (GPC) using poly[bis(trifluoroethoxy)phosphazene] as a standard. The absolute value of M_w for **19** determined by light scattering was found to be $7.4 \times 10.^4$

Synthesis and Properties of Small-Molecule Cyclic (Aryloxy)carbophosphazenes 25–33. In analogous small-molecule model reactions, the cyclic carbophosphazene **12** was allowed to react with aryloxide nucleophiles to yield species **25–33**. These cyclic compounds were isolated as hydrolytically stable, white crystalline solids, the structures of which were confirmed by ^{31}P NMR spectroscopy and mass spectrometry. The ^{31}P NMR spectra consisted of singlet resonances at ca. +20 ppm. The electron impact mass spectra showed molecular ions, together with peaks assignable to the sequential loss of the aryloxide side groups. These data are summarized in Table III.

Table II

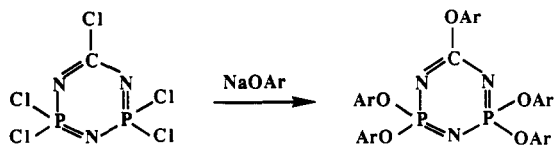
$-[-N_3P_2CR_5-]-_n$	GPC	elem anal., calc/found		% yield
16	$M_w = 1.2 \times 10^5$	64.02/63.33	C	70
	$M_n = 2.3 \times 10^4$	4.34/4.15	H	
		7.23/7.38	N	
		0.00/0.01	Cl	
17	$M_w = 2.0 \times 10^5$	71.60/71.45	C	48
	$M_n = 4.0 \times 10^4$	7.60/7.62	H	
		4.87/4.89	N	
		0.00/0.10	Cl	
18	$M_w = 1.1 \times 10^5$	38.15/40.95	C	57
	$M_n = 2.6 \times 10^4$	2.07/2.48	H	
		4.31/5.05	N	
		0.00/0.05	Cl	
19	$M_w = 1.5 \times 10^5$	77.86/76.86	C	55
	$M_n = 1.2 \times 10^4$	6.45/5.85	H	
		3.58/3.95	N	
		0.00/0.07	Cl	
20	$M_w = 1.4 \times 10^5$	59.10/58.80	C	51
	$M_n = 2.6 \times 10^4$	4.82/5.08	H	
		5.74/5.09	N	
		0.00/0.28	Cl	
21	*a*	75.37/77.05	C	19
		5.70/5.62	H	
		4.32/2.86	N	
		0.00/0.04	Cl	
22	$M_w = 1.2 \times 10^5$	56.54/56.21	C	70
	$M_n = 2.4 \times 10^4$	4.05/4.20	H	
		4.82/4.87	N	
		0.00/0.04	Cl	
23	$M_w = 9.0 \times 10^4$	46.92/45.96	C	55
	$M_n = 4.3 \times 10^4$	2.18/2.06	H	
		4.56/4.79	N	
		0.00/0.08	Cl	
24	$M_w = 1.1 \times 10^5$	46.92/46.16	C	73
	$M_n = 4.7 \times 10^4$	2.18/2.19	H	
		4.56/4.99	N	
		0.00/0.03	Cl	

[a] The molecular weight of this compound could not be determined due to insolubility.

Table III

$N_3P_2CR_5$	^{31}P,[a] ppm	MS, calc/found	$N_3P_2CR_5$	^{31}P,[a] ppm	MS, calc/found
25	20.2	581/581	**30**	20.6	961/961
26	20.3	861/861	**31**	19.5	871/971
27	20.3	976/976	**32**	19.6	921/921
28	20.2	1171/1171	**33**	20.2	921/921
29	21.3	731/731			

[a] These values were obtained in THF.



12 25-33

Thermal Transition Behavior of the Poly(carbophosphazenes) 15–24. The glass transition temperature (T_g) of a polymer is believed to be a measure of the reorientational freedom of the macromolecular chain. Classical polyphosphazenes possess one of the most inherently flexible polymer backbones known. When the side groups are small and flexible, this feature generates some of the lowest glass transition temperatures found in synthetic polymers. For example, the T_g of $[NPCl_2]_n$ **2** is −63 °C,[2b] that of $[NPF_2]_n$ −96 °C,[2b] and of $[NP(OBu)_2]_n$ −105 °C.[10] However, the presence of more rigid and bulky aryloxy side groups leads to a significant increase in T_g. For example, the T_g of $[NP(OPh)_2]_n$ is −6 °C, 72 °C higher than that of **2**.[9] In this section the glass transition temperatures of the poly(carbophosphazenes) **13** and **16–24** are discussed. This provides insight into the effect on the thermal transition behavior of the replacement of skeletal phosphorus atoms by carbon.

Table IV

$-[-N_3P_2CR_5-]-_n$	T_g, °C	$-[NPR_2-]-_n$	T_g,[c] °C
13	−21	2	−63
16	18	3	−6
17	74	4	50
18	45	5	15
19	55	6	39
20	37	7	13
21	*a*	8	93
22	52	9	*b*
23	31	10	*b*
24	−20	11	*b*

[a] The T_g of this compound could not be detected. [b] This is not a known compound. [c] For compound **2**, see ref 2b. For compounds **3**, **4**, **6**, and **8**, see ref 9. For compound **5**, see ref 12. For compound **7**, see ref 13. The T_g of compound **9** has not been determined. However, the T_g of the ethyl ester, $-[-NP(OPhCO_2Et)_2-]-_n$, is 7 °C; see ref 14.

The T_g values for the poly(carbophosphazenes) **13** and **16–24**, together with those of their classical polyphosphazene analogues, are shown in Table IV. In every case, the glass transition temperature of the poly(carbophosphazene) is ca. 16–42 °C higher than that of the corresponding classical polyphosphazene with the same side group. This indicates that the poly(carbophosphazene) skeleton is inherently less flexible than that of the classical polyphosphazenes. This is in spite of the fact that steric interactions between side groups would be expected to be less severe in poly(carbophosphazenes) (five side groups per repeating unit) than in the classical analogues (six side groups per repeating unit). One possible explanation for the lower skeletal flexibility of poly(carbophosphazenes) involves the inherent differences in the π-bond character of C=N and P=N bonds. Torsions about C=N bonds in the polymer backbone would follow the normal pattern for "organic-type" $p\pi-p\pi$ bonds, in which maximum π-bond overlap occurs at only two points in the 360° bond twisting profile. Hence, an appreciable barrier must be surmounted before the bond can undergo significant torsion. The P=N bond is believed to be of the $d\pi-p\pi$ type. Five alternative 3d orbitals at phosphorus can interact with a $2p_z$ orbital at nitrogen. Hence, significant π overlap is possible at any point in the 360° torsional profile. Therefore, the barrier to torsion will be low. Another possible explanation is that the smaller size of the main-chain carbon atoms compared to that of phosphorus might generate more severe steric interactions between side groups in poly(carbophosphazenes), and this could lead to higher T_g values.

The variations in T_g within the group of poly(carbophosphazenes) studied closely parallel those found previously for classical polyphosphazenes. Thus, the T_g values increase with increasing steric bulk, linearity, symmetry, and rigidity of the side group. For example, the glass transition temperatures increase in the order **13** (R = Cl) −45 °C < **16** (R = OPh) 18 °C < **19** (R = $OPhC(CH_3)_2Ph$) 55 °C < **17** (R = $OPhC(CH_3)_3$) 74 °C. This trend can be explained by increased steric interactions between side groups and the lower free volume when side groups with these characteristics are present. Comparison of the T_g values of **23** and **24** allows insight into the effect of side-group asymmetry on the skeletal flexibility. For polymer **23**, which contains a linear *p*-(trifluoromethyl)phenoxy side group, the T_g is 51 °C higher than for **24**, in which the trifluoromethyl substituent has an ortho orientation. This

difference can be rationalized in terms of free volume arguments. Thus, the more asymmetric aryloxy side group in **24** would be expected to generate more free volume compared to the situation in **23**.

Some single-substituent poly(aryloxyphosphazenes) are microcrystalline.[2b,9] No evidence for T_m transitions was found for the poly(carbophosphazenes). This suggests that polymers **13** and **16–24** are amorphous. The backbone carbon atoms that bear only one substituent may generate a more irregular side-group disposition than in classical polyphosphazenes, and this would hinder crystallization.

Experimental Section

Equipment and Materials. The cyclo(carbophosphazene) **12** was synthesized by a modification of the method of Fluck et al.[5] A two-step route was employed as described below using phosphorus pentachloride, ammonium chloride, and cyanamide, which were obtained from Aldrich. 1,1,2,2-Tetrachloroethane and nitrobenzene were dried over molecular sieves (Davison 4 Å). Compound **12** was sublimed twice before use and was stored in a drybox (Vacuum Atmospheres). Tetrahydrofuran and diethyl ether (Aldrich) were distilled from sodium benzophenone ketyl. All phenols were obtained from Aldrich and were sublimed or distilled under vacuum before use. All reactions and manipulations were carried out under an atmosphere of dry argon using either a drybox or standard Schlenk techniques.

^{31}P (^1H decoupled) NMR spectra were obtained with a JEOL FX-90Q NMR spectrometer operating at 36.2 MHz and with a Bruker WP-360 NMR spectrometer operating at 146 MHz. ^{31}P NMR chemical shifts are relative to 85% phosphoric acid as external reference, with positive shift values downfield from the reference. ^1H NMR and ^{13}C NMR spectra were recorded with the use of a Bruker WP-360 NMR spectrometer operating at 360 and 90 MHz, respectively. Chemical shifts are relative to external TMS. Infrared spectra were obtained with the use of a Perkin-Elmer 283B grating spectrometer. Elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN. Gel permeation chromatography (GPC) and differential scanning calorimetry (DSC) were carried out as described previously.[11]

Synthesis of $N_3P_2CCl_5$ 12. Step 1. Phosphorus pentachloride (624 g, 3.0 mol) and ammonium chloride (53 g, 1.0 mol) were suspended in a mixture of 1,1,2,2-tetrachloroethane (500 mL) and nitrobenzene (400 mL). The reaction mixture was heated at 90 °C under argon until evolution of chlorine was no longer detected (approximately 2 days). The solution was cooled slowly to room temperature. The product, NP_3Cl_{12}, crystallized as colorless needles, which were purified by repeated washings with 1,1,2,2-tetrachloroethane and diethyl ether (^{31}P δ = 21.8 ppm; yield 50%). **Step 2.** NP_3Cl_{12} (266 g, 0.5 mol) was suspended in hexane (1000 mL) with overhead stirring. A solution of cyanamide (21 g, 0.5 mol) in diethyl ether was added dropwise under argon to the stirred suspension, which was cooled to 0 °C. The reaction mixture was heated to 35 °C for 4 days. The solvent was removed under vacuum and white, crystalline **12** was isolated from the resultant oil by two vacuum sublimations (yield 29 g (20%); ^{31}P δ = 36.2 ppm).

Synthesis of $[N_3P_2C(OC_6H_4C(CH_3)_3)_5]_n$ 17. Compound **12** (1.0 g, 3.44 mmol) was polymerized in an evacuated thick-walled glass tube at 120 °C. After ca. 3.5 h, the tube contents were dissolved in a tetrahydrofuran solution of sodium *p-tert*-butylphenoxide. The latter was prepared by adding a solution of *p-tert*-butylphenol (10.0 g, 66.7 mmol) in THF (50 mL) to a suspension of sodium metal (3.0 g, 130 mmol) in THF (50 mL) followed by refluxing for 16 h. After 24 h, the ^{31}P NMR spectrum indicated that complete chlorine atom replacement in **12** had occurred. The polymeric product was isolated by sequential precipitations of the concentrated reaction mixture into distilled water (twice) and methanol (once) to afford a white powder, yield 1.4 g (48%).

The synthesis of polymers **16** and **18–24** followed the procedure described above for **17**. Purification of **19**, **20**, and **22–24** was effected by precipitation into distilled water (twice), methanol (once), and hexane (twice). Polymer **18** was purified by dialysis in methanol. Polymers **16–24** were isolated as fine white powders. The synthesis of **21** resulted in a product that was only sparingly soluble in hot THF, which hampered both its purification and characterization.

Synthesis of $N_3P_2C(OC_6H_4C(CH_3)_3)_5$ 26. Compound **12** (0.5 g, 1.8 mmol) was dissolved in THF (25 mL) and to it was added dropwise a solution of sodium *p-tert*-butylphenoxide in THF, prepared by addition of *p-tert*-butylphenol (0.81 g, 5.4 mmol) and sodium (0.25 g, 11 mmol) in THF (20 mL) followed by refluxing for 16 h. After 2 h, the ^{31}P NMR spectrum indicated that complete substitution had occurred. The product, **26**, was purified by column chromatography (methylene chloride/hexane) and was obtained as white crystals from hexane, yield 0.9 g (65%).

The synthesis of compounds **25** and **27–33** followed the procedure outlined above. Compounds **25–31** were obtained as white crystalline solids and compounds **32** and **33** were obtained as colorless oils.

Acknowledgment. This work was supported by the U.S. Army Research Office (H.R.A., S.M.C., and I.M.) and Bayer A.G. and the F.R.G. Ministry of Science Technology (O.N. and G.R.). The work was carried out at the Pennsylvania State University. We thank Dr. Robert E. Singler and Marie K. Potts of U.S. Army Materials Technology Laboratory for the light scattering measurements.

References and Notes

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Registry No. **13** (homopolymer), 121425-35-2; **13** (SRU), 132492-02-5; **25**, 121440-63-9; **26**, 132491-93-1; **27**, 132491-94-2; **28**, 132491-95-3; **29**, 132492-00-3; **30**, 132491-96-4; **31**, 132491-97-5; **32**, 132491-98-6; **33**, 132491-99-7; $N_3P_2CCl_5$, 57332-66-8; PCl_2, 10026-13-8; NH_4Cl, 12125-02-9.