Macromolecules **1989,** *22,* 4179–4190 **4179**

In the case of microporous membranes with grafted polyelectrolyte brushes within the pores, one would have a permanently altered membrane with particular properties depending on the polyelectrolyte molecule.

Experimental data on brush conformation are limited. Webber, Anderson, and Jhon[22] have performed a study on solvent flow through membranes with adsorbed diblock copolymers and measured the effect of solvent quality, molecular weight, etc., on the hydrodynamic thickness of the polymer layer. Hadziioannou et al. and Tauton et al.[20,21] have measured the forces between surfaces with adsorbed copolymers. These are some ways of probing the segment density in a brush. Direct measurements of segment density could be made by small-angle neutron scattering (SANS)[28-30] or evanescent wave induced fluorescence experiments.[31,32] As suggested by Milner et al., one could probe the end segment density distribution by fluorescent tagging of end segments and relate it to the total segment density distribution. This, as mentioned by them, would be a more robust test of the parabolic potential theory. Hydrodynamic thickness measurements can also be used,[33,34] as mentioned earlier, as indirect methods, although the detailed picture can only be obtained by SANS or fluorescent tagging.

Acknowledgment. We greatly appreciate various insightful and valuable discussions with Prof. C. G. Montgomery of the Department of Physics, The University of Toledo, and Noubar Tcheurekdjian of S. C. Johnson and Son Inc.

References and Notes

(1) Napper, D. H. *Polymeric Stabilization of Colloidal Dispersions*; Academic: London, 1983.
(2) Witten, T. A.; Pincus, P. A. *Macromolecules* **1986**, *19*, 2509.
(3) Scheutjens, J.; Fleer, G. J. *Macromolecules* **1985**, *18*, 1882.
(4) Hesselink, F. Th. *J. Colloid Interface Sci.* **1977**, *60*, 448.
(5) Pefferkorn, E.; Scmitt, A.; Varoqui, R. *Biopolymers* **1982**, *21*, 1451.
(6) Idol, W. K.; Anderson, J. L. *J. Membr. Sci.* **1986**, *28*, 269.
(7) Alexander, S. *J. Phys.* (*Les Ulis, Fr.*) **1977**, *38*, 983.
(8) de Gennes, P.-G. *Macromolecules* **1980**, *13*, 1069.
(9) de Gennes, P.-G. *Adv. Colloid Interface Sci.* **1987**, *27*, 189.
(10) Scheutjens, J. M. H. M.; Fleer, G. J. *J. Phys. Chem.* **1979**, *83*, 1619.
(11) Cosgrove, T.; Heath, T.; van Lent, B.; Leermakers, F.; Scheutjens, J. *Macromolecules* **1987**, *20*, 1692.
(12) Edwards, S. F. *Proc. Phys. Soc.* **1965**, *85*, 613.
(13) de Gennes, P.-G. *Rep. Prog. Phys.* **1969**, *32*, 187.
(14) Dolan, A. K.; Edwards, S. F. *Proc. R. Soc., London A* **1974**, *337*, 509.
(15) Dolan, A. K.; Edwards, S. F. *Proc. R. Soc., London A* **1975**, *343*, 427.
(16) Helfand, E. J. *J. Chem. Phys.* **1975**, *62*, 999.
(17) Jones, I. S.; Richmond, P. J. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 1062.
(18) Ploehn, H. J.; Russel, W. B.; Hall, C. K. *Macromolecules* **1988**, *21*, 1075.
(19) Milner, S. T.; Witten, T. A.; Cates, M. E. *Macromolecules* **1988**, *21*, 2610.
(20) Hadziioannou, G.; Patel, S.; Granick, S.; Tirrell, M. *J. Am. Chem. Soc.* **1986**, *108*, 2869.
(21) Tauton, H. J.; Toprakcioglu, C.; Fetters, L. J.; Klein, J. *Nature* **1988**, *332*, 712.
(22) Webber, R. M.; Anderson, J. L.; Jhon, M. S. in session on "Block Copolymers in Solutions and Interfaces", 62nd Colloid and Surface Science Symposium; June 19–22, 1988, University Park, PA.
(23) Miklavic, S. J.; Marcelja, S. *J. Phys. Chem.* **1988**, *92*, 6718.
(24) Papenhuijzen, J.; Van der Schee, H. A.; Fleer, G. J. *J. Colloid Interface Sci.* **1985**, *104*, 540.
(25) Van der Schee, H. A.; Lyklema, J. *J. Phys. Chem.* **1984**, *88*, 6661.
(26) Hoeve, C. A. J. *J. Polym. Sci.* **1970**, *C30*, 361.
(27) Roe, R. J. *J. Chem. Phys.* **1974**, *60*, 4192.
(28) Cosgrove, T.; Cohen Stuart, M. A.; Vincent, B. *Adv. Colloid Interface Sci.* **1986**, *24*, 143.
(29) Cosgrove, T.; Heath, T. G.; Ryan, K. in session on "Polymers at Interfaces", Annual AIChE meeting; Nov 15–20, 19878 New York.
(30) Auvray, L.; Cotton, J. P.*Macromolecules* **1987**, *20*, 202.
(31) Caucheteux, I.; Ausserre, D.; Hervet, H.; Rondelez, F. *Phys. Rev. Lett.* **1985**, *54*, 1948.
(32) Caucheteux, I.; Ausserre, D.; Hervet, H.; Rondelez, F. in session on "Polymers at Interfaces", Annual AIChE meeting, Nov 15–20, 1987, New York.
(33) Varoqui, R.; Dejardin, P. *J. Chem. Phys.* **1977**, *66*, 4395.
(34) Cohen Stuart, M. A.; Waajen, F. H. W. H.; Cosgrove, T.; Vincent, B.; Crowley, T. L. *Macromolecules* **1984**, *17*, 1825.

Poly[(aryloxy)phosphazenes] with Phenylphenoxy and Related Bulky Side Groups. Synthesis, Thermal Transition Behavior, and Optical Properties

Harry R. Allcock,* Michael N. Mang, and Alexa A. Dembek

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Kenneth J. Wynne

Chemistry Division, Office of Naval Research, Arlington, Virginia 22217.
Received November 29, 1988; Revised Manuscript Received March 31, 1989

ABSTRACT: The effect of steric hindrance on the synthesis of poly[(aryloxy)phosphazenes] that bear bulky aryloxy substituents is discussed. The syntheses of poly[(aryloxy)phosphazenes] with the general formula $[NP(OAr')_x(OAr'')_y]_n$, where OAr′ and OAr″ are phenoxy, 2-methylphenoxy, 4-methylphenoxy, 2-phenylphenoxy, 3-phenylphenoxy, 4-phenylphenoxy, 4-benzylphenoxy, 4-cumylphenoxy, and 4-*tert*-butylphenoxy and $x + y = 2$, are described. These polymers were prepared by the interaction of the corresponding sodium aryloxide with poly(dichlorophosphazene) in dioxane at 150 °C in an autoclave. This procedure allows the synthesis of poly[(aryloxy)phosphazenes] with bulky side groups while avoiding equilibration depolymerization. The influence of side group structural parameters on the thermal transition behavior of the polymers is discussed. The refractive indices of the polymers were measured by using a modified critical angle method at $\lambda = 632$ nm and were found to vary between 1.561 and 1.686.

A wide variety of poly(organophosphazenes) has been prepared by the replacement of the chlorine atoms in soluble poly(dichlorophosphazene) by organic nucleophiles[1] such as amines, alkoxides, or aryl oxides.[2] The properties of these polymers vary widely depending on the structure of the organic substituents attached to the skeletal phos-

0024-9297/89/2222-4179$01.50/0 © 1989 American Chemical Society

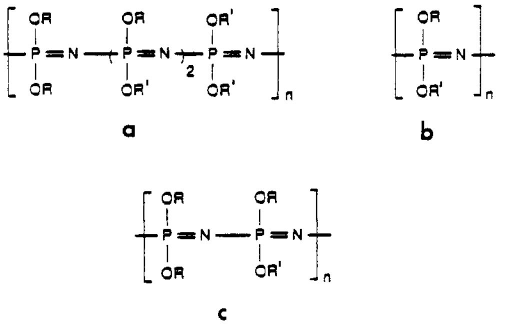


Figure 1. Possible side group distributions in mixed-substituent polyphosphazenes: (a) statistical distribution with equal numbers of different side groups (OR and OR′); (b) "ideal" distribution with equal numbers of different side groups; (c) "ideal" distribution when different side groups are present in 1:3 ratios.

phorus atoms.[3-5] For example, different organic substituents yield low-temperature elastomers,[6,7] microcrystalline materials,[2] or brittle glasses.[1] The properties of the polyphosphazene may be modified further by the incorporation of two or more different substituents (Figure 1).[8,9] Because of the large number of polymer structures available in this system, an opportunity exists to develop molecular structure–property correlations that may eventually allow the prediction of properties.

One objective of this work was to examine the variation in thermal transition and optical properties of poly[(aryloxy)phosphazenes] as a function of changes in side group structure. For example, aromatic side groups might be expected to generate high refractive indices. The use of different side groups would provide absorption or transmission in different regions of the spectrum. In addition, the types of side groups should influence the amorphous or microcrystalline character and hence determine the transparency. Materials for linear or nonlinear optical experiments should also possess a high glass transition temperature, a feature that should also depend on side group structure.

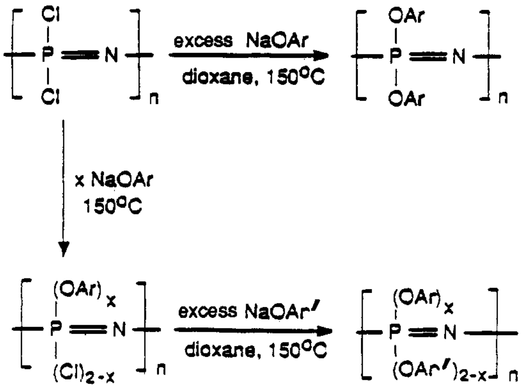
Results and Discussion

General Factors Involved in Synthesis. In general, the glass transition temperature of a polyphosphazene increases with increasing substituent size and rigidity.[10-12] Thus, rigid, glasslike polyphosphazenes should be accessible by the incorporation of large, rigid, sterically hindered side groups, such as aryloxy units, into the polymer. However, the complete replacement of the chlorine atoms in poly(dichlorophosphazene) by aryloxy groups is a difficult process because of steric retardation effects.[2] Thus, it was necessary to use a synthetic approach that would overcome the steric inhibition to full substitution while, at the same time, preventing thermally induced depolymerization. In the following sections, we describe a method that accomplishes this objective and allows the preparation of highly hindered single-substituent or mixed-substituent poly[(aryloxy)phosphazenes].

Conventional Synthetic Procedure. Although some nucleophiles react with poly(dichlorophosphazene) at low temperatures,[13] the steric size of aryloxide ions requires more forcing reaction conditions. The traditional synthesis method[2] allows poly(dichlorophosphazene) to react with a large excess of a sodium aryloxide in a high boiling solvent, such as toluene or xylene, for 3 days or longer. At longer reaction times and elevated temperatures, the kinetically favored linear macromolecules often equilibrate to more thermodynamically stable oligomers.

Modified Synthetic Procedure. For the present studies, we have used a modified synthetic procedure, originally described by Futumura et al.[14] In this procedure, the halogen replacement reaction is carried out in a solvent such as dioxane with a boiling point in the 100 °C/1 atm range, in a sealed reaction vessel at temperatures up to 150 °C. For example, poly(dichlorophosphazene) in dioxane was allowed to react with 4 equiv of sodium aryl oxide in the presence of tetra-*n*-butylammonium bromide at 150 °C in a stirred autoclave for 24 h to yield polymers **1**–**6** (Scheme I). The rate of the substitution reaction is increased by virtue of the higher reaction temperature, and complete replacement of chlorine by aryloxy units can be effected.

Scheme I



Reaction Conditions and Polymer Stability. It was first necessary to determine the stability of the phosphazene skeleton under these forcing reaction conditions. Some poly[(aryloxy)phosphazenes] are known to undergo molecular weight decline at temperatures as low as 100 °C.[15] It was also important to ascertain if the substituted polymer undergoes molecular weight decreases *after* the halogen replacement reaction is complete but before the reaction mixture is cooled to room temperature. If this occurred, the advantages of the method would be lost.

Thus, the following experiments were performed. Two samples of $[NP(OC_6H_5)_2]_n$ were synthesized from the same batch of poly(dichlorophosphazene). The first was prepared at 100 °C in refluxing dioxane (**1a**), and the second was synthesized with the use of an autoclave at 150 °C (**1b**). After isolation, *both* polymers had weight-average molecular weights of 1.2×10^6 (as determined by gel permeation chromatography). Thus, if depolymerization occurred in the autoclave at 150 °C, it occurred at the same rate as in the reaction carried out at 100 °C. This is unlikely. Polymers **1a** and **1b** were then dissolved in dioxane and were placed in an autoclave vessel at 150 °C for 24 h. The molecular weight of polymer **1a** declined from 2×10^6 to 7×10^5, while the molecular weight of **1b** remained unchanged. Thus, the polymer prepared in the autoclave appeared to have a higher thermal stability than the polymer prepared by conventional methods. We speculate that this is a consequence of a lower concentration of unreacted chlorine remaining in **1b**.

Limits of Substituent Steric Size: Ortho-Substituted Aryloxy Groups. One goal of this investigation was to assess the steric size limit for substituents attached to a polyphosphazene chain. Aryloxy groups with substituents in the meta and para position have been attached to polyphosphazenes previously, but no fully derivatized, ortho-substituted poly[(aryloxy)phosphazenes] have been reported. The synthesis of $[NP(OC_6H_4CH_3\text{-}o)_2]_n$ (**7**) and $[NP(OC_6H_4C_6H_5\text{-}o)_2]_n$ (**8**) was, therefore, attempted to determine whether a high loading of *o*-methylphenoxy or *o*-phenylphenoxy groups could be introduced by using the synthetic method described above.

First, several small-molecule, model compound reactions[16] were carried out in which the cyclic trimer, (NP-

$Cl_2)_3$, and the cyclic tetramer, $(NPCl_2)_4$, were allowed to react with sodium *o*-methylphenoxide or sodium *o*-phenylphenoxide. In all four cases, total replacement of chlorine atoms by aryloxy units occurred in the presence of tetra-*n*-butylammonium bromide within 48 h at 100 °C.

The corresponding reactions at 150 °C were then attempted at the high polymeric level with $(NPCl_2)_n$, using 2 equiv of sodium *o*-methylphenoxide or sodium *o*-phenylphenoxide for each chlorine atom. Complete chlorine replacement did not occur. The concentration of the nucleophile was then increased, and longer reaction times were used. Even under these forcing conditions, only 85% of the chlorine atoms in **7** and 76% of the chlorine atoms in **8** could be replaced. Remarkably, these polymers remained soluble in organic media and did not cross-link even after repeated precipitations into water and exposure to atmospheric moisture. Less shielded P–Cl bonds would have hydrolyzed to P–OH units and formed cross-links under the same conditions. This result emphasizes the difficulty associated with replacement of a chlorine atom geminal to a bulky ortho-substituted aryloxy group even by an unhindered nucleophile such as water. For these systems, a degree of halogen replacement of 75%–85% is apparently the maximum that can be achieved with this procedure.

Reduction of Polymer Crystallinity by Preparation of Mixed-Substituent Poly[(aryloxy)phosphazenes]. The absence of microcrystallinity is an important requirement for a polymer that is to be considered for uses in optical fibers, lenses, or nonlinear optical devices. Most known single-substituent poly[(aryloxy)phosphazenes] are microcrystalline solids. However, it is known that the incorporation of two different substituents randomly along the phosphazene chain can disrupt and lower the symmetry of the system and the crystallinity. Some mixed-substituent poly(organophosphazenes) are elastomeric materials with low glass transition temperatures.[6,9] In this work, the challenge was to prepare polymers that would be amorphous but have high glass transition temperatures.

Two different classes of mixed-substituent poly[(aryloxy)phosphazenes] were prepared during the course of this investigation, with the differences being based on the ratios of the side groups (Table I). In the first series, the different side groups were present in equimolar amounts (**9–25**). In the second series, the side groups were present in the ratio of one to three (**26–40**). Compounds **1–42** are shown in Charts I–III.

Mixed-substituent polymers **9–25**, which contained equal numbers of both types of side groups, were prepared in the following manner. Poly(dichlorophosphazene) was allowed to react with a sufficient amount of the first nucleophile to replace only one-half of the available chlorine atoms. The product was then treated with an excess of the second nucleophile (Scheme I). It is probable that the initial replacement of chlorine would follow a mainly nongeminal pattern. Replacement of the remaining chlorine atoms by the second nucleophile would give a polymer with a final distribution of repeating units close to that of a nongeminal (all (OR)(OR′)) distribution (see Figure 1).

In the second series, only one-third of the chlorine atoms was replaced by the first nucleophile, and the remaining halogen was then replaced by an excess of the second aryl oxide. The process yielded polymers **26–40**, in which the different side groups are present in a 1:3 ratio. In the ideal case, a random distribution of equal numbers of (OR)(OR) or (OR)(OR′) side group pairs would be present (see Figure 1).

The mixed-substituent polymers described here were amorphous solids. Polymers **14**, **21**, **27**, **31**, and **37** all showed one weak endothermic transition in addition to the glass transition, as revealed by differential scanning calorimetry. However, films of these polymers were not birefringent when viewed between crossed polarizers. Reports have appeared of mixed-substituent poly[(aryloxy)phosphazenes] that are either crystalline[8] or show evidence of crystal–crystal type phase transitions.[9]

Differences between Sequential and Simultaneous Addition of Nucleophiles. Sequential addition of the nucleophiles is necessary in order to achieve precise control over the ultimate composition of the derivative polymer. If the halogen replacement reaction is carried out with a mixture of nucleophiles, each in excess of the amount needed for replacement of the corresponding P–Cl units, slight differences in the rates of reaction would yield polymers with a side group stoichiometry different from that of the original reagent mixture. Sequential addition of the different nucleophiles avoids this complication and allows the composition of the product to be inferred from the stoichiometry of the first reagent.

Polymers **41** and **42** were synthesized to compare the physical properties of species prepared by using sequential or simultaneous addition of two nucleophiles. Polymer **41** was prepared by allowing poly(dichlorophosphazene) to react with 1 equiv of sodium *p*-phenylphenoxide at 150 °C for 8 h. Three equivalents of sodium *p*-methylphenoxide were then added, and the mixture was heated to 150 °C for 16 h. Polymer **42** was prepared by allowing an equimolar mixture of sodium *p*-phenylphenoxide and sodium *p*-methylphenoxide to react with poly(dichlorophosphazene) for 24 h at 150 °C.

The ^1H NMR spectrum of **41** showed unresolved peaks for the aromatic and aliphatic protons in the ratio 1:0.25, compared with the theoretical ratio 1:0.23. Polymer **42** had an integrated aromatic:aliphatic ratio of 1:0.23. These data, and the results of the elemental microanalyses, suggest that the compositional differences between the two polymers are very small. However, the two polymers do show different thermal transition behavior. Polymer **41**, prepared by sequential nucleophile addition, had a glass transition temperature of 42 °C and an additional endothermic transition at 108 °C. The T_g of polymer **42** was 46 °C, with a second endothermic transition occurring at 131 °C.

Differences in the pattern of substitution, or randomness of substitution, may account for the small differences in the thermal transition behavior of these polymers. For example, the pattern of substitution in polymer **42** should be more random than that of **41**. In **41**, the first nucleophile would be expected to react in a nongeminal pattern to give a polymer with a more regular structure.

Sequential addition of the nucleophiles was necessary when ortho-substituted aryloxy groups were incorporated into mixed-substituent poly[(aryloxy)phosphazenes]. As discussed earlier, complete replacement of the chlorine atoms in poly(dichlorophosphazene) by ortho-substituted aryloxy groups is not possible even under forcing reaction conditions. However, polymers could be prepared in which 25% of the chlorine atoms were first replaced by *o*-methylphenoxy groups (**28**) or *o*-phenylphenoxy groups (**29**), and the remaining chlorine atoms were then replaced by *p*-phenylphenoxy groups. In addition, related polymers in which 50% of the chlorine atoms were replaced by *o*-methylphenoxy groups (**10**, **23**) or *o*-phenylphenoxy groups (**13**, **24**) have also been prepared.

Table I
Reaction Stoichiometries and Characterization Data for 1–42[a]

	reactant stoichiometry, equiv/P=N					^{31}P NMR			elemental anal., %				
compd	nucleophile 1	time, h	nucleophile 2	time, h	purif method[b]	shift, ppm[c]	M_w	M_n	element	calcd	found	T_1, °C	n_{632nm}
1	4.0 $NaOC_6H_5$	24			A	−20.0	1.1×10^6	4.6×10^4	C	62.36	61.88	147	1.619
									H	4.33	4.64		
									N	6.06	5.86		
									Cl	0	0.03		
2	4.0 $NaOC_6H_4CH_2C_6H_5$	24			A	−19.7	1.9×10^6	9.5×10^4	C	75.93	75.61	11	1.639
									H	5.35	5.34		
									N	3.41	3.30		
									Cl	0	0.16		
3	4.0 $NaOC_6H_4C(CH_3)_2C_6H_5$	24			B				C	77.11	76.12	119	1.614
									H	6.42	5.84		
									N	3.00	3.01		
									Cl	0	0.90		
4	4.0 $NaOC_6H_4C(CH_3)_3$	24			A	−19.0	2.5×10^6	1.5×10^5	C	69.95	69.80	135	1.561
									H	7.63	7.28		
									N	4.08	4.04		
									Cl	0	<0.50		
5	4.0 $NaOC_6H_4C_6H_5$-*m*	24			A	−20.7	1.5×10^6	1.0×10^5	C	75.22	75.26		1.657
									H	4.70	4.98		
									N	3.66	3.55		
									Cl	0	0.03		
6	4.0 $NaOC_6H_4C_6H_5$-*p*	24			B				C	75.22	74.77		
									H	4.70	4.55		
									N	3.60	3.68		
									Cl	0	0.01		
7[d]	20.0 $NaOC_6H_4CH_3$-*o*	67			B	−22.0, br	1.7×10^6	7.0×10^4	C	64.86	59.62		1.594
									H	5.41	5.30		
									N	5.40	5.62		
									Cl	0	4.10		
8[d]	16.0 $NaOC_6H_4C_6H_5$-*o*	84			A	−24.0, br	*e*		C	75.22	63.89		1.646
									H	4.70	4.52		
									N	3.66	5.02		
									Cl	0	5.02		
9	1.0 $NaOC_6H_4C_6H_5$-*p*	8	3.0 $NaOC_6H_5$	16	A	−19.6	1.5×10^6	4.7×10^4	C	70.13	69.61		1.646
									H	4.90	4.78		
									N	4.54	4.52		
									Cl	0	0.13		
10	1.0 $NaOC_6H_4CH_3$-*o*	24	3.0 $NaOC_6H_4C_6H_5$-*p*	24	A	−19.9	1.1×10^6	1.2×10^5	C	70.02	69.98		1.627
									H	5.02	4.85		
									N	4.36	4.37		
									Cl	0	0.65		
11	1.0 $NaOC_6H_4CH_2C_6H_5$	8	3.0 $NaOC_6H_4C_6H_5$-*p*	16	A	−19.1	1.5×10^6	1.1×10^5	C	75.57	71.40		1.649
									H	5.04	5.36		
									N	3.53	3.26		
									Cl	0	0.04		
12	1.0 $NaOC_6H_4C(CH_3)_2C_6H_5$	8	3.0 $NaOC_6H_4C_6H_5$-*p*	16	A	−18.9	1.1×10^6	5.5×10^4	C	76.25	75.39		1.635
									H	5.64	5.61		
									N	3.29	3.34		
									Cl	0	0.30		
13	1.0 $NaOC_6H_4C_6H_5$-*p*	18	12.0 $NaOC_6H_4C_6H_5$-*o*	72	A	−22.0, br	1.2×10^6	2.5×10^5	C	75.19	74.80		1.637
									H	4.73	5.25		
									N	3.65	3.29		
									Cl	0	0.82		
14	1.0 $NaOC_6H_4C_6H_5$-*m*	18	3.0 $NaOC_6H_4C_6H_5$-*p*	24	A	−19.2	8.9×10^5	5.1×10^4	C	75.22	74.38	121	1.667
									H	4.70	4.83		
									N	3.66	3.25		
									Cl	0	0.14		
15	1.0 $NaOC_6H_4C(CH_3)_3$	8	3.0 $NaOC_6H_4C_6H_5$-*p*	16	A	−18.4	2.5×10^6	1.5×10^5	C	72.75	72.91		1.613
									H	6.06	5.58		
									N	3.86	3.44		
									Cl	0	0.06		
16	1.0 $NaOC_6H_4C_6H_5$-*m*	8	3.0 $NaOC_6H_5$	16	A	−20.5	1.0×10^6	4.8×10^4	C	70.13	70.83		1.639
									H	4.90	4.64		
									N	4.54	4.31		
									Cl	0	0.10		
17	1.0 $NaOC_6H_4C_6H_5$-*m*	8	3.0 $NaOC_6H_4CH_2C_6H_5$	16	A	−19.9	9.2×10^5	1.2×10^5	C	75.59	75.45		1.644
									H	5.03	4.90		
									N	3.53	3.48		
									Cl	0	0.15		
18	1.0 $NaOC_6H_4C_6H_5$-*m*	8	3.0 $NaOC_6H_4C(CH_3)_2C_6H_5$	16	A	−19.9	2.0×10^6	1.5×10^5	C	76.25	76.17		1.629
									H	5.64	5.79		
									N	3.29	3.12		
									Cl	0	0.09		
19	1.0 $NaOC_6H_4C(CH_3)_2C_6H_5$	8	3.0 $NaOC_6H_5$	16	A	−20.0	1.2×10^6	4.6×10^4	C	72.23	71.80		1.613
									H	5.73	5.06		
									N	4.01	3.87		
									Cl	0	0.31		

Table I (Continued)

	reactant stoichiometry, equiv/P=N								elemental anal., %				
compd	nucleophile 1	time, h	nucleophile 2	time, h	purif method^b	^{31}P NMR shift, ppm^c	M_w	M_n	element	calcd	found	T_1, °C	n_{632nm}
20	1.0 $NaOC_6H_4C(CH_3)_2C_6H_5$	8	3.0 $NaOC_6H_4C(CH_3)_3$	16	A	−19.5	1.4×10^6	9.5×10^4	C	74.05	73.98		1.588
									H	6.96	6.52		
									N	3.46	3.35		
									Cl	0	0.05		
21	1.0 $NaOC_6H_4C(CH_3)_2C_6H_5$	8	3.0 $NaOC_6H_4CH_2C_6H_5$	16	A	−19.7	1.6×10^6	9.5×10^4	C	76.56	76.69	140	1.619
									H	5.92	6.05		
									N	3.19	2.94		
									Cl	0	0.11		
22	1.0 $NaOC_6H_4CH_2C_6H_5$	8	3.0 $NaOC_6H_5$	16	A	−20.0	1.5×10^6	9.7×10^4	C	71.02	70.25		1.623
									H	4.98	5.13		
									N	4.36	4.21		
									Cl	0	0.18		
23	1.0 $NaOC_6H_4CH_3$-*o*	18	3.0 $NaOC_6H_5$	24	A	−20.9	8.5×10^5	4.1×10^5	C	63.67	62.73		1.609
									H	4.93	4.88		
									N	5.71	5.87		
									Cl	0	0.86		
24	1.0 $NaOC_6H_4C_6H_5$-*o*	18	3.0 $NaOC_6H_5$	24	A	−24.2, br	9.6×10^5	1.2×10^5	C	70.35	69.14		1.633
									H	4.59	5.26		
									N	4.56	4.44		
									Cl	0	2.34		
25	1.0 $NaOC_6H_4C(CH_3)_3$	8	3.0 $NaOC_6H_5$	16	A	−19.8	7.7×10^5	9.0×10^4	C	66.89	66.52		1.573
									H	6.32	6.51		
									N	4.88	4.57		
									Cl	0	0.33		
26	0.5 $NaOC_6H_5$	8	5.5 $NaOC_6H_4C_6H_5$-*p*	16	B				C	73.06	70.67		1.654
									H	4.64	4.28		
									N	4.06	3.92		
									Cl	0	0.01		
27	0.5 $NaOC_6H_4CH_2C_6H_5$	8	3.5 $NaOC_6H_4C_6H_5$-*p*	18	B				C	75.40	75.28	152	1.661
									H	4.87	4.91		
									N	3.59	3.53		
									Cl	0	0.17		
28	0.5 $NaOC_6H_4CH_3$-*o*	24	3.5 $NaOC_6H_4C_6H_5$-*p*	96	A	−18.8	3.8×10^5	1.0×10^5	C	73.29	72.06		1.654
									H	4.86	5.13		
									N	3.98	3.86		
									Cl	0	0.17		
29	0.5 $NaOC_6H_4C_6H_5$-*o*	8	3.5 $NaOC_6H_4C_6H_5$-*p*	16	A	−20.0	9.1×10^5	2.0×10^5	C	75.20	71.15		1.661
									H	4.70	4.70		
									N	3.66	3.38		
									Cl	0	0.11		
30	0.5 $NaOC_6H_4C(CH_3)_2C_6H_5$	8	4.0 $NaOC_6H_4C_6H_5$-*p*	16	A	−18.3	9.9×10^5	3.7×10^4	C	75.73	74.32		1.650
									H	5.23	4.99		
									N	4.46	3.35		
									Cl	0	0.12		
31	1.5 $NaOC_6H_4C_6H_5$	12	2.5 $NaOC_6H_4C(CH_3)_3$	16	B				C	73.98	72.03	140	1.634
									H	5.40	5.25		
									N	3.75	3.54		
									Cl	0	0.08		
32	0.5 $NaOC_6H_4C_6H_5$-*m*	8	3.5 $NaOC_6H_4C_6H_5$-*p*	16	B				C	75.22	74.86		1.686
									H	4.70	4.70		
									N	3.66	3.59		
									Cl	0	0.11		
33	1.5 $NaOC_6H_4C_6H_5$-*m*	8	2.5 $NaOC_6H_5$	16	A	−20.5	5.6×10^5	1.3×10^4	C	73.06	72.26		1.644
									H	4.64	4.98		
									N	4.06	3.74		
									Cl	0	0.16		
34	1.5 $NaOC_6H_4C_6H_5$-*m*	8	2.5 $NaOC_6H_4CH_2C_6H_5$	16	A	−20.2	1.4×10^6	1.2×10^5	C	76.48	75.29		1.648
									H	4.94	4.60		
									N	3.64	3.50		
									Cl	0	0.25		
35	1.5 $NaOC_6H_4C_6H_5$-*m*	8	2.5 $NaOC_6H_4C(CH_3)_2C_6H_5$	16	A	−20.1	7.8×10^5	1.1×10^5	C	75.74	75.66		1.640
									H	5.20	4.98		
									N	3.46	3.35		
									Cl	0	0.03		
36	1.5 $NaOC_6H_4C_6H_5$-*m*	8	2.5 $NaOC_6H_4C_6H_5$-*p*	16	A	−20.1	5.5×10^5	1.0×10^5	C	75.22	75.65		1.675
									H	4.70	5.19		
									N	3.66	3.26		
									Cl	0	0.03		
37	0.5 $NaOC_6H_5$	8	3.5 $NaOC_6H_4C(CH_3)_2C_6H_5$	16	A	−19.9	1.1×10^6	1.0×10^5	C	75.02	74.79	155	1.610
									H	6.12	6.27		
									N	3.43	3.21		
									Cl	0	0.23		
38	0.5 $NaOC_6H_4CH_2C_6H_5$	8	3.5 $NaOC_6H_4C(CH_3)_2C_6H_5$	16	A	−19.8	2.1×10^6	9.8×10^4	C	76.84	76.84		1.619
									H	6.18	6.36		
									N	3.09	2.96		
									Cl	0	0.14		

Table I (Continued)

	reactant stoichiometry, equiv/P=N					^{31}P NMR			elemental anal., %				
compd	nucleophile 1	time, h	nucleophile 2	time, h	purif method[b]	shift, ppm[c]	M_w	M_n	element	calcd	found	T_1, °C	n_{632nm}
39	0.5 $NaOC_6H_4C_6H_5$-*m*	8	3.5 $NaOC_6H_4C(CH_3)_2C_6H_5$	16	A	−19.8	3.0 × 10^6	1.7 × 10^5	C	76.68	77.72		1.627
									H	6.05	6.50		
									N	3.14	3.17		
									Cl	0	0.14		
40	1.5 $NaOC_6H_4CH_2C_6H_5$	8	2.5 $NaOC_6H_4C_6H_5$-*p*	16	A	−19.4	9.8 × 10^5	9.9 × 10^4	C	76.68	76.71		1.630
									H	6.05	6.24		
									N	3.14	2.94		
									Cl	0	0.08		
41	1.0 $NaOC_6H_4C_6H_5$-*p*	8	3.0 $NaOC_6H_4CH_3$-*p*	16	A	−18.9	1.9 × 10^6	9.9 × 10^4	C	71.02	70.31	108	
									H	4.98	4.97		
									N	4.36	4.65		
									Cl	0	0.26		
42	2.0 $NaOC_6H_4C_6H_5$-*p*	24[e]	2.0 $NaOC_6H_4CH_3$-*p*	24	A	−18.8	2.1 × 10^6	9.3 × 10^4	C	71.02	71.28	131	
									H	4.98	4.91		
									N	4.36	4.15		
									Cl	0	0.12		

[a] Compounds **43–45** have been prepared prevously. See ref 10. [b] See Experimental Section. [c] THF/$CDCl_3$. [d] Complete chlorine replacement was not achieved. Characterization data suggest that the composition of **7** is $[NP(OC_6H_4CH_3\text{-}o)_{1.70}Cl_{0.30}]_n$ and that of **8** is $[NP(OC_6H_4C_6H_5\text{-}o)_{1.52}Cl_{0.48}]_n$. [e] Gel permeation chromatography was not attempted on this polymer because of the large number of residual P–Cl units.

Possibility of Side Group Exchange in the Substitution Reaction. Organophosphazenes are known to undergo side group exchange reactions.[17,18] These processes could affect the physical properties of the final polymers. The available evidence suggests that, under the conditions used here, aryloxy groups attached to the phosphazene skeleton were not displaced by different aryl oxide ions during the sequential preparation of mixed-substituent polyphosphazenes. The microanalytical data for polymers **9–42** and the integrated ^{1}H NMR spectra of polymers **41** and **42** showed that the products had the composition expected based on the ratios of the reactants used in the substitution reaction.

Spectroscopic Characterization. The polymers were studied by a combination of ^{31}P and ^{1}H NMR spectroscopy, gel permeation chromatography, differential scanning calorimetry, and elemental microanalysis. The characterization data are listed in Table I. The structural examination of polymers **5**, **9**, and **34** will be discussed as representative examples of each class of polymer prepared.

The ^{31}P NMR spectrum of polymer **5** in THF/$CDCl_3$ consisted of a singlet centered at −20.7 ppm, indicative of a high degree of chlorine replacement. Gel permeation chromatography suggested that the polymer had a high molecular weight, with a weight-average molecular weight of 1.5 × 10^6 and the broad, bimodal molecular weight distribution typical of polyphosphazenes ($M_w/M_n = 15$). The glass transition temperature of this polymer was 37 °C.

The mixed-substituent polymer **9** yielded a singlet ^{31}P NMR spectrum at −19.6 ppm, which is typical of aryloxy-substituted polyphosphazenes. Even though three different phosphorus environments are probably present, the chemical shift differences are insignificant, making line broadening negligible. The ^{1}H NMR spectrum of **9** showed only aromatic protons, and integration of the peaks did not provide information about the level of incorporation of the different side groups. However, the microanalytical data are consistent with the structure shown in Table I. Polymer **9** had a GPC weight-average molecular weight of 1.5 × 10^6. This polymer had a glass transition temperature of 43 °C.

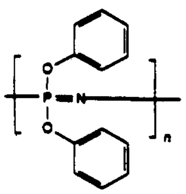
The ^{31}P NMR spectrum of polymer **34** consisted of a singlet at −20.2 ppm, and the integrated ^{1}H NMR spectrum suggested that the side groups are present in a 1:3 ratio. The elemental microanalysis was also consistent with that structure. Gel permeation chromatography suggested that the weight-average molecular weight was 1.4 × 10^6, with a broad molecular weight distribution ($M_w/M_n = 12$). Polymer **34** had a glass transition temperature of 25 °C.

Relationship between Side Group Structure and Thermal Transition Behavior. In polyphosphazenes, as in other polymer systems, the flexibility of the skeleton defines the maximum materials flexibility that can be expected. For example, skeletal systems that are comprised of bonds that have a high torsional barrier cannot be expected to generate materials flexibility or low-temperature elasticity. The polyphosphazene skeleton (together with the polysiloxane backbone) has one of the most flexible backbones known. This undoubtedly explains why $[NPCl_2]_n$ has a T_g at −65 °C[19] and $[NPF_2]_n$ has a T_g at −96 °C.[20] The low inherent barrier to backbone torsional motions, coupled with the small size of fluorine or chlorine as side groups, is presumably responsible for this behavior.[21]

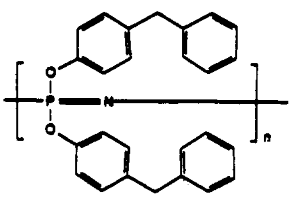
However, superimposed on the character of the backbone is the influence by side groups.[22] This influence is minimal if the side group itself is highly flexible; for example, the T_g of $[NP(O(CH_2)_3CH_3)_2]_n$ is −105 °C. However, rigid, bulky side groups raise the glass transition temperature markedly.[22] $[NP(OC_6H_5)_2]_n$ (**1**) has a T_g of −6 °C, a value that is 90 °C higher than that of $[NPF_2]_n$. In this work and in earlier studies,[8,9] it was found that larger aromatic side groups cause the T_g of the polymer to increase further, although not in a completely predictable manner. Moreover, the simple relationships that often hold for organic copolymers[23] seem not to apply to mixed-substituent polyphosphazenes.

Any attempt to provide even a qualitative explanation of the way in which T_g values vary with side group structure must take into account a complex group of interconnected influences. We prefer to view these phenomena in terms of three types of contributions. First, side groups can restrict the torsional motions of the skeletal bonds by *intra*molecular interactions, usually with other side groups but sometimes with skeletal atoms. The interactions may involve van der Waals- or polar-type forces. Second, *inter*molecular steric or polar interactions between the side groups on neighboring polymer molecules may "anchor" side chains to each other and limit the conformational freedom of both participating molecules. An extreme consequence would be the stacking of side groups from neighboring chains,[24,25] side chain liquid crystallinity, or the generation of conventional microcrystallinity. Fi-

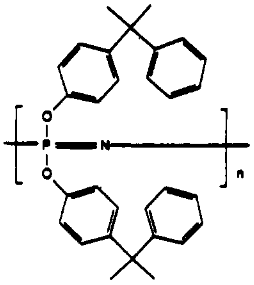
Chart I



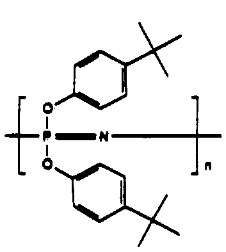
T_g = -6°C
1



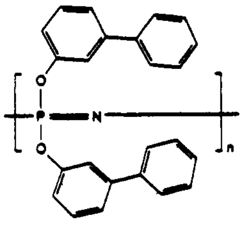
T_g = 6°C
2



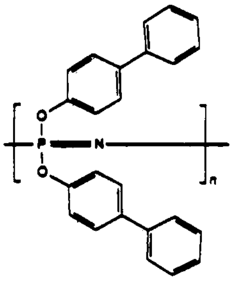
T_g = 39°C
3



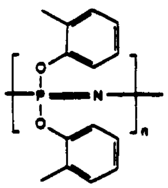
T_g = 50°C
4



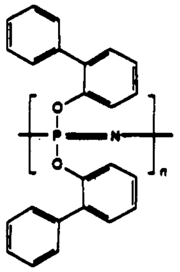
T_g = 37°C
5



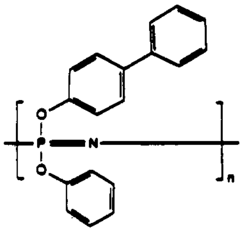
T_g = 93°C
6



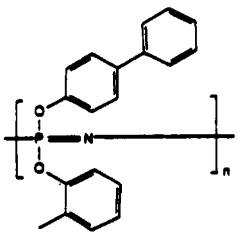
T_g = 13°C
7



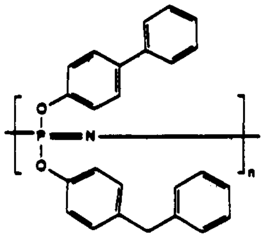
T_g = 67°C
8



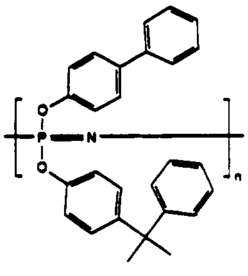
T_g = 43°C
9



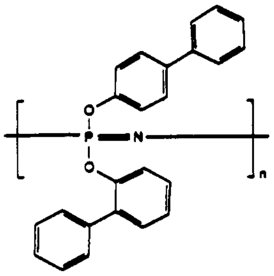
T_g = 52°C
10



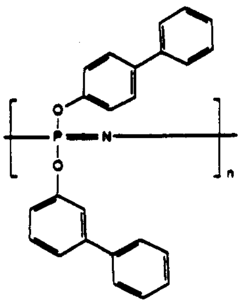
T_g = 34°C
11



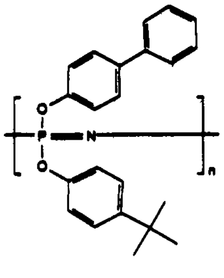
T_g = 51°C
12



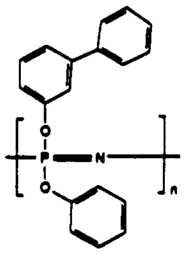
T_g = 57°C
13



T_g = 56°C
14



T_g = 57°C
15



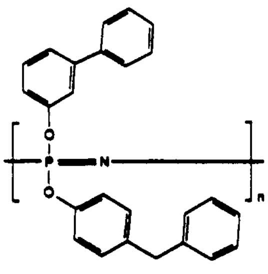
T_g = 16°C
16

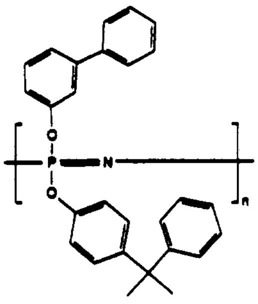
nally, molecular asymmetry in the disposition of side groups along the chain, especially when side groups are present with markedly different dimensions, or when highly flexible side groups are present, will generate free volume in the solid. This would facilitate molecular reorientation and lead to materials flexibility. The first effect is a purely molecular phenomenon. The second two are solid-state effects.

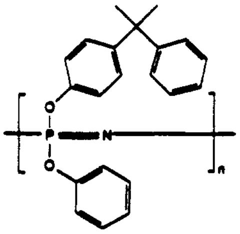
The compounds synthesized in this present work allow an insight into the relative importance of these three factors in aryloxy-substituted phosphazenes. Some conclusions will be drawn first from the behavior of the single-substituent polymers 1–8. The effect of introducing a second substituent will then be considered.

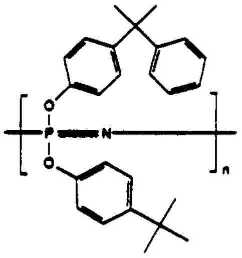
For the single-substituent polymers 1–6 and two related polymers described in the literature,[10] the glass transition

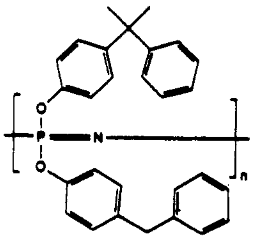
Chart II

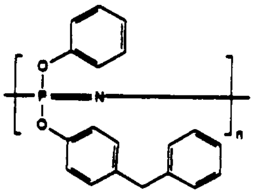

T_g = 19°C
17

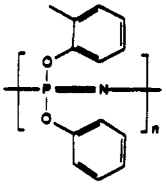

T_g = 27°C
18

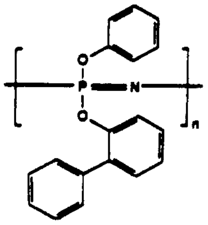

T_g = 19°C
19

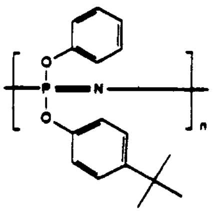

T_g = 39°C
20

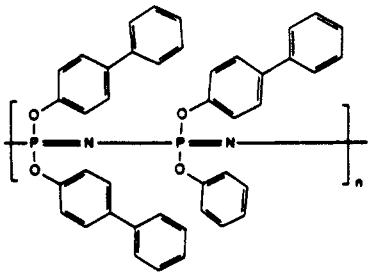

T_g = 9°C
21

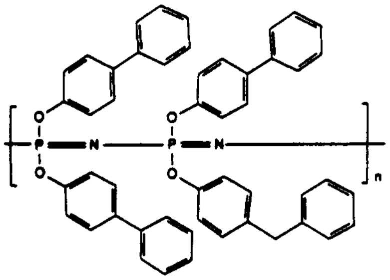

T_g = 7°C
22

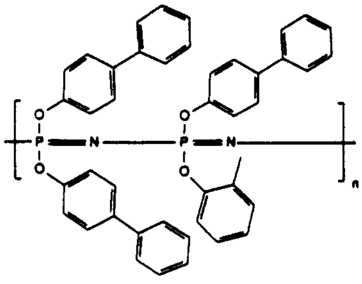

T_g = 11°C
23

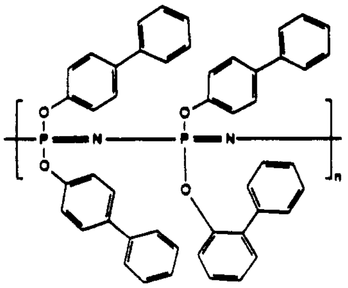

T_g = 40°C
24

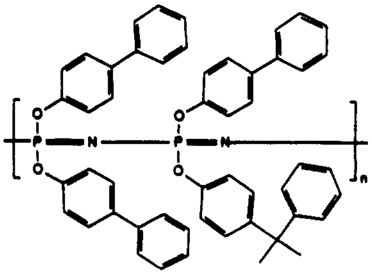

T_g = 17°C
25


T_g = 63°C
26


T_g = 60°C
27


T_g = 65°C
28

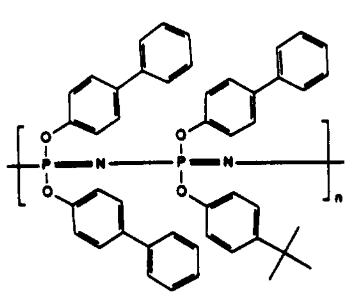

T_g = 59°C
29

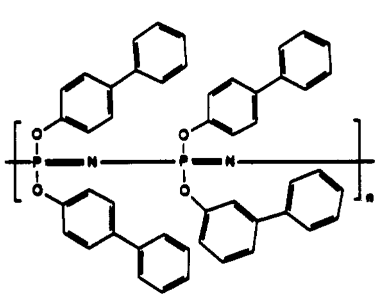

T_g = 59°C
30

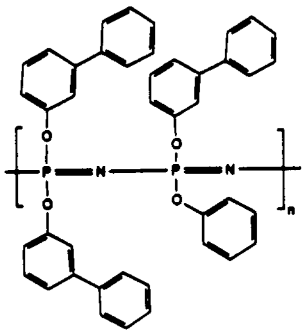
temperature rises with side group changes in the following order: $OC_6H_4C_2H_5$-*p* (**44**) (−18 °C)[10] < OC_6H_5 (**1**) (−6 °C) < $OC_6H_4CH_3$-*p* (**43**) (0 °C)[10] < $OC_6H_4CH_2C_6H_5$ (**2**) (6 °C)[26] < $OC_6H_4C_6H_5$-*m* (**5**) (37 °C) ≈ $OC_6H_4C(CH_3)_2C_6H_5$ (**3**) (39 °C) < $OC_6H_4C(CH_3)_3$ (**4**) (50 °C)[9] < $OC_6H_4C_6H_5$-*p* (**6**) 93 °C). As a general trend, side groups that contained only one aryl ring (**1**, **43**, **44**) generated lower T_g values than those that contained two aryl units (**2**, **3**, **5**, **6**). This is not surprising since two of the influences mentioned above would be greater for the bulkier side groups in **2**, **3**, **5**, and **6** than for the side groups that contain only one aryl ring.

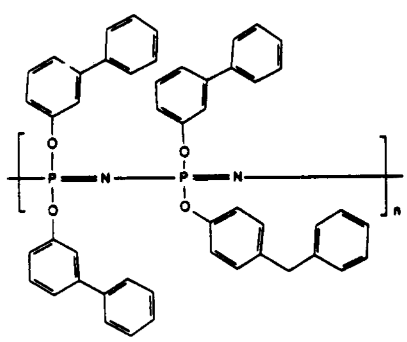
However, the presence of an angular structure within each double-ring side group has a distinct influence on the properties (see, for example, Figure 2). The T_g value of 93 °C measured for $[NP(OC_6H_4C_6H_5\text{-}p)_2]_n$ (**6**) is the highest yet found for an (aryloxy)phosphazene polymer.[27] Yet the

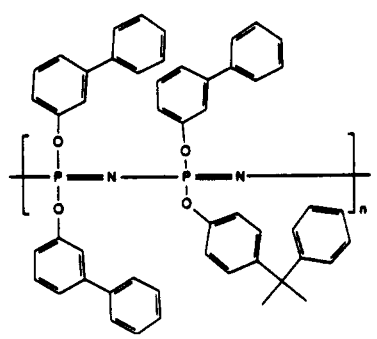
Chart III

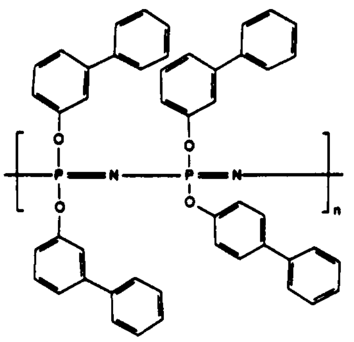

T_g = 68°C
31

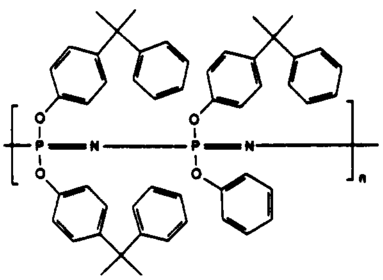

T_g = 64°C
32

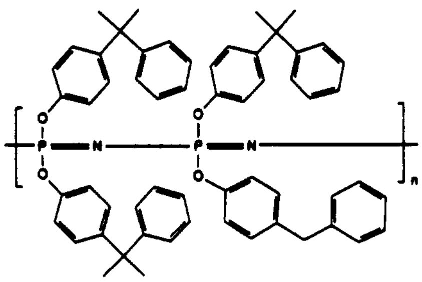

T_g = 27°C
33

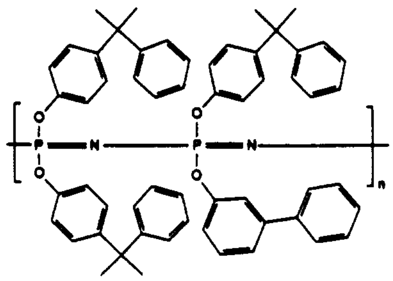

T_g = 25°C
34

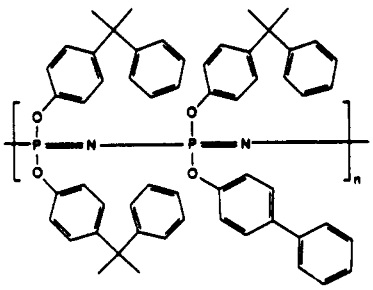

T_g = 32°C
35

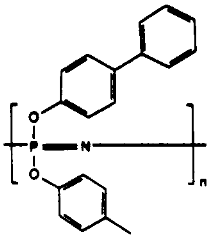

T_g = 38°C
36

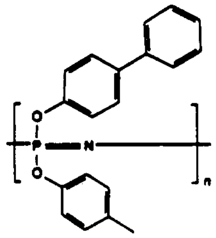

T_g = 18°C
37


T_g = 22°C
38


T_g = 33°C
39


T_g = 29°C
40


T_g = 42°C
41


T_g = 46°C
42

meta orientation of the two rings in **5** lowers the T_g by 56 °C. Similarly, the presence of an intervening methylene unit in **2** lowers the T_g by 87 °C compared to **6**, and a connecting $C(CH_3)_2$ unit in **3** lowers the transition by 54 °C. We interpret these effects in terms of a high efficiency of intra- and intermolecular packing for the linear, rigid aryl units in **6**, contrasted with the ability of the angular side groups in **2**, **3**, and perhaps **5** to undergo side chain "avoidance" motions as skeletal conformational changes occur.[28] The shape of the side groups in **2**, **3**, and **5** would also be expected to generate more free volume and hence permit more extensive molecular movement than would be possible in the case of **6**. It should be noted also that all the polymers mentioned above, except **5**, showed T_1 or T_m transitions, and this is a further indication of strong intermolecular interactions.

The seemingly anomolous high T_g values of polymers such as **4** that contain *p*-*tert*-butylphenoxy side groups can be understood in terms of the bulk, symmetry, and rigidity of the *tert*-butyl unit. The T_g of **4** is 50 °C higher than the value reported for its *p*-methylphenoxy counterpart.

The mixed substituent polymers provide a further insight into the influence of side group structure on physical properties. First, consider the series of polymers **9–15** in which each skeletal phosphorus bears one *p*-phenylphenoxy side group and one other aryloxy unit. All the T_g values in this series fall within a fairly narrow range of 34–57 °C in spite of the broad variations in cosubstituent dimensions. In fact, if species **11** is excluded (with its bulky but flexible cosubstituent group), the range is only from 43 to 57 °C. We interpret this to mean that the rigidity of the polymer and the intermolecular interactions are dominated by the one *p*-phenylphenoxy group per repeating unit. This side group is so bulky, rigid, and symmetrical that it overwhelms all other influences. Of these polymers, only **14** showed detectable crystallinity.

As the ratio of *p*-phenylphenoxy side groups increases from 50% to 75% of the total, the effects mentioned above become even more obvious. The overwhelming influence of the *p*-phenylphenoxy unit becomes manifest in the very narrow range of T_g values from 59 to 68 °C found for polymers **26–27** and **29–32**. Within this series, changes in the minor cosubstituent from $OC_6H_4C(CH_3)_2C_6H_5$ (**30**), through $OC_6H_4C_6H_5$-*o* (**29**), $OC_6H_4CH_2C_6H_5$ (**27**), and OC_6H_5 (**26**), to $OC_6H_4C_6H_5$-*m* (**32**) raise the T_g by only 5 °C, a value that is close to the experimental error of the measurement. Only the *tert*-butylphenoxy group (in **31**) appears to have a significant influence as a cosubstituent. Thus, it appears that small or more flexible side groups buried within a matrix of *p*-phenylphenoxy units have little influence on the glass transition temperature. However, the second substituent, even in 25% concentration, may be sufficient to eliminate crystallinity.

Polymers in which 75% of the side groups are *m*-phenylphenoxy units (**33–36**) are influenced hardly at all by the shape and dimensions of the minor cosubstituent. Polymers **33–36** were all noncrystalline and had T_g values within the range 27–38 °C. The single-substituent polymer (**5**) (T_g = 37 °C) also falls within the same range. The lower T_g values within this series are associated with the presence of minor cosubstituents such as OC_6H_5 or $OC_6H_4CH_2C_6H_5$, which probably generate free volume within the solid-state matrix.

Similarly, the series of polymers **37–40** in which 75% of the side groups are $OC_6H_4C(CH_3)_2C_6H_5$ units have T_g values that mainly reflect the size and shape characteristics of the majority side group. The crystalline single-substituent polymer (**3**) has a T_g of 39 °C. Replacement of 25% of these side groups by $OC_6H_4C_6H_5$-*m* units (**39**) lowers the T_g by only 6 °C. The $OC_6H_4C_6H_5$-*p* group lowers the T_g by 10 °C, the $OC_6H_4CH_2C_6H_5$ unit by 17 °C, and the OC_6H_5 group by 21 °C. This last polymer is crystalline.

In earlier papers, we discussed the steric influence of small side groups in terms of their influence on the torsional freedom of a polyphosphazene backbone.[21,22] However, it is clear from the present results that this simple intramolecular interpretation is no longer sufficient when the side groups are bulky aryloxy units. Yeung, Frank, and Singler, using excimer fluorescence spectroscopy, found that the aryl rings of **1** and **43** were stacked at temperatures between −80 and 150 °C.[29] The formation of liquid-crystalline-type stacks of side groups[30,31] will drastically affect the reorientational freedom of the polymer chain. Under these circumstances, the solid-state properties appear to be dominated by strong side group interactions and by free volume effects. In this sense, the rotational freedom of a side group becomes as important as or more important than the conformational freedom of the backbone.

Optical Properties. a. UV–Visible and Infrared Spectroscopy of Mixed-Substituent Poly[(aryloxy)phosphazenes]. The optical absorption characteristics of polymers **1–40** were examined by UV–vis spectroscopy in solution and by infrared spectroscopy in the solid state. No absorbances were detected in the near-UV to visible region between 280 and 800 nm. The absorbances between 245 and 280 nm showed little fine structure and are characteristic of the aromatic side groups. The phosphazene P–N skeleton absorbs at wavelengths shorter than 180 nm[1]. No evidence was found for extended conjugation in any of the aromatic side groups.

The infrared spectra of **1–40** showed absorbances expected for poly[(aryloxy)phosphazenes]. No strong absorptions were found between the C—H stretch region (3100–2800 cm^{-1}) and the C═C stretch region (1600 cm^{-1}). Absorbances for the P═N skeleton (1250–1200 cm^{-1}) were detected.

b. Refractive Index Measurements. The refractive indices of polymers **1–40** were measured at λ = 632 nm by using a modified critical angle method[32] (Figure 3). Films of the polymers were cast on one surface of a heavy flint glass equilateral prism, which was mounted on a calibrated rotational stage. The films were illuminated by a HeNe laser, and the prism was rotated so that the angle the incident beam made with the polymer–glass interface passed through the critical angle. The apparatus was calibrated with poly(methyl methacrylate) and polycarbonate. Good agreement with literature values for these polymers was obtained. However, no readily available samples of polymers with refractive indices in the range found for these polyphosphazenes could be obtained for comparison. The refractive indices are shown in Table I. The values vary from 1.561 (**4**) to 1.686 (**32**). In general, the polymers with phenylphenoxy substituents only had the highest refractive indices, values that are among the highest measured for synthetic high polymers. This suggests that the polymers described here may be particularly useful as lenses or waveguides.

Experimental Section

Equipment and Materials. Hexachlorocyclotriphosphazene was provided by Ethyl Corp. Poly(dichlorophosphazene) was prepared according to a previously published procedure.[1] Dioxane was distilled from sodium benzophenone ketyl under an atmosphere of dry argon before use. Tetra-*n*-butylammonium bromide was dried by azeotropic removal of water from a benzene solution, followed by recrystallization from benzene and drying under high vacuum. Phenols were purified by distillation under reduced pressure or sublimation, as appropriate. Manipulation of reagents before the substitution reaction was carred out by using standard Schlenk and drybox techniques. Substitution reactions were performed with the use of a Buchi BEP280 stirred autoclave equipped with an inert gas manifold and a Lauda KS-6 circulator. All transfers of reagents into the autoclave were performed under an atmosphere of dry argon by using modified Schlenk techniques. ^{31}P and ^{1}H NMR spectra were recorded on a JEOL FX90Q spectrometer operated at 36.23 and 89.55 MHz, respectively. Molecular weights were determined by using a Hewlett-Packard HP1090 gel permeation chromatograph equipped with a refractive index detector. The samples were eluted with a 0.1% by weight solution of tetra-*n*-butylammonium bromide in tetrahydrofuran, through Polymer Laboratories PL Gel columns. Approximate molecular weight calibrations were performed by using narrow molecular weight distribution polystyrene standards. Poly[bis-

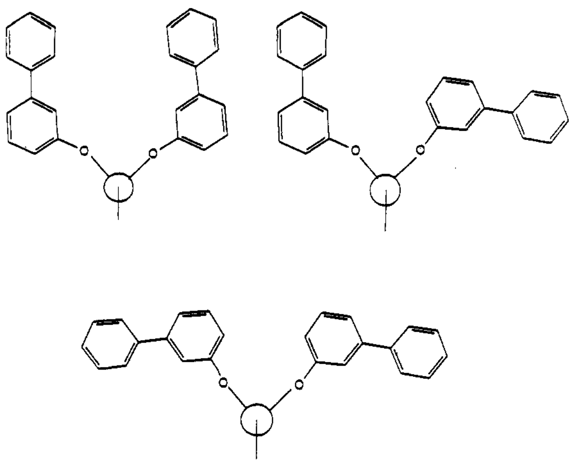


Figure 2. Projection down axis of P–N bond illustrating possible side group rotational isomers for a $[NP(OC_6H_4C_6H_5\text{-}m)_2]$ repeat unit.

Figure 3. Apparatus used for refractive index measurements.[36] HeNe laser (A) illuminates polymer film (C)–prism (B) interface. Rotation of prism until total internal reflection occurred allowed calculation of critical angle θ_c.

(trifluoroethoxy)phosphazene] samples, provided by Drs. R. Singler and G. Hagnauer of the U.S. Army Materials Technology Laboratories, were used as controls for the GPC work. These fractionated samples were of known molecular weights as determined by GPC measurements and light scattering. Good agreement between our GPC data and the standards was obtained. UV–vis spectra of the polymers as solutions in tetrahydrofuran were obtained with a Hewlett-Packard 8450A spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1710 FTIR instrument. Thin films of the polymers were cast on NaCl plates. The refractive indices were measured by using the apparatus described in the text. The poly(methyl methacrylate) and polycarbonate calibration standards were obtained from Aldrich. Prisms (Spindler & Hoyer) were 30 mm × 30 mm equilateral heavy flint glass, with $n_{632} = 1.723\,09$. Elemental microanalyses were obtained by Galbraith Laboratories, Knoxville, TN.

Synthesis of Poly[(aryloxy)phosphazenes]. Poly[(aryloxy)phosphazenes] 1–40 were synthesized in a similar manner but were purified differently depending on the solubility of the product polymer in various solvents at room temperature. The reactant stoichiometries, reaction times, and method of purification for each sample are listed in Table I.

General Preparation of Soluble Polymers (Purification Method A). Poly(dichlorophosphazene) (5.00 g, 43.2 mmol) was dissolved in dioxane (250 mL). Solutions of the nucleophiles were prepared by the slow addition of a dioxane solution (50 mL) of the phenol (10 mol % excess) to a stirred suspension of sodium metal and tetra-*n*-butylammonium bromide (0.50 g, 1.5 mmol) in dioxane (100 mL). The mixtures were heated to reflux until the sodium had dissolved. The poly(dichlorophosphazene) solution was then transferred to the autoclave by syringe; the solution containing nucleophile A was transferred to the autoclave, and the mixture was stirred at 150 °C for the time indicated in Table I. The mixture was then cooled to room temperature, and the solution of nucleophile B was transferred to the autoclave by syringe. The mixture was reheated to 150 °C for the times listed in Table I and was allowed to cool to room temperature. The contents were then removed by using a cannula. The reaction mixture was concentrated to a volume of approximately 150 mL by rotary evaporation. The product was then isolated by precipitation from the concentrated reaction solution into distilled water. The polymer was purified further by successive precipitations from tetrahydrofuran into distilled water, until no precipitate of silver chloride was detected after the addition of several drops of aqueous silver nitrate to the precipitant solution. The product was further purified by Soxhlet extraction with methanol for 72 h, followed by Soxhlet extraction with hexanes for 72 h. The polymer was dried under high vacuum for 48 h before characterization.

General Preparation of Insoluble Polymers (Purification Method B). Those polymers that were insoluble in the reaction solvents at room temperature were prepared by following the procedure outlined above, with the following modifications. After completion of the substitution reaction at 150 °C, the reaction mixture was cooled to room temperature. The product precipitated from the cooled mixture and was then collected by filtration. The product was washed with large quantities of distilled water to remove occluded salts and was purified by Soxhlet extraction with methanol for 96 h and hexanes for 96 h. The product was dried under high vacuum for 48 h before characterization.

Acknowledgment. This work was supported by the Office of Naval Research. We thank Dr. C. Kolich of Ethyl Corp. for his suggestions regarding the synthesis technique. We also thank Dr. C.-H. Wang of the University of Utah for his suggestions regarding the refractive index measurements. A more detailed assessment of the optical properties is being made in his laboratory.

References and Notes

(1) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216–4218.
(2) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709–1715.
(3) *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; ACS Symposium Series 360, American Chemical Society: Washington, D.C., 1988; pp 250–313.
(4) Allcock, H. R. *Chem. Eng. News* **1985**, *63*(11), 22–36.
(5) Singler, R. E.; Schneider, N. S.; Hagnauer, G. L. *Polym. Eng. Sci.* **1975**, *15*(5), 321–338.
(6) Rose, S. H. *J. Polym. Sci.* (*B*) **1968**, *6*, 837–839.
(7) Tate, D. P. *J. Polym. Sci., Polym. Symp.* **1974**, *48*, 33–45.
(8) Beres, J. J.; Schneider, N. S.; Desper, C. R.; Singler, R. E. *Macromolecules* **1979**, *12*, 566–575.
(9) Dieck, R. L.; Goldfarb, L. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 361–369.
(10) Singler, R. E.; Hagnauer, G. L.; Schneider, N. S.; Laliberte, B. R.; Sacher, R. E.; Matton, R. W. *J. Polym. Sci., Chem. Ed.* **1974**, *12*, 433–444.
(11) Allcock, H. R.; Connolly, M. S.; Sisko, J. T.; Al-Shali, S. *Macromolecules* **1988**, *21*, 323–334.
(12) Allen, G. W.; Lewis, C. J.; Todd, S. M. *Polymer* **1970**, *11*, 44–60.
(13) Allcock, H. R.; Cook, W. J.; Mack, D. P. *Inorg. Chem.* **1972**, *11*, 2584–2590.
(14) Futamura, S.; Valaitis, J. K.; Lucas, K. R.; Fieldhouse, J. W.; Cheng, T. C.; Tate, D. P. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 767–777.
(15) Allcock, H. R.; Moore, G. Y.; Cook, W. J. *Macromolecules* **1974**, *7*, 571–575.
(16) Allcock, H. R. *Acc. Chem. Res.* **1979**, *12*, 351–358.
(17) Allcock, H. R.; Smeltz, L. A. *J. Am. Chem. Soc.* **1976**, *98*, 4143–4149.
(18) Ferrar, W. T.; Marshall, A. S.; Whitefield, J. *Macromolecules* **1987**, *20*, 317–322.
(19) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709–1715.
(20) Allcock, H. R.; Kugel, R. L.; Stroh, E. G. *Inorg. Chem.* **1972**, *11*, 1120.
(21) Allcock, H. R.; Allen, R. W.; Meister, J. J. *Macromolecules* **1976**, *9*, 950–955.
(22) Allen, R. W.; Allcock, H. R. *Macromolecules* **1976**, *9*, 956–960.
(23) Wunderlich, B. In *Thermal Characterization of Polymeric Materials*; Turi, E. A., Ed.; Academic Press: New York, 1981.
(24) Shaefer, J.; Stejskal, E. O.; Percahk, D.; Skolnick, J.; Yaris, R. *Macromolecules* **1985**, *18*, 368–373.
(25) Boyer, R. F. *J. Macromol. Sci. Phys.* **1976**, *B12(2)*, 253–301.
(26) Desper, C. R.; Schneider, N. S.; Higginbotham, E. *J. Polym. Sci., Polym. Lett. Ed.* **1977**, *15*, 457–461.
(27) Previous reports (Allen, G.; Lewis, C. J.; Todd, S. M. *Polymer* **1970**, *11*, 44–60. Rieck, U.; Magill, J. H. *Polym. Commun.* **1987**, *28*, 107–108) place the T_g of 6 at 43 and 73 °C, respectively. The discrepancies might be the result of cyclic oligom-

ers present in the samples used in the earlier investigations.
(28) Side group rotamers have been identified from the crystal structure of $[NP(OC_6H_4\text{–}CH_3\text{-}o)_2]_4$. Allcock, H. R.; Birdsall, W. J.; Al-Shali, S.; Dembek, A. A.; Parvez, M.; Mang, M. N., manuscript in preparation.
(29) Yeung, A. S.; Frank, C. W.; Singler, R. E. *Polym. Prepr.* 1986, *27(2),* 214–215.
(30) Kim, C.; Allcock, H. R. *Macromolecules* 1987, *20,* 1727–1728.
(31) Singler, R. E.; Willingham, R. A.; Lenz, R. W.; Furukawa, A.; Finkelmann, H. *Macromolecules* 1987, *20,* 1728–1729.
(32) *Optical Properties of Polymers*; Meeten, G. H., Ed.; Elsevier: New York, 1986.

Solid-State NMR Studies on the Molecular Structure and Dynamics of Poly(diethylsiloxane) Polymorphs†

Gerhard Kögler, Alfred Hasenhindl, and Martin Möller*

Institut für Makromolekulare Chemie, Hermann-Staudinger-Haus, Stefan Meier Strasse 31, D-7800 Freiburg, Federal Republic of Germany. *Received January 12, 1989; Revised Manuscript Received April 5, 1989*

ABSTRACT: Molecular structure and segmental motion of different crystalline modifications of high molecular weight poly(diethylsiloxane) have been investigated by variable-temperature MAS ^{13}C and ^{29}Si NMR experiments. The observations were discussed in correlation to thermodynamic data. Cooperative changes of the motional state of the molecular backbone and the side chains are observed at the solid transitions detected by differential scanning calorimetry (DSC) experiments. Structural differences of the α- and β-polymorph are indicated. Annealing experiments allow determination of the β-modification as the equilibrium modification. The stepwise loss of long-range order at the onset of different motional processes, which results in the formation of a "liquid crystal" type phase of these highly flexible long chain molecules, is discussed with respect to the amphiphilic constitution of poly(diethylsiloxane) having an inorganic backbone substituted by organic side groups.

Introduction

In a recent review we discussed experimental data and general characteristics of the mesomorphic phases (i.e., neither fully ordered like a rigid crystal nor without long-range correlation in the molecular packing like an amorphous melt or glass) of highly flexible chain molecules.[1] Because of the lack of a rigid, nonspheric mesogenic subunit in the molecular structure and the fact that the molecules are typically packed in a hexagonal cylinder lattice, we distinguished those mesophases as a matter of principle from liquid crystals. Featuring the most important aspect of the partially disordered structure we described them according to B. Wunderlich as conformationally disordered crystals, i.e., Condis crystals.[2]

Solid-state NMR experiments showed the dynamic nature of the disordering. It has been possible to monitor the type and the changes of segmental motions within the mesomorphic phase and at the corresponding phase transitions for typical examples, i.e., poly(*trans*-1,4-butadiene),[3,4] cycloalkanes,[5–7] and *n*-alkanes.[8,9] The results may be summarized by describing those mesophases as a state where the molecules are arranged in regularly packed virtual cylinders, in which, however, they can move surprisingly unrestricted. Fast liquidlike conformational interconversion processes of carbon–carbon single bonds and, in addition, translational diffusion are characteristic. This reptational motion of chain molecules through the lamellae can explain the formation of extended chain crystals.[10,11]

In addition to the compounds mentioned above, which consist of linear nonpolar molecules, there is a second class of highly flexible molecules for which mesomorphic or even liquid crystalline behavior has been reported. These are various polyphosphazenes,[12–14] poly(di-*n*-alkylsilanes),[15,16] poly(diethylsiloxane),[17–27] and poly(dipropylsiloxane).[28,29]

Table I
Glass Transition, Melting, and Solid–Solid Transition Temperatures of Inorganic–Organic Hybrid Polymers

	transition temp, K			
polymer	T_g	T_d	T_m	ref
poly(di-*n*-hexylsilane)		315	>453	15, 16
poly(diethylsiloxane)	134	206/280 214/290	319	22
poly(dipropylsiloxane)	164	218/333	479	17, 24
poly[bis(trifluoroethoxy)-phosphazene]	207	363	515	13
poly[bis(*p*-chlorophenoxy)-phosphazene]	273	442	629	12

It is common to these compounds that they consist of an inorganic backbone that is symmetrically substituted by organic side chains. In general, the rotational barriers for bonds of second- and third-row elements are low. Thus in most cases, the molecular backbone and often also the side chains of polyphosphazenes, polysiloxanes, and polysilanes are highly flexible. This flexible character is demonstrated by the very low glass transition temperatures listed in Table I, together with the solid–solid transitions reported in the literature.

In the present paper we compare data from variable-temperature NMR and differential scanning calorimetry experiments in order to get a detailed picture of the conformations, conformational changes, and variations of the motional state of PDES at the different transitions.

Experimental Section

Polymerization. Hexaethylcyclotrisiloxane was obtained from Petrarch Chem. The monomer was used as supplied. The PDES sample was prepared by ring-opening polymerization of hexaethylcyclotrisiloxane in the presence of KOH as initiator.[30] High molecular weight fractions were seperated from oligomers by repeated precipitation in methanol.

For gel permeation chromatography, styragel columns with a length of 30 cm and a diameter of 7.7 mm were used. The particle size was 10 μm; the pore size was 10^6, 10^5, 10^4, and 10^3 Å. The temperature was 300 K and toluene was used as solvent. GPC

---

* To whom correspondence should be sent.

† Dedicated to Prof. Dr. P. Rempp at the occasion of his 60th birthday.

0024-9297/89/2222-4190$01.50/0 © 1989 American Chemical Society