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Registry No. (2IPN)(MAn) (alternating copolymer), 120743-21-7.

References and Notes

(1) (a) Delaire, J. A.; Rodgers, M. A. J.; Webber, S. E. *J. Phys. Chem.* **1984**, *88*, 6219. (b) Bai, F.; Chang, C.-H.; Webber, S. E. *Macromolecules* **1986**, *19*, 588, 2484, 2798. (c) Webber, S. E. *Macromolecules* **1986**, *19*, 1658. (d) Delaire, J. A.; Rodgers, M. A. J.; Webber, S. E. *Eur. Polym. J.* **1986**, *22*, 189. (e) Delaire, J. A.; Sanquer-Barrie, M.; Webber, S. E. *J. Phys. Chem.* **1988**, *92*, 1252. (f) Bai, F.; Webber, S. E. *Macromolecules* **1988**, *21*, 628. (g) Morishima, Y.; Kobayashi, T.; Nozakura, S.; Webber, S. E. *Macromolecules* **1987**, *20*, 807. (h) Bai, F.; Chang, C. H.; Webber, S. E. *ACS Symp. Ser.* **1988**, *358*, 384.

(2) (a) Morishima, Y.; Kobayashi, T.; Furui, T.; Nozakura, S. *Macromolecules* **1987**, *20*, 1707. (b) Morishima, Y.; Nozakura, S. *J. Polym. Sci., Polym. Symp.* **1986**, 741. (c) Morishima, Y.; Kobayashi, T.; Nozakura, S. *J. Phys. Chem.* **1985**, *89*, 4081.

(3) (a) Chu, D.-Y.; Thomas, J. K. *Macromolecules* **1984**, *17*, 2142. (b) Harrop, R.; Williams, P. A.; Thomas, J. K. *J. Chem. Soc., Chem. Commun.* **1985**, 280.

(4) (a) Guillet, J. E.; Wang, J.; Gu, L. *Macromolecules* **1986**, *19*, 2793. (b) Arora, K. S.; Turro, N. J. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 259.

(5) Fox, R. B.; Price, T. R.; Cozzens, R. F.; Echols, W. H. *Macromoles* **1974**, *7*, 937.

(6) Shirota, Y.; Yoshimura, M.; Matsumoto, A.; Mikawa, H. *Macromolecules* **1974**, *7*, 4.

(7) Wang, Y.-G.; Morawetz, H. *Makromol. Chem. Suppl.* **1975**, *1*, 283.

(8) Morishima, Y.; Lim, H. S.; Nozakura, S.; Sturtevant, J. L. *Macromolecules* **1989**, *22*, 1148.

(9) Fales, H. M.; Jaouni, T. M.; Babashak, J. F. *Anal. Chem.* **1973**, *45*, 2302. Adrnt, F. *Organic Syntheses Collec Vol 2*; Wiley: New York, 1969; p 165.

(10) Demas, J. N. *Excited State Lifetime Measurements*; Academic Press: New York, 1983.

(11) (a) Lappalainen, E. Koskimies, S. *J. Polym. Sci., Polym. Lett. Ed.* **1986**, *24*, 17. (b) Trivedi, B. C.; Culbertson, B. M. *Maleic Anhydride*; Plenum Press: New York, 1982; p 307. (c) Cowie, J. M. G. *Alternating Copolymers*; Plenum Press: New York, 1985. (d) Hill, D. J. T.; O'Donnell, J. M.; O'Sullivan, P. W. *Macromolecules* **1985**, *18*, 9.

(12) Hellensleben, M. L.; Lumme, I. *Die Makromol. Chem.* **1976**, *144*, 261.

(13) Elias, H. G. *Macromolecules*; Plenum Press: New York, 1984; p 764.

(14) Akimoto, A. Engel, D.; Schulz, R. C. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 673.

(15) (a) Webber, S. E.; Bai, F.; Chang, C.-H. *Macromolecules* **1986**, *19*, 588. (b) Fox, R. B.; Price, T. R.; Cozzens, R. F.; McDonald, J. R. *J. Chem. Phys.* **1972**, *57*, 534. (c) Reid, R. F.; Soutar, I. *J. Polym. Sci.* **1978**, *16*, 23.

(16) Ohno, N.; Okuda, T.; Nitta, K.; Sugai, S. *J. Polym. Sci.*, Polym. *Phys. Ed.* **1978**, *16*, 513.

(17) Barbieri, B. W.; Strauss, U. P. *Macromolecules* **1985**, *18*, 411.

(18) Somersall, A. C.; Guillet, J. E. *Macromolecules* **1973**, *6*, 218.

(19) (a) Turner, D. C.; Brand, Ludwig *Biochemistry* **1968**, *7*, 3381. (b) Wong, M.; Thomas, J. K.; Gratzel, M. *J. Am. Chem. Soc.* **1976**, *98*, 2291.

(20) Treloar, F. E. *Chem. Scr.* **1976**, *10*, 219.

(21) (a) Holden, D. A.; Guillet, J. E. *Macromolecules* **1980**, *13*, 289. (b) Ng, D.; Yoshiki, K.; Guillet, J. E. *Macromolecules* **1983**, *16*, 568. (c) Bai, F.; Chang, C.-H.; Webber, S. E. *Macromolecules* **1986**, *19*, 2484.

(22) Dean, K. R.; Webber, S. E. *J. Luminesc.*, in press.

(23) Fox, R. B.; Price, T. R.; Cozzens, R. F.; McDonald, J. R. *J. Chem. Phys.* **1972**, *57*, 534.

(24) Holden, D. A.; Kovarova, J.; Guillet, J. E.; Engel, D.; Rhein, T. H.; Schulz, R. C. *Eur. Polym. J.* **1983**, *19*, 1071.

(25) Tada, K.; Fueno, T.; Furukawa, J. *J. Polym. Sci., A-1* **1966**, *4*, 2987.

(26) Berlman, I. B. *Energy Transfer Parameters of Aromatic Molecules*; Academic: New York, 1973.

(27) The rate constant for energy migration is given by $k_{DD} = (1/\tau_D)(R_o/R_D)^6$ where τ_D is the singlet lifetime, R_o is the Forster radius, and R_D is the average chromophore separation. The number of hops is $n = 2k_{DD}\tau_D = 2(R_o/R_D)^6$ and the average excitation displacment is $L = (2nR_D)^{1/2}$.

(28) Alexandru, L.; Somersall, A. C. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2013.

(29) Morishima, Y.; Itoh, Y.; Nozakura, S. *Chem. Phys. Lett.* **1982**, *91*, 258.

Organosilylphosphazene Oligomers and Polymers: Synthesis via (Lithioaryloxy)phosphazenes[1]

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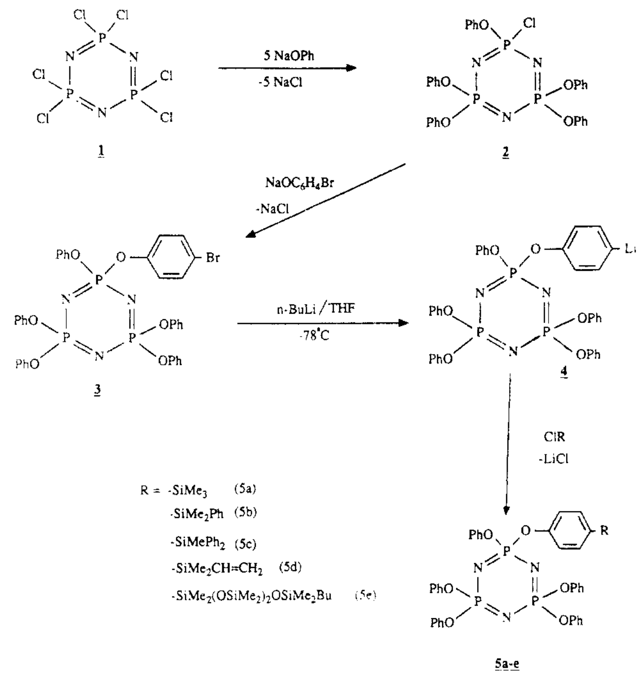
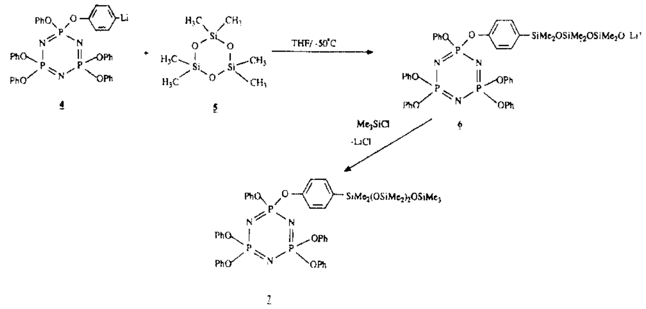
ABSTRACT: (Lithioaryloxy)phosphazenes have been used as reaction intermediates for the synthesis of phosphazenes that bear organosilicon side groups. The synthetic pathways were developed at two levels, first with the use of small-molecule cyclic phosphazenes as reaction models and second with high polymeric phosphazenes. The cyclic small molecule $N_3P_3(OPh)_5OC_6H_4Br$-*p* was first lithiated to $N_3P_3(OPh)_5OC_6H_4Li$-*p*, and this compound was allowed to react with a range of organochlorosilanes or with hexamethylcyclotrisiloxane to yield the species $N_3P_3(OPh)_5OC_6H_4R$-*p*, where R is $SiMe_3$, $SiMe_2Ph$, $SiMePh_2$, $SiMe_2CH{=}CH_2$, $SiMe_2(OSiMe_2)_2OSiMe_2Bu$, and $SiMe_2(OSiMe_2)_2OSiMe_3$. At the high polymer level, the macromolecule $[NP(OC_6H_4Br)_2]_n$ was subjected to partial lithiation followed by coupling to chlorosilanes or to ring-opening addition of $(OSiMe_2)_3$ to generate polymers with OC_6H_5 and OC_6H_4Br-*p* side groups as well as OC_6H_4R'-*p* units, where R′ is $SiMe_3$, $SiMe_2Ph$, $SiMePh_2$, or $SiMe_2(OSiMe_2)_2OSiMe_3$. Molecular structural characterization was obtained by NMR, IR, microanalytical, and mass spectrometric methods. Glass transition temperatures for the high polymers were in the range +45 to −68 °C.

The synthesis of new macromolecules derived from the inorganic elements provides opportunities for the extension of both polymer chemistry and inorganic chemistry into fields as diverse as solid-state science, electronics research,

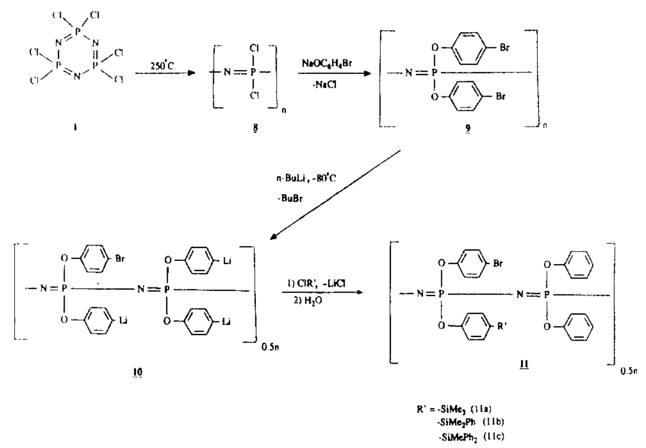
Scheme I



Scheme II



Scheme III



and biomedicine.[2,3] Organosilicon polymers and polyphosphazenes are playing a major role in these developments.

Poly(organosiloxanes), polysilanes, polysilazanes, and polyphosphazenes have different structure–property characteristics, some of which are mutually exclusive. However, the possibility of a *combination* of features that are characteristic of, for example, polysiloxanes and polyphosphazenes offers a synergism of solid-state and surface properties that is appealing for future research.

We have published several papers on the synthesis and properties of high molecular weight polyphosphazenes that bear organosilane or organosiloxane side groups.[4-9] The emphasis in previous work has been on the preparation of small-molecule cyclic phosphazenes with organosilicon side groups and on the subsequent ring-opening polymerization of these to linear high polymers.[5-9] Recently, Neilson, Wisian-Neilson, and their co-workers have reported a different approach in which poly((methylaryl)phosphazenes) were lithiated by metal–hydrogen exchange reactions, followed by coupling of the side groups to organosilicon units.[10] In earlier studies, we explored the preparation of (lithioaryloxy)phosphazenes and their coupling to chlorophosphines, gold halide, or chlorotin units.[11-14] Here we describe an extension of these reactions to the linkage of organosilicon units to (aryloxy)phosphazenes. In addition, a new type of reaction is reported in which a lithioaryloxy side group attached to a phosphazene induces the ring-opening linkage of a cyclosiloxane to the aryloxy unit. As in most of our previous studies,[15] the development of this chemistry was carried out at the small-molecule model system level first, before transposition of the optimized reaction conditions to the macromolecular systems.

Results and Discussion

Synthesis and Lithiation of $N_3P_3(OPh)_5(OC_6H_4Br\text{-}p)$ (3). Following the approach described in earlier work,[12] hexachlorocyclotriphosphazene (1) was converted first to $N_3P_3(OPh)_5(Cl)$ (2) which, in turn, was allowed to react with *p*-bromophenoxide ion to yield 3 (Scheme I). The metal–halogen exchange reaction with excess *n*-butyllithium in tetrahydrofuran (THF) at −78 °C then yielded 4. The lithio derivative is exceedingly sensitive to minute traces of water and must be used immediately to prevent its conversion to $[NP(OPh)_2]_3$.

Reactions of Cyclic Trimeric Lithioaryloxy Derivative 4 with Organosilicon Halides and Hexamethylcyclosiloxane. Rapid addition of $ClSiMe_3$, $ClSiMe_2Ph$, $ClSiMePh_2$, $ClSiMe_2CH{=}CH_2$, or $ClSiMe_2(OSiMe_2)_2OSiMe_2Cl$ to 4 yielded species **5a**–**e**. Compound **5e** was formed by reaction of the terminal chlorine atom with excess *n*-butyllithium present in the mixture. The reaction of 4 with hexamethylcyclotrisiloxane (5) (Scheme II) induced a siloxane ring-opening reaction to give **6**. Treatment of intermediate **6** with trimethylchlorosilane yielded the stable product **7**. The products detected by thin layer chromatography and ^{29}Si NMR experiments[24] were consistent with a mechanism that involved the ring opening of D_3 and/or linkage of chlorophosphazenes through linear oligomeric siloxane units. No evidence was obtained that long-chain siloxane side units were formed under the reaction conditions employed. In all the reactions that involved species 4, a delay of only 3 min in the addition of the chlorosilane or cyclosiloxane reduced the yield of 7 or its analogues by at least 20%. The decreased formation of 7 was accompanied by an increase in the formation of $[NP(OPh)_2]_3$.

Synthesis and Lithiation of High Polymeric $[NP(OC_6H_4Br\text{-}p)_2]_n$. The synthesis and lithiation of $[NP(OC_6H_4Br\text{-}p)_2]_n$ (**9**) has been investigated earlier by Allcock, Evans, and Fuller.[11,12] The first phase of the present polymer synthesis route followed the same reaction pathway. Hexachlorocyclotriphosphazene (**1**) was polymerized in the molten state to poly(dichlorophosphazene) (**8**). Treatment of this intermediate with *p*-bromophenoxide yielded poly[bis(*p*-bromophenoxy)phosphazene] (**9**) (Scheme III).

Treatment of **9** with excess of *n*-butyllithium brought about replacement of only 75–80% of the bromine atoms by lithium. This is presumably a consequence of the charge buildup on the side groups as lithiation occurs. Polymer **10** was then allowed to react with $ClSiMe_3$,

Table I
Characterization Data for $N_3P_3(OPh)_5OC_6H_4R$-*p*

R	compd	mp, °C	% yield	mass spectral data		elem anal.		
				found	calcd		found	calcd
Br	**3**	51–52	79	771	771	C	55.98	55.78
						H	3.78	3.89
						Br	10.34	9.74
$SiMe_3$	**5a**	oil	65	766	766	C	61.18	61.51
						H	5.00	5.11
						N	5.49	5.36
$SiMe_2Ph$	**5b**	oil	53	827	827	C	63.84	63.51
						H	4.87	4.76
						N	5.07	5.14
$SiMePh_2$	**5c**	oil	58	889	889	C	66.14	65.42
						H	4.76	4.77
						N	4.72	4.78
$SiMe_2CH{=}CH_2$	**5d**	oil	45	777	777	C	61.77	62.63
						H	4.92	5.27
						N	5.40	5.33
$SiMe_2(OSiMe_2)_2OSiMe_2Bu$	**5e**	oil	30	1026[a]	996	C	55.95	55.96
						H	6.18	5.95
						N	4.08	4.13
$SiMe_2(OSiMe_2)_2OSiMe_3$	**7**	oil	41	987	987	C	54.68	54.70
						H	5.72	5.39
						N	4.25	4.47

[a] Parent peak represents molecular ion peak minus two methyl groups. Other fragments included loss of $SiMe_2$, $OSiMe_2$, $SiMe_3$, and OC_6H_5 units.

Table II
^1H NMR and Infrared Data for $N_3P_3(OPh)_5(OC_6H_4R$-*p*$)$[a,b]

R (compd)	signal	^1H NMR (δ, $CDCl_3$)	IR,[c] cm^{-1}
Br (**3**)	PhO, OC_6H_4Br	7.3–6.9	3050, 1610
$SiMe_3$ (**5a**)	PhO	7.2–6.9 (m, 29 H)	3030, 1610
	$SiMe_3$	0.27 (s, 9 H)	1263, 850, 800
$SiMe_2Ph$ (**5b**)	PhO	7.1–6.9 (m, 29 H)	3050, 1610
	$SiMe_2$	0.30 (s, 6 H)	1260, 850, 800
	SiPh	6.8–6.6 (m, 5 H)	1115
$SiMePh_2$ (**5c**)	PhO	7.2–6.9 (m, 29 H)	3030, 1610
	SiMe	0.33 (s, 3 H)	1260, 855, 798
	$SiPh_2$	6.8–6.7 (m, 10 H)	1112
$SiMe_2(CH{=}CH_2)$ (**5d**)	PhO	7.2–6.9 (m, 29 H)	3030, 1610
	$SiMe_2$	0.33 (s, 6 H)	1260, 850, 800
	$CH{=}CH_2$	6.3–5.7 (m, 3 H)	
$SiMe_2(OSiMe_2)_2OSiMe_2Bu$ (**5e**)	PhO	7.2–6.9 (m, 29 H)	3030, 1610
	$SiMe_2$	0.7–0.4 (s, 24 H)	1264, 845, 800
	Bu	1.5–0.9 (m, 9 H)	2950
$SiMe_2(OSiMe_2)_2OSiMe_3$ (**7**)	PhO	7.2–6.9 (m, 29 H)	3030, 1610
	$SiMe_2$	0.4 (s, 6 H)	1254, 840, 800
	$(OSiMe_2)_2$-$OSiMe_3$	0.1 (s, 21 H)	1050, 1030

[a] All compounds gave a singlet in the ^{31}P NMR, δ (THF) = 8.6 ppm. [b] ^1H NMR taken in $CDCl_3$: chemical shifts are reported relative to external TMS = 0 ppm. A pulse delay of 10 s was used to avoid signal saturation and reduced integral intensities. [c] All compounds gave a P=N stretch in the 1230–1260-cm^{-1} region. Aliphatic C–H signals were observed in the 2940-cm^{-1} region.

$ClSiMe_2Ph$, and $ClSiMePh_2$ to yield species **11a–c**. The efficiency of the coupling reaction decreased with increases in the number of phenyl groups in the chlorosilane, presumably for steric reasons. Thus, when $ClSiMe_3$ was used as a reagent, 75% of the side groups bore $SiMe_3$ units, but with $ClSiMePh_2$, only 35–40% of the aryloxy units bore organosilicon units. The overall lithiation and coupling process was not nearly as reproducible as at the small-molecule level. Polymer **10** is insoluble in THF at -80 °C, presumably as a consequence of lithioaryloxy unit agglomeration and the increased ionic character of the polymer. Thus, the efficiency of lithiation may be impared by premature precipitation of **10**. The effectiveness of the coupling reaction may also be lowered by the heterophase character of the reaction at the lower temperatures, although the polymer always redissolved as the electrophile was added. As discussed for the model compound reaction, any delay in the coupling reaction increases the probability that the lithio units will react preferentially with traces of water rather than with the organosilicon electrophile. Thus, the final polymers contained bromo, hydrogen, and organosilicon units in the para positions of the aryloxy side groups. This is reflected in the analytical data reported in Table III. The physical properties of these polymers are discussed later.

It should be noted that attempts to carry our similar reactions with the use of $ClSiMe_2CH{=}CH_2$ or $ClSiMe_2(OSiMe_2)_2OSiMe_2Cl$ led invariably to cross-linking of the chains.

Structure Proof and Properties of Polymers 11a–c. Elemental microanalysis and ^1H NMR spectroscopy were used in tandem to estimate the ratios of the different side groups in polymers **11a–c**. The ^1H NMR spectrum was used to deduce the ratio of methyl to phenyl protons in the polymer, and this was used as a basis for the calculated elemental analysis values. A summary of these data, together with ^{13}C and ^{29}Si NMR chemical shifts for **13** and **7**, is presented in Tables III and IV.

The linkage of organosilicon units to the aryloxyphosphazene polymer brought about changes in the physical properties. The precursor polymer (**9**) is a microcrystalline material with a T_g at 15 °C and a T_m at 125 °C. Introduction of $SiMe_3$ and $SiMe_2Ph$ units eliminated the microcrystallinity and gave rise to elastomeric character. Replacement of bromine atoms in **9** by $SiMe_3$ units raised the T_g to 28 °C, whereas the introduction of

Table III
Characterization Data for $[NP(OC_6H_4R')_x(OC_6H_5)_y(OC_6H_4Br)_z]_n$

R′ (compd)	x	y^a	M_n	M_w	T_g, °C	elem anal.		
							calcd	found
Br (9)	2.00	0	6.0×10^4	2.0×10^6	15 (T_m = 125 °C)	C	39.05	40.26
						H	2.07	2.49
						N	3.60	3.72
						Cl	0	0.27
$SiMe_3$ (**11a**)	1.50	0.45	3.4×10^5	3.1×10^6	27	C	57.70	56.93
						H	6.46	6.34
						N	4.08	3.87
						Br	1.16	1.16
$SiMe_2Ph$ (**11b**)	1.20	0.72	1.1×10^5	2.5×10^6	6	C	63.00	62.51
						H	5.38	5.00
						N	3.28	3.16
						Br	5.05	4.39
$SiMePh_2$ (**11c**)	0.7	1.1	9.3×10^5	2.5×10^6	45	C	66.92	66.45
						H	4.78	4.67
						N	3.63	2.61
						Br	4.16	4.82
$(SiMe_2O)_3SiMe_3$ (**13**)	0.6	0.6	8.4×10^4	2.0×10^6	−67	C	43.15	43.81
						H	5.32	5.66
						N	2.81	2.71
						Br	12.80	12.82
						Si	14.85	14.71

[a] $x + y + z = 2$; values estimated from ^1H NMR integration.

Table IV
^1H NMR Data for $[NP(OC_6H_4R')_x(OC_6H_5)_y(OC_6H_4Br)_z]_n$

R′ (compd)	x	y	signal	^1H NMR (δ, $CDCl_3$)[a,c]	IR,[b] cm^{-1}	
$SiMe_3$ (**11a**)	1.50	0.45	Ph	7.1–6.9 (9 H)	aromatic	3030
			$SiMe_3$	0.17–0.15 (14 H)		1610
					SiMe	1264
						800
$SiMe_2Ph$ (**11b**)	1.20	0.72	Ph	7.1–6.9 (9 H)	aromatic	3030
			SiPh	6.8–6.6 (6 H)		1610
			SiMe	0.2 (7 H)	SiPh	1120
					SiMe	1260
						804
$SiMePh_2$ (**11c**)	0.7	1.1	Ph	7.1–6.9 (18 H)	aromatic	3030
			SiPh	6.9–6.7 (5 H)		1608
			SiMe	0.15 (16 H)	SiPh	1130
					SiMe	1260
						800
$(SiMe_2O)_3SiMe_3$[d] (**13**)	0.6	0.6	Ph	7.1–6.8 (17 H)	aromatic	3030
			SiMe	0.2 (81 H)		1608
					SiMe	1254
						800
					SiOSi	1080
						1010

[a] All line shapes were broad due to the solution viscosity. A pulse delay of at least 10 s was used to avoid signal saturation and reduced integral intensities. [b] All compounds exhibited P═N stretch in 1230–1260-cm^{-1} region. [c] All compounds gave a singlet in the ^{31}P NMR at δ ($CDCl_3$) = −21.4 ppm. [d] Polymer 13 had the idealized structure of $[NP(OC_6H_4R')_{0.6}(OC_6H_5)_{0.6}(OC_6H_4Br)_{0.8}]_n$. The high bromine content results from the inability to use a large excess of *n*-BuLi to generate 11.

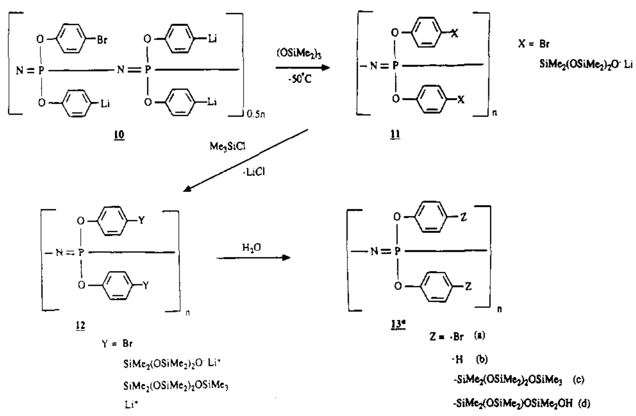
$SiMe_2Ph$ groups lowered the T_g slightly to 6 °C. The organosilicon groups also altered the solubility dramatically. Polymer **9** is insoluble in aliphatic hydrocarbons, but **11a** and **11b** are soluble in hexane. The increased steric size of the $SiMePh_2$ side group in **11c** results both in a stiffening of the polymer relative to **11a** and **11b** and a reduced solubility in aliphatic hydrocarbon solvents. (However, the T_g of 45 °C represents a marked decrease in chain torsional mobility, even though the substitution is at the outer fringe of the side-group structure.)

Polymers **11a–c** were film-forming materials when cast from concentrated solutions in THF. The films showed some optical birefringence under crossed polarizers, but no evidence of microcrystalline melting transitions could be detected from differential scanning calorimetry thermograms. All three materials as films could be cross-linked by exposure to γ radiation (1–3 Mrad), a process that probably involves free-radical cleavage of the aliphatic carbon–hydrogen bonds.[16,17] The three polymers showed hydrophobic surface character, with contact angle values for water droplets of 105° (**11a**), 103° (**11b**), and 101° (**11c**). These can be compared to the values of 101° for $[NP(OPh)_2]_n$ and 101° for $[NP(OC_6H_4Br)_2]_n$.

Ring-Opening Interaction of $(OSiMe_2)_3$ with (Lithioaryloxy)phosphazene Polymers. As discussed, at the phosphazene cyclic trimer model level, side groups that bear lithioaryloxy units cleave a cyclotrisiloxane skeleton to form a pendent linear siloxane appendage. With high polymeric phosphazenes, such a reaction offers prospects for graft polymerization and cross-linking, as well as for the introduction of linear oligosiloxane side units.

Although many examples have been reported of the ring-opening polymerization of $(OSiMe_2)_3$ under the influence of alkyllithium reagents,[18-20] such reactions normally take place at room temperature or above. However, (lithioaryloxy)phosphazenes must be used at −80 to −40

Scheme IV



[a] The various methods of analysis indicated the proportion of z units in this polymer were Br (40%), H (30%) and siloxane units derived from (c) and/or (d) (30)%.

°C to avoid side reactions. Thus, it was of interest to determine the course of the reaction between **10** and $(OSiMe_2)_3$ at these lower temperatures.

As a model reaction, the ring cleavage of $(OSiMe_2)_3$ under the influence of *phenyllithium* at −80 °C was examined. The reaction was monitored by vapor-phase chromatography following deactivation of the system by the addition of $ClSiMe_3$. At these temperatures, a complex ring–ring and ring–chain siloxane redistribution process occurred to yield at least 10 products. The same reaction, carried out in the presence of $Me_3SiOSiMe_3$ as a chain-termination and -transfer agent, yielded four main products, two of which were identified by vapor-phase chromatography/mass spectrometry as $PhSiMe_2OSiMe_2OSiMe_3$ and $PhSiMe_2(OSiMe_2)_2OSiMe_3$. Thus, the evidence exists that, even at −80 °C, an aryllithium unit can cleave $(OSiMe_2)_3$ and generate pendent siloxane chains.

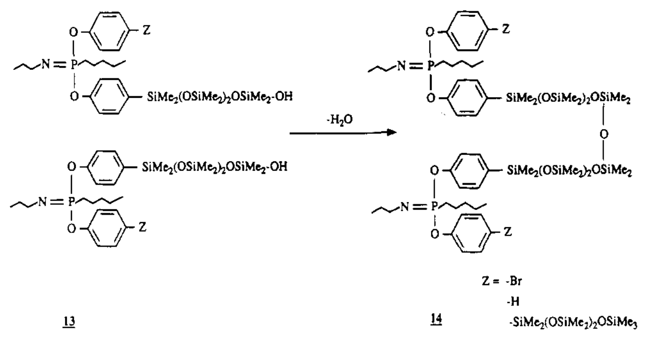
The analogous reaction between high polymer **10** and $(OSiMe_2)_3$ (Scheme IV) was carried out, with care taken to avoid the presence of excess *n*-butyllithium. An excess of this reagent might be expected to induce the independent polymerization of $(OSiMe_2)_3$. Following the reaction between **10** and $(OSiMe_2)_3$, the system was treated with $ClSiMe_3$ at room temperature in order to deactivate the terminal $\sim SiMe_2O^-Li^+$ units by conversion to $\sim SiMe_2OSiMe_3$.[20]

The reactions carried out as described in the Experimental Section yielded a homogeneous solution of a siloxyl-substituted polyphosphazene in THF, a solution system that was stable for several weeks at room temperature. However, total removal of the solvent was accompanied by light cross-linking, and the resultant rubbery elastomer, though swellable in organic media, would not redissolve.[21] The surface contact angle of 109° measured for this polymer is consistent with an enhanced hydrophobic character that can be attributed to the presence of the organosiloxane side groups.

A likely cross-linking mechanism is shown in Scheme V. It is proposed that, at room temperature, the deactivation of $\sim SiMe_2O^-Li^+$ units by $ClSiMe_3$ is not 100% effective.[20] Low concentrations of residual $\sim SiMe_2O^-Li^+$ side units that survive the deactivation process would be converted to $\sim SiMe_2OH$ groups during the subsequent workup procedures. In solution, these units are sufficiently well separated that they do not interact strongly. However, removal of the solvent would favor condensation of silanol end units and generate cross-links.

The alternative explanation that $\sim SiMe_2O^-Li^+$ units might react with residual bromoaryloxy groups on another chain is considered to be less likely. Attempts to deliberately favor a process of this type, by allowing **9** at −78 °C to react with only half the *n*-butyllithium needed for complete lithiation, followed by treatment with $(OSiMe_2)_3$, did not generate cross-links in solution. Moreover, no cross-linking was detected if the cyclosiloxane addition was omitted, and this suggests that precursor **10** is not the major source of cross-link formation.

Scheme V



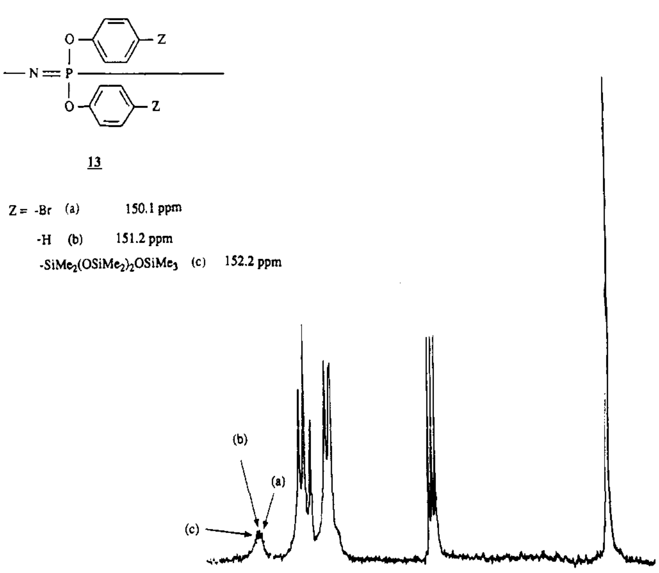


Figure 1. ^{13}C NMR of polymer **13** taken as a swollen gel in $CDCl_3$. Peak assignments for the ipso carbons were based upon chemical shifts of authentic samples of $(NP(OPh)_2)_3$ and $(NP(OC_6H_4Br-p)_2)_3$.

The concentration of cross-links in polymer **14** was so low that they were close to the limit of detectability by standard analytical methods. For example, the infrared spectra could be interpreted satisfactorily in terms of the aryloxyphosphazene and linear oligosiloxane units. However, no absorptions expected from cross-links could be detected. Elemental microanalyses (see Table III) provided a satisfactory proof of the general structure but were not sufficiently sensitive to yield evidence of cross-link structure.

^{13}C NMR spectroscopy showed the existence of two different types of $SiMe_2$ signals. These are (1) the methyl groups bonded to the silyl unit adjacent to the phenyl ring ($\delta = 0.71$ ppm) and (2) the methyl groups separated from the phenyl ring ($\delta = 0.34$ ppm). The influence of phenyl rings on carbon chemical shifts is well-known.[22,23] The ^{13}C NMR spectra also show three distinct C–O–P signals. These were assigned, as shown in Figure 1, and correspond to the three different types of phenyl rings that exist in **13**. The chemical shifts of these peaks correspond to the signals obtained from authentic samples of $[NP(OC_6H_5)_2]_3$ and $[NP(OC_6H_4Br)_2]_3$.

The ^{29}Si NMR spectra provided supporting evidence for the structure of polymer **13** and for the existence of the Si–O–Si cross-links. As shown in Figure 2, the polymer

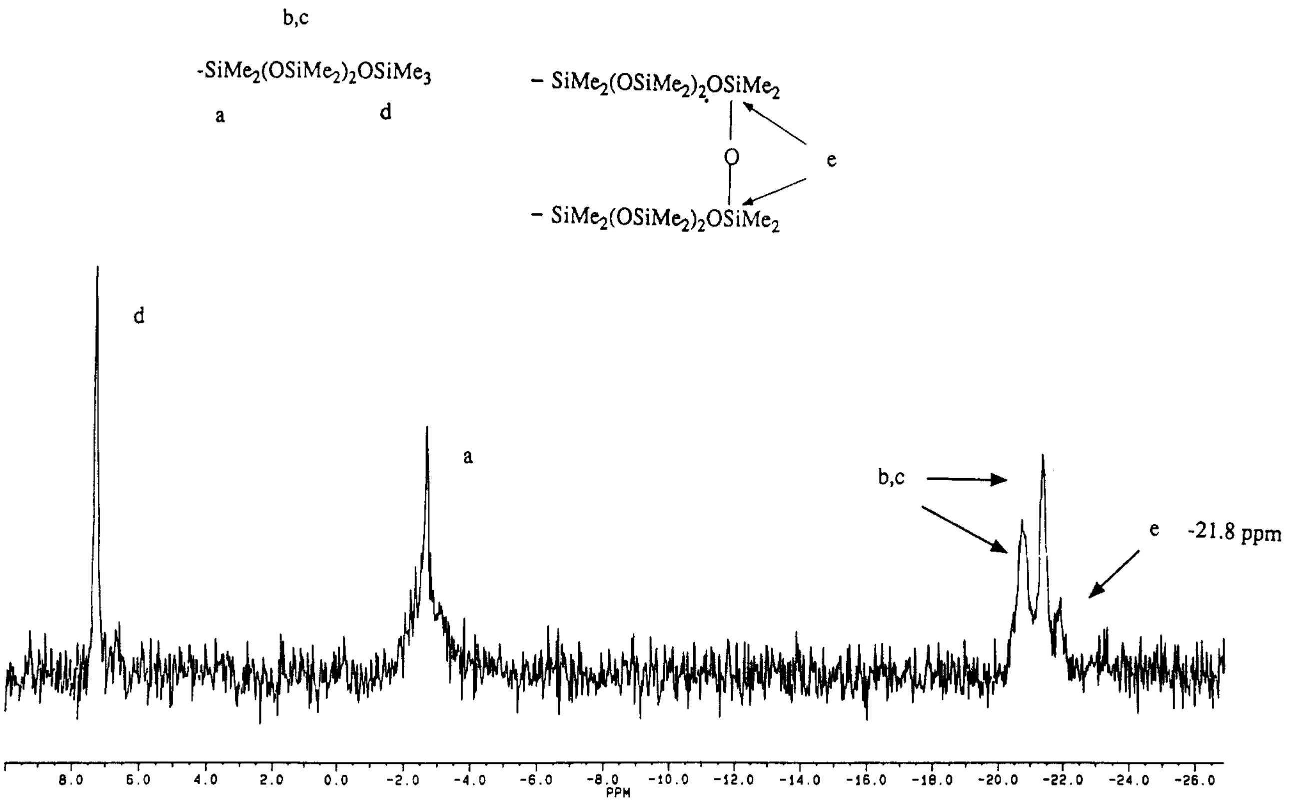
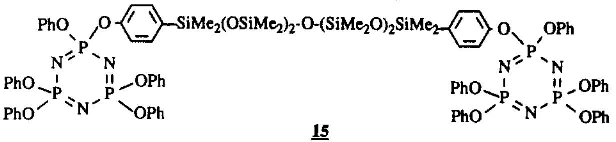


Figure 2. ^{29}Si NMR of polymer 13 taken as a swollen gel in $CDCl_3$. Peak assignments were based on the chemical shifts of various linear siloxanes as reported in ref 22. The chemical shifts are reported relative to external TMS = 0 ppm. Line broadening was the result of the heterogeneous nature of the sample.

contains silicon atoms in four different environments. The two downfield signals (δ = 7.3 and −2.8 ppm) are from silicon atoms that bear only one oxygen atom. Silicon atoms bonded to a phenyl ring are known to generate upfield chemical shifts.[22] The peak at −2.8 ppm is attributed to a structure of this type. The central two silicon atoms are flanked by two oxygen atoms: such a unit is known as a "D" unit. The D units in this polymer generated two different signals in the −20 to −22 ppm region, because they are flanked by different types of silicon atoms. The shoulder on the upfield side of the D unit signals (at −21.8 ppm) has two possible origins. It could represent longer oligosiloxane chain units formed by the addition of an additional $(OSiMe_2)_3$ molecule to the terminal anionic site of a trisiloxy side group. Alternatively, the signal could arise from cross-links of the type shown in Scheme V.

However, the best evidence for the proposed cross-linking mechanism comes from a model compound experiment in which $N_3P_3(OPh)_5(OC_6H_4Li)$ (4) was allowed to react with $(OSiMe_2)_3$. Although the main product from this reaction was species 7, small quantities of ring-linked compounds, such as 15, were detected by mass spectrometry experiments. Moreover, the ^{29}Si NMR spectrum of the reaction mixture contained weak signals that corresponded to the shoulder found in the high polymeric system.[24]



15

Experimental Section

Equipment. ^{31}P (36.2-MHz) and ^{13}C (22.5-MHz) NMR spectra were obtained with the use of a JEOL FX90Q spectrometer. High-field ^{1}H NMR spectra were obtained by using a Bruker WP-200 MHz spectrometer. The ^{29}Si NMR spectra were measured by means of a Bruker AM-300 instrument operated at 59.6 MHz. The signal was enhanced by the use of the INEPT polarization transfer method.[25] The Si/H coupling constant was estimated to be 7.6 Hz. Infrared spectra were recorded on a Perkin-Elmer 1710 FT-IR spectrophotometer. Perkin-Elmer System 7 thermal analysis equipment was used to obtain glass transition information. Small-molecule products were purified by means of a Waters Associates preparative HPLC system 500, with the use of two Prep-Pak 500 silica gel columns in series. Gravity-driven chromatography was carried out using 60/200-mesh silica gel, with elution by silicone grease-free solvents obtained by distillation. Polymer molecular weights were measured by means of a Hewlett-Packard 1090 liquid chromatography unit. The molecular weights were estimated by comparison with polystyrene standards obtained from Waters Associates. Polymer surface water contact angles were measured with use of a Rame-Hart contact angle goniometer (values are accurate to ±1°). The films were cast from concentrated THF solutions filtered through clean glass wool. The solvent was allowed to evaporate slowly in a dust-free environment.

Materials and Procedures. All reaction mixtures were protected by an atmosphere of dry argon (Matheson) using standard Schlenk line techniques. Tetrahydrofuran and dioxane (Omnisolv) were dried and distilled from sodium benzophenone ketal. *n*-Butyllithium (Aldrich), as 1.6 or 2.5 M solutions in hexane, was used as received. The silanes and siloxanes (Petrarch) were distilled under dry nitrogen and stored over 3-Å molecular sieves. Hexamethylcyclotrisiloxane (5) was purified by sublimation in a static vacuum (0.2 Torr, 25 °C) and was stored in an atmosphere of dry nitrogen before use. Hexachlorocyclotriphosphazene (1) was provided by Ethyl Corporation and was purified by recrystallization from hexane, followed by fractional sublimation at 30 °C/0.5 mm. Phenol (Aldrich) was dried by azeotropic removal of water with benzene. Elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN.

Pentaphenoxychlorocyclotriphosphazene (2). This compound was synthesized by a variation of the method reported earlier.[12] Sodium phenoxide (14.3 g, 0.15 mol) was prepared from phenol and sodium (3.51 g, 0.16 mol) in THF (125 mL) at 66 °C. This solution was then added to hexachlorocyclotriphosphazene (10.0 g, 0.03 mmol) in THF (150 mL). The products included

$N_3P_3(OPh)_5Cl$ (**2**) and $[NP(OPh)_2]_3$. Compound **2** was isolated by preparative scale high-pressure liquid chromatography and was recrystallized from methanol. ^{31}P NMR in CH_2Cl_2 (D_2O lock): AB_2, $\delta_A = 21.8$ ppm, $\delta_B = 6.5$ ppm, $J_{PNP} = 58$ Hz. Mp 62–65 °C.

Pentaphenoxy(*p*-bromophenoxy)cyclotriphosphazene (3). Compound **2** was allowed to react with a slight excess of sodium *p*-bromophenoxide in THF at 66 °C. Purification of the product (**3**) was effected by extraction with diethyl ether, followed by column chromatography. Recrystallization from methanol yielded **3** (mp 51–52 °C) in 62% yield. ^{31}P NMR in CH_2Cl_2 (D_2O lock): $\delta = 8.2$ ppm.

Pentaphenoxy(*p*-(trimethylsilyl)phenoxy)cyclotriphosphazene (5a). This synthesis is typical of those used for the preparation of **5a–e**. Compound **3** (0.66 g, 1.14 mmol) was dissolved in freshly dried THF (100 mL) and cooled to −78 °C by means of a dry ice/acetone bath. *n*-Butyllithium (4.3 mL of a 1.6 M solution, 6.84 mmol) was added slowly to the mixture. Trimethylchlorosilane (1.3 mL, 10 mmol) was then added quickly to the stirred solution. The reaction mixture was allowed to warm to room temperature, and the solvent was removed under reduced pressure. The resultant oil was extracted with methylene chloride, and the extract was dried over $MgSO_4$. The solids were removed by filtration, and removal of the solvent yielded a pale-green oil. Purification by preparative HPLC using hexane:CH_2Cl_2 (3:2) as an eluent yielded **5a**. The characterization data and yields are listed in Tables I and II.

Pentaphenoxy(*p*-(dimethylphenylsilyl)phenoxy)cyclotriphosphazene (5b). The reaction was carried out as in the previous example, with the use of **3** (1.5 g, 1.95 mmol), *n*-butyllithium (9.73 mL of a 1.6 M solution, 15.6 mmol), and dimethylphenylchlorosilane (2.65 g, 25 mmol). The final purification was by means of column chromatography over silica gel with hexane:CH_2Cl_2 (3:2) used as the eluent.

Pentaphenoxy(*p*-(methyldiphenylsilyl)phenoxy)cyclotriphosphazene (5c). The same procedures as described above were used for the reaction of **3** (2.0 g, 2.6 mmol) with *n*-butyllithium (9.73 mL of a 1.6 M solution, 15.6 mmol), followed by treatment with methyldiphenylchlorosilane (5.6 g, 25 mmol). The oily product was purified by column chromatography over silica gel using hexane:CH_2Cl_2 (3:2) as the eluent.

Pentaphenoxy(*p*-(dimethylvinylsilyl)phenoxy)cyclotriphosphazene (5d). Compound **3** (1.0 g, 1.3 mmol) in THF (100 mL) was allowed to react at −78 °C with *n*-butyllithium (4.80 mL of a 1.6 M solution, 7.78 mmol), and the product was treated with dimethylvinylchlorosilane (2.7 mL, 2.4 g, 20 mmol). Column chromatography on silica gel with hexane:ethyl acetate (9:1) used as the eluent was employed for the final purification.

Pentaphenoxy(*p*-(butyloctamethyltetrasiloxanyl)phenoxy)cyclotriphosphazene (5e). To a solution of **3** (5.0 g, 6.5 mmol) in THF (250 mL) at −78 °C was added *n*-butyllithium (2.5 mL of a 2.5 M solution, 6.2 mmol). 1,7-Dichlorooctamethyltetrasiloxane (6.9 g, 19.5 mmol) was then added. The solution was allowed to warm to room temperature to maximize the coupling of the organosilicon unit to the phosphazene. The mixture was then cooled again to −78 °C and was treated with excess *n*-butyllithium to replace the terminal chlorine atoms by butyl groups. Trimethylchlorosilane was then added to quench any unreacted *n*-butyllithium. The product was isolated as an oil after column chromatography on silica gel using hexane: methylene chloride (1:1) as an eluent.

Reaction of 4 with Hexamethylcyclotrisiloxane. A dry, round-bottomed flask was charged with **3** (1.0 g, 1.3 mmol) and THF (50 mL), and the solution was cooled to −50 °C by means of a dry ice/acetonitrile bath. *n*-Butyllithium (0.8 mL of a 1.6 M solution in hexane, 1.3 mmol) was then added, and the mixture was stirred. After 3 min, a solution of hexamethylcyclotrisiloxane (0.5 g, 2.24 mmol) in THF (5 mL) was added. The mixture was allowed to warm to room temperature, and an excess of trimethylchlorosilane (1.4 mL, 11.2 mmol) was added to terminate the pendent siloxane chains. The mixture was heated at 66 °C for 8 h, and the product (**7**) was isolated by removal of the volatile materials at reduced pressure, followed by chromatography of the residue on silica gel using hexane:CH_2Cl_2 (4:1) as an eluent. The product was an oil (yield, 520 mg, 41%).

Poly[(*p*-(trimethylsilyl)phenoxy)(*p*-bromophenoxy)phenoxyphosphazene] (11a). Poly[bis(*p*-bromophenoxy)phosphazene] (**9**) was prepared by allowing excess (3 equiv/PCl) sodium *p*-bromophenoxide to react with poly(dichlorophosphazene) in refluxing dioxane for 48–72 h. The fully substituted polymer was purified by multiple reprecipitations into H_2O (3 times) and hexanes (4 times), followed by Soxhlet extraction for 2 days with EtOH. Polymer **9** was always thoroughly dried by heating under vacuum (24 h at 50 °C) before use.

Polymer **9** is not directly soluble in THF. However, it is soluble in warm dioxane. Removal of most of the dioxane, followed by the addition of THF, yields a solution of the polymer. The reactions of this polymer were carried out in a 500-mL round-bottomed flask equipped with a mechanical stirrer, with the reaction mixtures protected by an atmosphere of dry nitrogen. The addition funnels that contained the *n*-butyllithium and the chloroorganosilane were attached to the flask *before* the vessel was cooled to −78 or −50 °C, to minimize exposure of these reagents to atmospheric moisture. The following procedure is typical of that used for all three polymers in this series.

Thus, polymer **9** (3.0 g, 15.51 mmol) was dissolved in dry THF (250 mL), and the solution was cooled to −78 °C (dry ice/acetone bath). To this solution was added *n*-butyllithium (62.1 mL of a 2.5 M solution, 155.1 mmol, 10 equiv excess). After 3 min, freshly distilled trimethylchlorosilane (21.5 g, 200 mmol) was added, and the mixture was stirred and allowed to warm to room temperature. The mixture was then concentrated to 75–100 mL and the polymer was isolated by precipitation into ethanol. The polymer was dried in vacuum, dissolved in THF, reprecipitated twice into water and 3 times into hexane/2-propanol or hexane/ethanol (1:1), and then subjected to Soxhlet extraction with ethanol for 48 h. The characterization data are summarized in Tables III and IV.

Poly[(*p*-(dimethylphenylsilyl)phenoxy)(*p*-bromophenoxy)phenoxyphosphazene] (11b). Polymer **9** (2.0 g, 10.3 mmol) was dissolved in THF (200 mL), cooled, and treated as described above with *n*-butyllithium (25 mL of a 2.5 M solution, 62.5 mmol) and dimethylphenylchlorosilane. The characterization data are summarized in Tables III and IV.

Poly[(*p*-(methyldiphenylsilyl)phenoxy)(*p*-bromophenoxy)phenoxyphosphazene] (11c). Similar procedures were used for the interaction of polymer **9** (2.0 g, 10.3 mmol) in THF (100 mL). It was treated at −80 °C with *n*-butyllithium (41.3 mL of a 2.5 M solution in hexane, 103.4 mmol) and allowed to react after 3 min with freshly distilled methyldiphenylchlorosilane (26 mL, 27.8 g, 120 mmol). Tables III and IV contain the characterization data.

Reaction of Polymer 10 with Hexamethylcyclotrisiloxane. Polymer **9** (2.0 g, 10.3 mmol) in THF (100 mL) was cooled to −50 °C and treated with *n*-butyllithium (6.4 mL of a 1.6 M solution, 10.2 mmol). After 3 min, a solution of $(OSiMe_2)_3$ (11.4 g, 51.5 mmol) in THF (15 mL) was added. The mixture was allowed to warm to room temperature and was then treated with excess trimethylchlorosilane and heated to 40 °C. Concentration of the mixture to ~50 mL was followed by precipitation into ethanol and H_2O. After precipitation into 2-propanol and vacuum drying, polymer **13** was no longer soluble in THF, DMF, toluene, hexane, dioxane, or glyme, although it swelled in these media. The characterization data are shown in Tables III and IV.

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Registry No. **1**, 940-71-6; **2**, 5032-39-3; **3**, 72811-83-7; **5a**, 120525-56-6; **5b**, 120525-57-7; **5c**, 120525-58-8; **5d**, 120525-59-9; **5e**, 120525-60-2; **7**, 120525-61-3; NaOPH, 139-02-6; $NaOC_6H_4Br$, 7003-65-8; butyllithium, 109-72-8; trimethylchlorosilane, 75-77-4; dimethylphenylchlorosilane, 768-33-2; methyldiphenylchlorosilane, 144-79-6; dimethylvinylchlorosilane, 1719-58-0; 1,7-dichlorooctamethyltetrasiloxane, 2474-02-4; hexamethylcyclotrisiloxane, 541-05-9.

References and Notes

(1) This is the seventh paper from our laboratory on organosilicon derivatives of phosphazenes. For the previous papers, see ref 4–9.

(2) Zeldin, M.; Wynne, K. J.; Allcock, H. R. *Inorganic and Organometallic Polymers*; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1987.

(3) Allcock, H. R. *Chem. Eng. News* **1985** *63* (Mar 18), 22.

(4) Allcock, H. R.; Brennan, D. J.; Allen, R. W. *Macromolecules* **1985**, *18*, 139.

(5) Allcock, H. R.; Brennan, D. J.; Graaskamp, J. M.; Parvez, M. *Organometallics* **1986**, *5*, 2434.

(6) Allcock, H. R.; Brennan, D. J.; Graaskamp, J. M. *Macromolecules* **1988**, *21*, 1.

(7) Allcock, H. R.; Brennan, D. J.; Dunn, B. S.; Parvez, M. *Inorg. Chem.* **1988**, *27*, 3226.

(8) Allcock, H. R.; Brennan, D. J. *J. Organomet. Chem.* **1988**, *341*, 231.

(9) Allcock, H. R.; Brennan, D. J.; Dunn, B. S. *Macromolecules*, in press.

(10) Wisian-Neilson, P.; Ford, R. R.; Neilson, R. H.; Roy, A. K. *Macromolecules* **1986**, *18*, 2091.

(11) Evans, T. L.; Fuller, T. J.; Allcock, H. R. *J. Am. Chem. Soc.* **1979**, *101*, 242.

(12) Allcock, H. R.; Evans, T. L.; Fuller, T. J. *Inorg. Chem.* **1980**, *19*, 1026.

(13) Allcock, H. R.; Fuller, T. J.; Evans, T. L. *Macromolecules* **1980**, *13*, 1325.

(14) Allcock, H. R.; Lavin, K. D.; Tollefson, N. M.; Evans, T. L. *Organometallics* **1983**, *2*, 267.

(15) Allcock, H. R. *Acc. Chem. Res.* **1979**, *12*, 351.

(16) Allcock, H. R.; Kwon, S.; Riding, G. H.; Fitzpatrick, R. J.; Bennett, J. L. *Biomaterials* **1988**, *9*, 509.

(17) Babic, D.; Souverain, D. M.; Stannett, V. T.; Squire, D. R.; Hagnauer, G. L.; Singler, R. E. *Int. J. Radiat. Appl. Instrum., Part C* **1986**, *28*, 169.

(18) Boileau, S. In *Ring Opening Polymerization*; McGrath, J. E., Ed.; ACS Symposium Series 286; American Chemical Society: Washington, DC, 1985; Chapter 2, pp 23–37.

(19) Wright, P. V. In *Ring-Opening Polymerization*; Ivin, K. J., Saegusa, T., Eds.; Elsevier: Amsterdam, 1985; Vol. 1, Chapter 14.

(20) Frye, C. L.; Salinger, R. M. *J. Org. Chem.* **1970**, *35*, 1308.

(21) However, polymer that retained some solvent did redissolve. Hence, purification by reprecipitation was possible.

(22) Exenrod, T. *NMR of Nuclei Other Than Proton*; Wiley: New York, 1974; Chapter 17.

(23) Silverstein, R. M.; Bassler, G. C.; Morril, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley Scientific: New York, 1981; Chapter 5, p 249.

(24) ^{29}Si NMR spectra of **15** contained four major signals at +7.5, −2.6, −20.6, and −20.9 ppm. A similar signal, corresponding to a siloxane cross-link, was detected at −21.7 ppm.

(25) Grignon-Dubois, M.; Laguerre, M.; Barbe, B.; Petraud, M. *Organometallics* **1984**, *3*, 1060.

Dependence of Miscibility on Copolymer Composition for Blends of Poly(vinyl chloride-*co*-vinyl acetate) and Poly(*n*-butyl methacrylate-*co*-isobutyl methacrylate)

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ABSTRACT: It has been so far reported that some polymer blends containing random copolymers can be miscible in a certain range of copolymer compositions even though the combinations of their corresponding homopolymers are immiscible. On the other hand, according to theory, there may exist some copolymer blends that are immiscible in a certain range of copolymer compositions even though their corresponding homopolymers are miscible with each other. For real blends with a possibility of such an immiscibility region, the dependence of miscibility on the copolymer composition was observed at the blend ratio 1/1. Poly(vinyl chloride-*co*-vinyl acetate) copolymers (VC·VAc) were immiscible with poly(*n*-butyl methacrylate-*co*-isobutyl methacrylate) copolymers (nBMA·iBMA) in a certain range of copolymer compositions of nBMA·iBMA, though every pair of VC·VAc copolymer/nBMA homopolymer, VC·VAc copolymer/iBMA homopolymer, and nBMA homopolymer/iBMA homopolymer was miscible.

Introduction

Recently, it has been demonstrated[1-4] that polymer blends containing random copolymers can be miscible in a certain range of copolymer compositions even though the combinations of their corresponding homopolymers are immiscible. Kambour et al.,[3] Paul and Barlow,[5] and ten Brinke et al.[6] explained such a miscibility, which is called a "miscibility window", by expressing the Flory–Huggins intermolecular interaction parameter, χ, in terms of the respective intersegmental parameters, χ_{ij}.[7] Shiomi et al.[4] showed various theoretical patterns of dependence of miscibility on the copolymer composition (miscibility map) for the copolymer blends having a common monomer, and they reported some experimental results corresponding to the theoretical miscibility maps.

The dependence of miscibility on the copolymer composition has been interpreted as follows.[3,5,6] For a mixture of two general random copolymers, 1 ($[(\mathrm{A1})_{x_1}(\mathrm{A2})_{x_2}\cdots(\mathrm{A}m)_{x_m}]_{r_1}$) and 2 ($[(\mathrm{B1})_{y_1}(\mathrm{B2})_{y_2}\cdots(\mathrm{B}n)_{y_n}]_{r_2}$), we can write the interaction parameter, χ, per segment between copolymers 1 and 2 as

$$\chi = \sum_{i=1}^{m}\sum_{j=1}^{n} x_i y_j \chi_{\mathrm{A}i\mathrm{B}j} - \sum_{i=1}^{m-1}\sum_{j=i+1}^{m} x_i x_j \chi_{\mathrm{A}i\mathrm{A}j} - \sum_{i=1}^{n-1}\sum_{j=i+1}^{n} y_i y_j \chi_{\mathrm{B}i\mathrm{B}j} \tag{1}$$

where $\chi_{\mathrm{A}i\mathrm{B}j}$, etc., are the segmental interaction parameters between the different segments A*i* and B*j*, etc., respectively, and x_i and y_j are the copolymer compositions expressed as the volume fraction for copolymers 1 and 2, respectively. When the intermolecular χ at a certain temperature is smaller than that at the critical point, χ_{crit}, that is,

$$\chi < \chi_{\mathrm{crit}} \tag{2}$$

two polymers are miscible with each other at that temperature, while they are immiscible when

$$\chi > \chi_{\mathrm{crit}} \tag{3}$$

According to the Flory–Huggins theory, χ_{crit} is given by

$$\chi_{\mathrm{crit}} = 1/2(r_1^{-1/2} + r_2^{-1/2})^2 \tag{4}$$

where r_1 and r_2 are the numbers of segments for polymers 1 and 2, respectively, when the segment is taken to be of

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