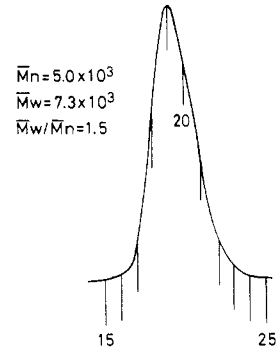

Figure 2. GPC of the methanol-insoluble polymer obtained by the copolymerization of N-PMI and PO with **3**.

protons of the polymerized N-PMI moiety. This spectrum implies that the polymer consists of both N-PMI and PO units. The mole fraction of PO in the polymer was calculated as 20% from the areas of signals a and e.

GPC[13] of the methanol-insoluble polymer obtained gives unimodal molecular weight distribution, as shown in Figure 2. The number-average molecular weight calculated from standardized polystyrene calibration is 5.0×10^3 and the molecular weight distribution ($\bar{M}_w/\bar{M}_n$) is 1.5. Thin layer chromatography (TLC)[14] of the polymer showed only one spot at a different position from those of homopolymers of N-PMI and of PO. GPC and TLC measurements suggest that the polymer obtained consists of only one component and is not a mixture of two homopolymers, i.e., a copolymer of N-PMI and PO is produced.

^{1}H NMR, GPC, and TLC analyses for the methanol-soluble polymer initiated with **3** revealed that it is a mixture of homopoly(PO) and copolymer of N-PMI and PO with high PO content. However, they actually could not be isolated separately.

It was confirmed by means of ^{1}H NMR that no copolymerization takes place with the other organozinc initiators. **1** and **4** only produced homopoly(N-PMI) (as the methanol-insoluble part) and homopoly(PO) (as the methanol-soluble part), respectively. The copolymerization in equimolar amount of PO and N-PMI (5 mmol each) with **3** also failed to incorporate appreciable amount of PO into the polymer and the mole fraction of PO in the polymer was less than 1% (by ^{1}H NMR).

Copolymerization of N-PMI and PO initiated with potassium *tert*-butoxide, which can initiate homopolymerization of both monomers, was carried out in a wide range of feed molar ratio of N-PMI to PO. No copolymerization took place but only homopoly(N-PMI) was obtained. Grignard reagents, alkyllithium and sodium naphthalenide gave also no copolymer at all but homopoly(N-PMI).

In conclusion, only **3** can give rise to the copolymerization of N-PMI and PO since the polymer obtained consisted of N-PMI and PO units (^{1}H NMR) and possessed only one component (GPC and TLC), though the type of their homopolymerization is quite different from each other. This is the first example of the copolymerization of an N-substituted maleimide with a cyclic ether.

Registry No. (N-PMI)(PO) (copolymer), 119770-35-3; Zn($OCH_3)_2$, 1184-55-0; $C_2H_5ZnOCH_3$, 15860-82-9.

References and Notes

(1) Simosaka, Y.; Tsuruta, T.; Furukawa, J. *Kogyo Kagaku Zasshi* **1963**, *66*, 1498.
(2) (a) Simionescu, C. I.; Grigoras, M.; Bicu, E.; Onofrei, G. *Polym. Bull. (Berlin)* **1985**, *14*, 79. (b) Rivas, B. L.; Pizarro, G. del C.; Canessa, G. S. *Polym. Bull. (Berlin)* **1988**, *19*, 123.
(3) Hagiwara, T.; Sato, J.; Hamana, H.; Narita, T. *Makromol. Chem.* **1987**, *188*, 1825.
(4) Ishimori, M.; Hagiwara, T.; Tsuruta, T.; Kai, Y.; Yasuoka, N.; Kasai, N. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1165.
(5) Ishimori, M.; Hagiwara, T.; Tsuruta, T. *Makromol. Chem.* **1978**, *179*, 2337.
(6) Hagiwara, T.; Ishimori, M.; Tsuruta, T. *Makromol. Chem.* **1981**, *182*, 501.
(7) Ishimori, M.; Tsuruta, T. *Kogyo Kagaku Zasshi* **1967**, *70*, 378.
(8) Ishimori, M.; Tomoshige, T.; Tsuruta, T. *Makromol. Chem.* **1969**, *128*, 52.
(9) Ishimori, M.; Tsuruta, T. *Makromol. Chem.* **1963**, *64*, 190.
(10) Tsuruta, T. *J. Polym. Sci., Part D* **1972**, *6*, 176.
(11) Purification of monomers are described in ref 3 for N-PMI and in ref 6 for PO.
(12) ^{1}H NMR was recorded at 60.0 MHz in deuterated chloroform at 35 °C.
(13) GPC was measured with column series of TSK gel G4000HXL-G3000HXL-G2000HXL (TOSOH Co., Tokyo) using THF as eluent. The exclusion limits of molecular weight: 4×10^5 for G4000HXL; 6×10^4 for G3000HXL; 1×10^4 for G2000HXL.
(14) TLC was performed on a silica gel plate (Merck silica 60) using ethanol/chloroform (8/2 v/v) as a developing solvent. R_f values for obtained copolymer, $0.02 < R_f < 0.28$; for homopoly(PO), $0.83 < R_f < 0.96$; for homopoly(N-PMI), $R_f = 0$.

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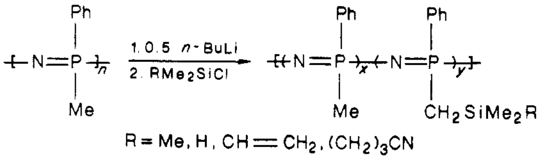
Poly(methylphenylphosphazene)-*graft*-poly(dimethylsiloxane)

Block and graft copolymers of polyphosphazenes are relatively few in number. Recently polystyrene-grafted aryloxy-[1] and alkyl/aryl-substituted[2] polyphosphazenes have been reported, but attempts to prepare copolymers with wholly inorganic silicon–oxygen and phosphorus–nitrogen monomeric units have not been successful.[3] We report here the first polyphosphazene-*graft*-polysiloxane copolymer in which the grafted siloxane chain is attached to the phosphazene backbone by the P–C–Si linkage.

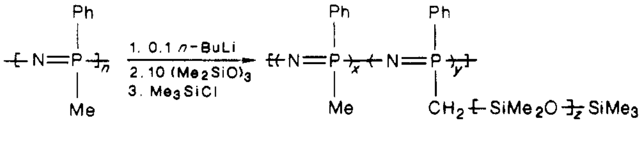
Earlier work in our laboratories has demonstrated that poly(methylphenylphosphazene), $[Me(Ph)P{=}N]_n$, can readily be derivatized by deprotonation-substitution reactions. For example, a series of silylated derivatives[4] have been prepared by sequential treatment of $[Me(Ph)PN]_n$ with n-BuLi and various chlorosilanes, RMe_2SiCl (eq 1).



$$\left[N{=}\overset{Ph}{\underset{Me}{P}}\right]_n \xrightarrow[2.\ RMe_2SiCl]{1.\ 0.5\ n\text{-}BuLi} \left[\left(N{=}\overset{Ph}{\underset{Me}{P}}\right)_x\left(N{=}\overset{Ph}{\underset{CH_2SiMe_2R}{P}}\right)_y\right] \qquad (1)$$

$$R = Me, H, CH{=}CH_2, (CH_2)_3CN$$

We have shown that the intermediate polymer anion in these reactions can also be used to prepare inorganic–organic graft copolymers[2] through initiation of addition polymerization of styrene. These reactions indicated that the polyphosphazene anion sites generated from n-BuLi and $[Me(Ph)PN]_n$ could be used to initiate ring opening of $(Me_2SiO)_3$ (eq 2).



$$\left[N{=}\overset{Ph}{\underset{Me}{P}}\right]_n \xrightarrow[\substack{2.\ 10\ (Me_2SiO)_3 \\ 3.\ Me_3SiCl}]{1.\ 0.1\ n\text{-}BuLi} \left[\left(N{=}\overset{Ph}{\underset{Me}{P}}\right)_x\left(N{=}\overset{Ph}{\underset{CH_2\left[SiMe_2O\right]_zSiMe_3}{P}}\right)_y\right] \qquad (2)$$

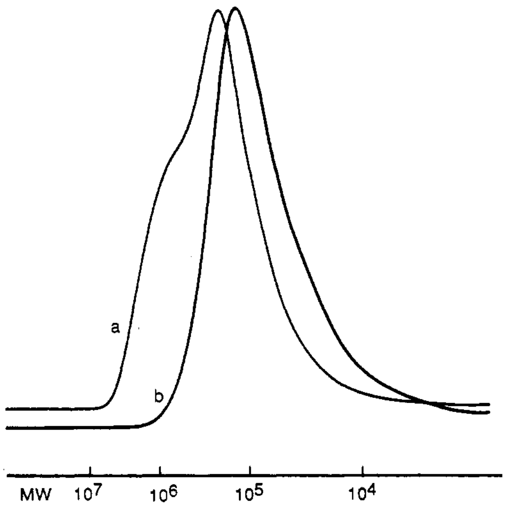


Figure 1. Molecular weight distributions determined by GPC (UV detector with 500, 10^4, 10^5, and 10^6 Å μStyragel columns) for (a) the graft copolymer and (b) the parent polymer $[Me(Ph)PN]_n$.

While initial reactions with the cyclic siloxane[5] appeared to be quite straightforward and, by size exclusion chromatographic (SEC) analysis, clearly yielded materials with some grafted components, closer investigation of the products revealed that low molecular weight components were also present. Subsequent alteration of the reaction conditions and purification procedures has, however, consistently given a pure graft copolymer with a phosphazene to silicone weight ratio of 37:63.

Optimized experimental reaction conditions consisted of initial anion preparation by dissolution of carefully dried $[Me(Ph)PN]_n$ (2.0 g, 14.6 mmol) in THF (freshly distilled from Na/benzophenone) followed by cooling to −78 °C, addition of *n*-BuLi (1.5 mmol, 0.6 mL, 2.5 M in hexane), and stirring for 1.5 h at −78 °C. Then a THF solution of $(Me_2SiO)_3$ (15.0 mmol, 3.34 g in 20 mL of THF) was added. The mixture was allowed to warm slowly and was stirred for 2 h at room temperature. A very viscous gel formed after ca. 30 min at room temperature and it was necessary to stir this mixture with a mechanical stirrer in order to optimize the grafting process. After no more than 2 h at room temperature (longer reaction times were accompanied by disappearance of the viscous gel and formation of large amounts of siloxane oligomers), the reaction was quenched by addition of Me_3SiCl (3.0 mmol). Quenching was accompanied by dissolution of the products as indicated by complete disappearance of the gel. The mixture was stirred overnight and the graft was precipitated by slow addition of the THF solution to water (ca. 800 mL). Subsequent reprecipitations from THF into acetone, decantation of the solvents, and drying in a vacuum oven for ca. 18 h at 80 °C afforded 2.8 g of the graft copolymer (49% yield) as an off-white solid.

Elemental analysis[6] and ^1H NMR spectroscopy[7] confirmed the phosphazene to silicone ratio predicted by the reagent stoichiometry, which was chosen to approximate a graft with 10% of the phosphazene monomer units containing grafted chains of ca. 30 monomeric siloxane units (i.e., in eq 2, $x = 9$, $y = 1$, $z = 30$). The ^{31}P NMR spectrum of the graft[7] contained only one signal. Similar simplicity was observed in the ^{31}P NMR spectra of the substituted-silyl polyphosphazene derivatives.[4] The ^{29}Si NMR spectra also contained only a single signal at δ −21.1. SEC analysis[8] of the graft (Figure 1) clearly shows an increased molecular weight[9] relative to the parent polymer, as well as the broadened, bimodal molecular weight distributions often observed for graft copolymers.[2,10] The absolute number-average molecular weight[9] ($M_n = 68\,000$) determined by membrane osmometry was in the same range as the value obtained by SEC and again shows a marked increase over the M_n value for the parent polymer ($M_n = 31\,000$).

The use of both refractive index and ultraviolet absorption detectors in the SEC experiments was particularly useful for studying the grafting process. Because the siloxane moiety does not absorb in the UV range (254 nm), it can be concluded that the broadening and the increase of the molecular weight distribution is due solely to grafting and not to formation of high molecular weight homopolysiloxane. Furthermore, the use of the refractive index detector provided an indication of the presence of low molecular weight, ungrafted siloxane oligomers. This was essential for determination of purity of the final graft since some low molecular weight siloxanes were produced in early reactions, presumably via chain transfer/cleavage processes.[11] It was also useful in demonstrating that insufficient stirring with a magnetic stirrer and reaction times in excess of 2 h were accompanied by increased amounts of oligomeric siloxanes.

Differential scanning calorimetry of the graft copolymer revealed three transitions (inflection points) in the graft copolymer. The weaker two of these corresponded to the glass transitions of the homopolymer components, e.g., −123 °C for the polysiloxane and 38 °C for the polyphosphazene. The third was a strong transition at −45 °C which is the T_m of poly(dimethylsiloxane). These data suggest that two phases exist within the copolymer.[12]

Thermal gravimetric analysis of the graft copolymer in air using a heating rate of 10 °C/min indicated that the onset of decomposition was at 436 °C with an inflection (ca. 50% weight loss) at 468 °C. This suggests that the grafted siloxane chains have enhanced the thermal stability of the graft copolymer relative to that of the parent polymer which typically shows an onset of decomposition at 395 °C in argon and at ca. 350–365 °C in air. This also compares favorably to the thermal stability of poly(dimethylsiloxane) and cross-linked silicones.[13] Similar enhancement of stability was observed for the simple silylated polyphosphazene, $\{[Me(Ph)PN][Me_3SiCH_2(Ph)PN]\}_n$.[4]

An additional factor worthy of note is that incomplete quenching of the reactions with Me_3SiCl caused cross-linking of the grafts upon extensive heating (e.g., overnight at 100 °C). These problems were usually alleviated by using a 2-fold excess of Me_3SiCl and by allowing the quenched reaction mixture to stir for ca. 18 h. Although this was generally sufficient, one batch of the graft copolymer still underwent slight cross-linking after 3 days at 100 °C. Nonetheless, the sample eventually formed a solution that could be filtered through a 1.0-μm filter. SEC analysis of the polymer in the filtered solution indicated a slightly lower molecular weight ($M_n = 60\,000$) relative to that of the graft before extensive heating.

In summary, this new graft copolymer demonstrates that the isoelectronic polysiloxane and polyphosphazene systems can be merged and the initial thermal analysis data indicate that such systems possess improved thermal stability. Further studies of a complete series of polyphosphazene-*graft*-polysiloxanes are in progress.

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References and Notes

(1) Gleria, M.; Bolognesi, A.; Porzio, W.; Catellani, M.; Destri, S.; Audisio, G. *Macromolecules* **1987**, *20*, 469.

(2) Wisian-Neilson, P.; Schaefer, M. A. *Macromolecules*, in press.

(3) (a) Allcock, H. R.; Brennan, D. J.; Graaskamp, J. M. *Macromolecules* **1988**, *21*, 1. (b) Allcock, H. R.; Brennan, D. J.; Allen, R. W. *Macromolecules* **1985**, *18*, 139.

(4) Wisian-Neilson, P.; Ford, R. R.; Roy, A. K.; Neilson, R. H. *Macromolecules* **1986**, *19*, 2089.

(5) Wisian-Neilson, P.; Islam, M. S.; Schaefer, M. A. *Phosphorus, Sulfur, Silicon, and the Related Elements*, in press.

(6) Elemental anal. Calcd: C, 43.55; H, 7.36; N, 3.82. Found: C, 43.88; H, 7.26; N, 4.20.

(7) ^{1}H NMR δ 0.06 (s, MeSi, 7), 1.36 (m, PCH, 1), 7.14, 7.73 (br m, Ph, 1.8); ^{29}Si NMR δ −21.1 (s); ^{31}P NMR δ 1.95 (s).

(8) Procedures, equipment, and operating procedures for SEC, membrane osmometry, NMR spectra, and thermal analysis are the same as those described in ref 2.

(9) SEC analysis (THF, 30 °C): M_w, 335 000; M_n, 87 000. Membrane osmometry (toluene, 35 °C): M_n, 68 000.

(10) Moore, L. D., Jr.; Adcock, J. I. *Characterization of Macromolecular Structure*; Publication 1573; National Academy of Sciences: Washington, DC, 1968; pp 289–296.

(11) Stark, F. O.; Falender, J. R.; Wright, A. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 2, pp 305–364.

(12) Krause, S.; Lu, Z.; Iskandar, M. *Macromolecules* **1982**, *15*, 1076.

(13) Critchley, J. P.; Knight, G. J.; Wright, W. W. *Heat-Resistant Polymers*; Plenum: New York, 1983; Chapter 6.

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