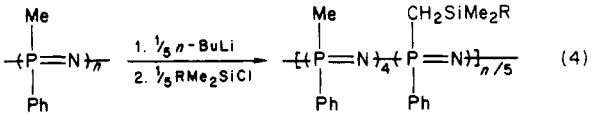

(4)

4a, R = Me
b, R = CH=CH$_2$

parent polymer (Table II). In these cases, very little disubstitution was observed, as evidenced by one very large singlet and only a small second singlet in the Me_2Si region of the ^1H NMR spectrum.[12] The elemental analyses of **4a,b** were less satisfactory than for **1** and **3a–c**, but this can be attributed to the more noticeable effect of even minor deviations in the stoichiometric measurements.

In summary, these reactions demonstrate that *under mild conditions, the poly(alkyl/arylphosphazenes) can be derivatized without chain degradation via sequential treatment with n-BuLi and chlorosilanes.* In this manner a series of silylated polymers that contain predominantly Ph, Me, and RMe_2SiCH_2 with minor portions of $(RMe_2Si)_2CH$ substituents attached to the polymer backbone were prepared. The potential for enhanced thermal stability and for further derivatization of these new materials via the reactive functional groups R are under investigation.

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(9) ^1H NMR ($CDCl_3$) δ 7.2, 7.3 (s, Ph), 1.4 (m, Me, CH_2, CH), 0.0, 0.1, –0.3 (m, Me_3Si); ^{13}C NMR ($CDCl_3$) δ 125.0–143.9 (m, Ph), 19.3–26.6 (m, Me, CH_2), 0.4, 3.1 (m, Me_3Si); ^{29}Si NMR ($CDCl_3$) δ –2.1.
(10) ^1H NMR ($CDCl_3$) δ 7.2, 7.8 (s, Ph), 1.4 (m, Me, CH_2), 0.8 (m, Si_2CH), 0.1, –0.1, –0.2 (m, Me_3Si); ^{29}Si NMR ($CDCl_3$) δ –2.1, –1.5.
(11) **3a**: ^{31}P NMR ($CDCl_3$) δ 4.0, –0.4(br s); ^1H NMR ($CDCl_3$) δ 7.8, 7.2 (s, Ph), 5.4–6.3 (m, CH=CH_2), 1.5 (m, Me, CH_2Si), 0.1, –0.2 (m, Me_2Si); ^{29}Si NMR ($CDCl_3$) δ –9.7. **3b**: ^{31}P NMR ($CDCl_3$) δ 4.3 (br sh), 3.5 (br s), 0.1 (br s); ^1H NMR ($CDCl_3$) δ 7.8, 7.2 (s, Ph), 0.8–2.3 (m, Me, CH_2Si), 0.3, 0.1, –0.3 (s, Me_2Si); ^{29}Si-($CDCl_3$) δ 6.3 (weak s, Si_2CH), –1.1 (s, $SiCH_2$). **3c**: ^{31}P NMR ($CDCl_3$) δ 3.9, 0.5 (br s); ^1H NMR ($CDCl_3$) δ 7.8, 7.1 (s, Ph), 4.7, 3.9 (s, SiH), 1.4 (br s, Me, CH_2), 0.1, –0.2 (m, Me_2Si); ^{29}Si NMR ($CDCl_3$) δ –18.5 (d, J_{H-Si} = 184.0 Hz).
(12) **4a**: ^{31}P NMR ($CDCl_3$) δ 7.3 (br sh), 3.8 (br s); ^1H NMR ($CDCl_3$) δ 7.6, 7.3, 7.1 (s, Ph), 1.2–1.7 (m, Me, CH_2), 0.0, –0.3 (m, Me_3Si); ^{29}Si NMR ($CDCl_3$) δ –1.4 (w s), –2.0 (str s). **4b**: ^{31}P NMR ($CDCl_3$) δ 2.0–10.3 (br, s); ^1H NMR ($CDCl3$) δ 7.7, 7.3, 7.1 (s, Ph), 5.2–6.0 (m, CH=CH_2), 0.8–1.6 (m, Me, CH_2Si), –0.3 (br s, Me_3Si); ^{29}Si NMR ($CDCl_3$) δ –9.8.

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Excimer Emission from Copolymers of Aromatic Monomers in Dilute Solution

In 1977 and 1978 Reid and Soutar[1,2] published a study in which they investigated the ratio of excimer and monomer fluorescence intensity, I_e/I_m, as a function of composition of copolymers containing aromatic and nonaromatic monomer residues. They assumed that only neighboring aromatic residues could form excimers and that energy migration along the polymer chain was limited to a contiguous sequence of such residues. This led them to conclude that $I_e/I_m = kf_{aa}\bar{l}_a$, where f_{aa} was the fraction of aromatic residues adjoining a similar residue, $\bar{l}_a$ was the mean sequence length of such residues, and k was a proportionality constant.

Reid and Soutar argued[1] that "the concentration of excimer sites must be modified to include only those traps which are within 'striking distance' of the migrating exciton" and justified in this way the proportionality of I_e/I_m on $\bar{l}_a$. They presented data on 1-vinylnaphthalene, 2-vinylnaphthalene, and styrene copolymers with methyl methacrylate[2] which were in agreement with this prediction. Later, a study of Anderson et al.[3] concerned with 1-vinylnaphthalene copolymers with methyl acrylate also behaved as predicted.

In spite of these reports, the relation of Reid and Soutar seems to be incompatible with a simple statistical argument. Let us assume that a sequence of aromatic monomer residues contains a fraction α of "traps", i.e., monomer residues whose configuration and/or conformation is required for excimer formation (presumably meso diads of such residues[4,5]). Then the probability that a sequence of n residues contains no such trap is $P(n) = (1 - \alpha)^{n-1}$. If we denote the I_e/I_m ratio in the aromatic homopolymer by $(I_e/I_m)_h$, then this ratio in a copolymer should be

$$I_e/I_m = (I_e/I_m)_h[1 - \sum_n W(n)(1 - \alpha)^{n-1}] \qquad (1)$$

where $W(n)$ is the weight fraction of sequences of n aromatic residues which will depend on the probability that an aromatic monomer is followed by a nonaromatic comonomer residue. It may be noted that the summation on the right of eq 1 vanishes for long-chain homopolymers, while the equation of Reid and Soutar has I_e/I_m increasing without limit as $\bar{l}_a$ is extended.[6]

There is another difficulty with the Reid–Soutar relation. Anderson et al.[3] found that the proportionality constant k was 6 times larger in 1-vinylnaphthalene copolymers with methyl acrylate than in the copolymers with methyl methacrylate. This was ascribed to the higher flexibility of the methyl acrylate copolymers. Yet the flexibility of a section of the chain consisting of a series of 1-vinylnaphthalene residues cannot depend on the na-

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ture of the comonomer by which the series is terminated. The difference between the fluorescence behavior of methyl acrylate and methyl methacrylate copolymers with the same distribution of sequences of the aromatic monomer residues can only be understood either if excimers can form from aromatic monomer residues separated by a comonomer or if energy migration is not limited by a comonomer residue. Both these effects might depend on the nature of the comonomer, which would affect the relative positioning of vinylnaphthalene residues separated by a comonomer. This interpretation is supported by the behavior of acenaphthylene copolymers, where the efficiency of excimer formation by interaction of next-to-nearest neighbors is strikingly dependent on the nature of the comonomer.[7,8]

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