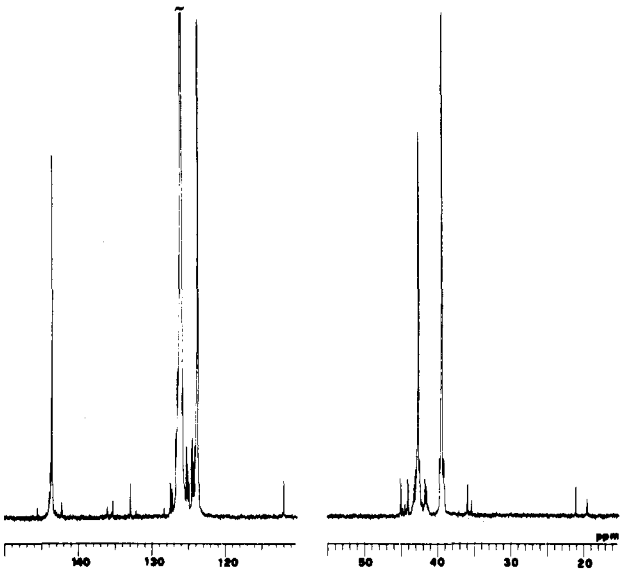

Figure 2. ^{1}H-decoupled ^{13}C NMR spectrum of sample 2 (HMDS scale). The resonances at 111.9, 127.1, 135.2, and 136.0 ppm are due to the presence of traces of styrene monomer in the sample.

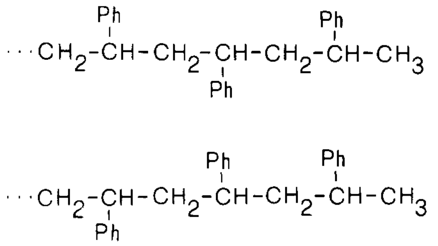

Figure 3. Fischer projection of the 2,4,6-triphenylheptyl end groups resulting after the insertion of three monomer units on M-H bonds. The two reported configurations are the only ones detected in the end groups of sample 2; Ph = C_6H_5.

oregular than sample 1. In fact, in the spectrum one can observe the resonances of some irregular stereosequences.[2] The amount of rrr stereochemical tetrads, evaluated according to the literature,[5] from the relative intensity of the resonances of the backbone methylene carbons is 80% in comparison with 99% for sample 1. Correspondingly the resonances of the PP end group also appear split due to different stereochemical environments (see Figures 2 and 3).

From the data reported in this paper it is therefore concluded that in the presence of the homogeneous syndiotactic catalysts TBT-MAO and TBZ-MAO the insertion of styrene is 100% secondary both in the propagation and in the initiation steps, even where it occurs on M-H bonds. The most important chain-transfer process involves β-hydrogen abstraction. Under our conditions most of the polymer chains are initiated on M-H bonds. The stereoregularity of the arrangement of the phenyl substituents of the end groups, with respect with those of the first neighboring monomer units, parallels that of the polymer chain.

Experimental Section. TBT, TBZ, and MAO were prepared according to the literature.[7,8] Sample 1 was prepared at 60 °C with TBT/MAO catalytic system as previously described,[2] collecting the boiling butanone-soluble fraction. Sample 2 was prepared by polymerizing at 90 °C for 4 h 0.17 mol of styrene dissolved in 40 mL of toluene, using 1.0 × 10^{-4} mol of TBZ and 0.45 g of MAO as catalyst. After the polymerization was stopped with 5 mL of methanol, the reaction mixture was poured into 200 mL of acetone. The precipitated solid was filtered, and the solution was cooled at −18 °C overnight. The solid crystallized at −18 °C was collected and dried, giving 0.5 g of oligomeric polystyrene (M_n = 1635; M_w = 2421). The ^{13}C NMR spectra were performed on an AM 250 Bruker Spectrometer, either at 120 °C (sample 1) or at 25 °C (sample 2), in solution of tetrachlorodideuterioethane containing hexamethyldisiloxane (HMDS) as internal chemical shift reference. Molecular weight of sample 2 was measured by GPC in o-dichlorobenzene.

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Registry No. TBT, 17520-19-3; TBZ, 24356-01-2; PhCH=CH_2, 100-42-5.

References and Notes

(1) Ishihara, N.; Seimiya, T.; Kuramoto, M.; Uoi, M. *Macromolecules* **1986**, *19*, 2465.
(2) Grassi, A.; Pellecchia, C.; Longo, P.; Zambelli, A. *Gazz. Chim. Ital.* **1987**, *117*, 65.
(3) Pellecchia, C.; Longo, P.; Grassi, A.; Ammendola, P.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 277.
(4) Weill, G.; Vogl, O. *Polym. Bull.* **1978**, *1*, 181.
(5) Sato, H.; Tanaka, Y. In *NMR and Macromolecules*; Randall, J. C., Ed.; ACS Symposium Series 247; American Chemical Society: Washington, DC, 1984; pp 181-196.
(6) Grant, D. M.; Paul, E. G. *J. Am. Chem. Soc.* **1964**, *86*, 2984.
(7) Zucchini, V.; Albizzati, E.; Giannini, V. *J. Organomet. Chem.* **1971**, *26*, 357.
(8) Zambelli, Al.; Ammendola, P.; Grassi, A.; Longo, P.; Proto, A. *Macromolecules* **1986**, *19*, 2703.

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Electronic Spectra of Hindered Silyl- and Organo-Substituted Polysilylenes†

High molecular weight polysilylenes are receiving considerable attention as photoresists[1] and photoconductors.[2] We have examined the absorption and emission spectra of a large number of linear polysilylenes[3] in order to provide photophysical evidence for the underlying causes for the photosensitivity of these unusual σ-backbone polymers and to gain insight into the mechanisms of charge and energy transport. These studies indicated that increasing the size of the substituent moieties bonded to the silicon main chain both reduced the transition energy for the first UV absorption[3] and increased the photosensitivity[1a,b] for alkyl-substituted polymers.

Although increasing the size of the substituent moiety has a pronounced effect on photosensitivity, this was not strongly reflected in the fluorescence quantum yields for these polymers. The small observed effect on the fluorescence quantum yields with substituent size increase (0.42 in poly(cyclohexylmethylsilylene) vs. 0.76 in poly(*n*-propylmethylsilylene)) may result from either an increased intersystem crossing rate or from more efficient internal conversion as the transition energy decreases. The phosphorescence behavior suggested that the immediate

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Table I
Absorption and Emission Spectral Data for Silyl- and Organo-Substituted Polysilylenes

substituents	$\bar{M}_w \times 10^{-3}$	abs max, nm	fluor max, nm	fluor yield	abs[a] width	fluor,[a] width
c-Hex, Me,[b,d] *t*-Bu, Me	119	312.0	347.5	0.034 ± 0.005	51.0	22.0
c-Hex, Me	141	317.0	345.0	0.42 ± 0.02	52.0	17.0
n-Pr, Me	270	308.0	340.0	0.76 ± 0.02	47.0	16.0
Me$_3$Si, Me	359	294.0	335.0	0.026 ± 0.01	50+	32.0[c]
Me$_3$Si, Me; Me$_2$	33	295.0	330.5	0.138 ± 0.007	50.0	16.0
Me$_3$Si, Me; *n*-Pr, Me	43	304.0	338.0	0.423 ± 0.017	45.0	16.0
Me$_3$Si, Me; *c*-Hex, Me	164	308.0	343.0	0.061 ± 0.005	45.0	18.0
Me$_3$Si, Me; Ph, Me	169	308.0	343.0	0.068 ± 0.005	51.0	18.0

[a] Full width at half-maximum in nanometers. [b] Equimolar comonomer feed ratios in all copolymers. [c] Shows structure at room temperature. [d] Insoluble in hexane, spectrum in toluene; all others are for hexane solutions.

We have synthesized and studied a series of novel polysilylenes having the even larger substituents, *tert*-butyl and trimethylsilyl. We report here the influence of these substituents on absorption and fluorescence emission spectra. From these studies, we conclude that the substituent size dependence of the fluorescence quantum yields is attributable to an increased rate of internal conversion with decreasing transition energy. The incorporation of the trimethylsilyl moiety, however, apparently also increases the intersystem crossing rate substantially, probably as a result of more effective spin–orbit coupling. Thus, trimethylsilyl substitution both reduces fluorescence yield and increases photochemical backbone scission, while *tert*-butyl substitution results in *decreased* photosensitivity as well as reduced fluorescence.

Experimental Section. Fluorescence and absorption spectra were obtained by using the apparatus previously described.[3] Quantum yields for fluorescence were measured by the technique of Renschler and Harrah[4] using *p*-terphenyl as a standard. Toluene and hexane were used as solvents in these measurements and were distilled from NaK alloy to remove water and other reactive impurities. Polymers were synthesized by the method of Zeigler[3,5] and purified by several precipitations from different solutions with nonsolvents.

Results and Discussion. The spectral characteristics of the polymers studied are summarized in Table I. The characteristics of the *n*-propylmethylsilylene and the cyclohexylmethylsilylene homopolymers have been previously reported[3] and are included here for comparison. With the exception of the cyclohexylmethylsilylene/*tert*-butylmethylsilylene copolymer, these data are for hexane solution. The insolubility of this highly branched polymer in hexane required the use of toluene to obtain solution spectra. At room temperature, other polysilylenes show little solvent influence on their spectra or emission quantum yields.[3]

Several striking observations are apparent from these data. The variation of transition energy with substituent size observed for the alkyl polymers does persist in the trimethylsilyl copolymers but the absorption maxima are substantially blue-shifted from their alkyl substituted analogues.[3] The fluorescence quantum yields for the trimethylsilyl polymers are substantially lower than those of their alkyl counterparts. Aromatic substitution in these copolymers does not cause spectral red shifts relative to alkyl substitution (cf. phenylmethylsilylene vs. cyclohexylmethylsilylene copolymers). The alkyl copolymer cyclohexylmethylsilylene/*tert*-butylmethylsilylene has a very low fluorescence quantum yield, comparable to that of the trimethylsilyl homopolymer.

In this study, no direct measurements of photochemical yield were made. The initial rates of bleaching of fluorescence for solutions of comparable absorbance were observed in the spectrometer and, while these rates are not a quantitative measure of photochemical sensitivity, they do give a rough estimate of the rate of scission of the polysilylene backbone. From this observation, we estimate that the trimethylsilyl polymers are 2–5 times more easily photolyzed in solution than the *n*-propylmethylsilylene homopolymer. Surprisingly, the *tert*-butyl-substituted copolymer appears *less* sensitive than the *n*-propylmethylsilylene homopolymer.

The observation here, that the polymers with the lowest quantum yields are the most photosensitive [(trimethylsilyl)methylsilylene homopolymer] *and* the least photosensitive (*tert*-butyl copolymer), seems to indicate that several competing factors are influencing the photochemical yield. The fluorescence yield is a measure of the ratio of the radiative decay rate to the rates of all other nonradiative deactivating processes. These include intersystem crossing, singlet-mediated photochemistry, and internal conversion. The relative stability of the *tert*-butyl-substituted copolymer combined with its low fluorescence quantum yield indicates that the increase in size of the *tert*-butyl moiety over the cyclohexyl has significantly increased the rates of nonreactive decay, in this case, most probably the internal conversion rate, without significantly affecting intersystem crossing. On the other hand, in the very photosensitive (trimethylsilyl)methylsilylene homopolymer with a similar fluorescence quantum yield, at least some of the photoreaction pathways (intersystem crossing, singlet photochemistry) have been enhanced.

It is tempting to conclude from this comparison that an increase in substituent size can increase the internal conversion rates. Siebrand and Siebrand and Williams[6] have shown that, in aromatic hydrocarbons, the rate of internal conversion increases as the transition energy decreases and is proportional to the anharmonicity of the molecular vibration(s) determining the Franck–Condon factors for internal conversion. For aromatic hydrocarbons, the C–H stretching vibrations are of highest energy and make the major contribution to internal conversion. With the introduction of the *tert*-butyl moiety on the silicon chains, the transition onset and fluorescence maximum energies are lowered and additional hydrogens added adjacent to the chain. Furthermore, the steric crowding with this substituent present may increase the vibrational anharmonicity for the methyl C–H and the Si–Si chain bonds. All of these factors favor an increased internal conversion rate. While the introduction of the trimethylsilyl moieties gives a size increase, even over the *tert*-butyl, they also may introduce additional photochemical reaction complexity such as side-chain cleavage and, through the internal heavy atom effect,[7] enhanced intersystem crossing. Here we feel that although additional, singlet, photoreaction pathways are possible, the principal effect is to increase the intersystem crossing rate, since we have previously shown[1a,b,3] that the triplet is the most likely photochemical precursor for alkylsilylene homo- and copolymers.

precursor to photochemistry is the triplet.[1a,b,2] Thus, it is probable that the size effects on the photochemistry result from distortions in the triplet rather than the singlet state.

The trimethylsilyl-containing copolymers show no regularity in the variation of fluorescence quantum yield with comonomer size. The smallest comonomer, dimethylsilylene, has a quantum yield intermediate between the largest and next largest comonomers. The absorption and fluorescence band maxima, however, are related to size in much the same fashion as in the alkyl series.

The similarity in behavior of the (trimethylsilyl)methyl-substituted copolymers with cyclohexylmethylsilylene and phenylmethylsilylene comonomers is striking. The absorption maxima, the fluorescence maxima, the fluorescence quantum yields, and the fluorescence bandwidths are the same within experimental error. Only the absorption bandwidths differ and this is most probably a consequence of a second, $\pi-\pi^*$, band at about 280 nm in the phenyl moieties. The phenylmethylsilylene and cyclohexylmethylsilylene homopolymers show entirely different behavior. The poly(phenylmethylsilylene) absorption maximum is shifted 20–22 nm to the red from that of poly(cyclohexylmethylsilylene), a phenomenon that has been attributed to mixing of the ring π states with the chain σ's.[3,8] Apparently the introduction of the trimethylsilyl substituents effectively quenches this $\pi-\sigma$ interaction. The large size of the trimethylsilyl may substantially alter the rotational configuration of the rings with respect to the silicon chain, making this $\pi-\sigma$ mixing less favorable.

Conclusions. The introduction of trimethylsilyl substituents onto polysilylene chains substantially reduces the fluorescence quantum yields over those of the alkyl-substituted polysilylenes. This decrease in fluorescence yield is accompanied by an apparent increase in photosensitivity. Since previous work suggests that triplets are the precursors to photochemistry in alkyl polysilylenes, we suggest that the heightened photosensitivity of these materials is due to an augmentation of the intersystem crossing rate, although the operation of singlet photochemistry, perhaps involving side-chain cleavage, cannot be rigorously ruled out at this time. The increased photosensitivity of the (trimethylsilyl)-substituted polysilylenes cannot be attributed to a substituent size effect since incorporation of a *tert*-butyl moiety in place of the trimethylsilyl group reduces the fluorescence yield without causing increased photochemical sensitivity.

In phenyl-substituted copolymers, the trimethylsilyl unit quenches the $\pi-\sigma$ mixing of the chain and ring states, since little difference exists in the spectroscopic properties between phenyl and cyclohexyl substitution in these copolymers. Work is continuing to ascertain the role of singlet states in the photochemistry of silyl-substituted polysilylenes and to characterize the applicability of these new polymers as resists.

Registry No. c-Hex(Me)SiCl$_2$ (homopolymer), 88002-85-1; (c-Hex(Me)SiCl$_2$)(t-Bu(Me)SiCl$_2$) (copolymer), 109281-90-5; Pr(Me)SiCl$_2$ (homopolymer), 88002-81-7; Me$_3$(Me)SiCl$_2$ (homopolymer), 109088-90-6; (Me$_3$Si(Me)SiCl$_2$)((Me)$_2$SiCl$_2$) (copolymer), 109281-91-6; (Me$_3$Si(Me)SiCl$_2$)(Pr(Me)SiCl$_2$) (copolymer), 109088-91-7; (Me$_3$Si(Me)SiCl$_2$)(c-Hex(Me)SiCl$_2$) (copolymer), 109088-92-8; (Me$_3$Si(Me)SiCl$_2$)(Ph(Me)SiCl$_2$) (copolymer), 109088-93-9.

References and Notes

(1) (a) Zeigler, J. M.; Harrah, L. A.; Johnson, A. W. *SPIE Adv. Resist Technol. Process. II* **1985**, *539*, 166–174. (b) Zeigler, J. M.; Harrah, L. A. U.S. Patents 4 587 205 and 4 588 801. (c) Hofer, D. C.; Miller, R. D.; Willson, C. G. *SPIE Adv. Resist Technol. Process. I* **1984**, *469*, 16.

(2) Kepler, R. G.; Zeigler, J. M.; Kurtz, S. R.; Harrah, L. A. *Phys. Rev. B* **1987**, *35*, 2818.

(3) (a) Harrah, L. A.; Zeigler, J. M. *Macromolecules* **1987**, *20*, 601. (b) Harrah, L. A.; Zeigler, J. M. *Symposium on Polymer Photophysics*, Meeting of the American Chemical Society, Sept, 1986, Anaheim, CA. (c) Harrah, L. A.; Zeigler, J. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1986**, *27*, 356.

(4) Renschler, C. L.; Harrah, L. A. *Anal. Chem.* **1983**, *55*, 798.

(5) (a) Zeigler, J. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1986**, *27*, 109–110. (b) Zeigler, J. M.; Harrah, L. A.; Johnson, A. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*, 424.

(6) (a) Siebrand, W. *J. Chem. Phys.* **1966**, *44*, 4055. (b) Siebrand, W.; Williams, D. F. *J. Chem. Phys.* **1967**, *46*, 403. (c) Siebrand, W. *J. Chem. Phys.* **1967**, *47*, 2411. (d) Siebrand, W.; Williams, D. F. *J. Chem. Phys.* **1968**, *49*, 1860.

(7) See, for example: Becker, R. S. *Theory and Interpretation of Fluorescence and Phosphorescence*; Wiley-Interscience: New York, 1968; pp 127–155.

(8) (a) Hague, D. N.; Prince, R. M. *Proc. Chem. Soc.* **1965**, 4690. (b) Pitt, C. G.; Jones, L. L.; Ramsey, B. G. *J. Am. Chem. Soc.* **1967**, *89*, 5471.

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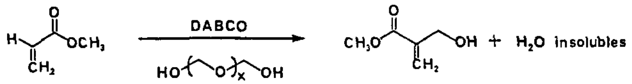
New Difunctional Methacrylate Ethers and Acetals: Readily Available Derivatives of α-Hydroxymethyl Acrylates

It has been reported that a number of aldehydes can be coupled with acrylate esters under mild conditions in the presence of DABCO (1,4-diazabicyclo[2.2.2]octane).[2-5] Using this approach, we have synthesized and polymerized the simplest derivative of methyl acrylate 1 obtained from formaldehyde (as formalin).[6]



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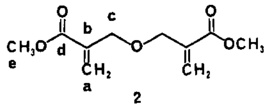
Compound 1 can also be made in ca. 30% yield from paraformaldehyde, the low molecular weight polymer of formaldehyde.[7] Workup of the reaction mixture by water extraction resulted in a water-insoluble fraction which did not display hydroxyl peaks in the IR. GC analysis indicated a complex mixture of products. Column chromatography[7] resulted in separation of the three main components 2–4.



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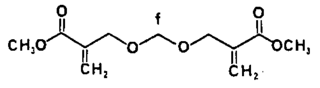

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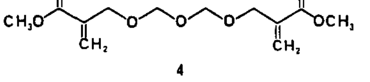

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Identification of these compounds involved purification and spectral characterization.[8] While none of the three displayed alcohol peaks in the IR, they all showed bands corresponding to ester and conjugated olefin groups. Peaks later identified as either and acetal bands were also observed. Most informative were the ^{13}C NMR spectra shown in Figure 1. Peaks were evident for all carbons found in the alcohol 1 but with significant differences in

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