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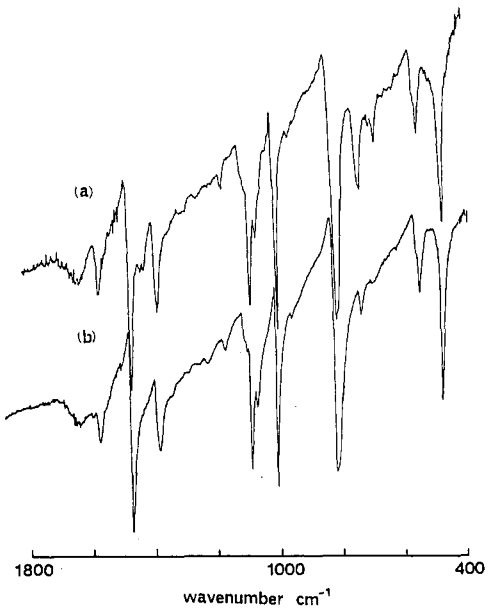

**Figure 1.** IR spectra of the obtained PPS (a) and commercially available PPS (noncuring type) (b).

diphenyl disulfide were necessary to give PPS quantitatively. Control experiments using diphenyl sulfide and thiophenol in the presence of $AlCl_3$ at room temperature did not give any polymer. These results suggest that the cation which is produced by cleavage of the S–S bond of diphenyl disulfide with the Lewis acid is an active species of this polymerization and substitutes electrophilically, on the phenyl ring as a Freidel–Crafts reaction.

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**Registry No.** PPS (homopolymer), 59371-97-0; PPS (SRU), 25212-74-2; $TiCl_4$, 7550-45-0; $AlCl_3$, 7446-70-0; $SbCl_5$, 7647-18-9; $WCl_5$, 13470-14-9; $C_6H_5SC_6H_5$, 139-66-2; thiophenol (homopolymer), 33411-63-1.

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# Poly[1-(trimethylsilyl)-2-propen-1-one]: The First Example of a Poly($\alpha,\beta$-unsaturated acylsilane)

Electronic excitation involving n → $\pi^*$ transitions in polymers containing pendant carbonyl chromophores results in photodegradation of the polymer via either the Norrish type I or type II mechanisms. In Norrish type I processes, a C–C bond adjacent to the carbonyl group is cleaved and CO is eliminated, resulting in the production of free-radical species. Norrish type II processes occur by a photoelimination reaction which involves hydrogen atoms at the carbon $\gamma$ to the carbonyl group which leads directly to main-chain scission,[1] whereas the type I process only leads to scission when the radical formed by $\alpha$-cleavage is a stable tertiary radical and there is little or no geminate recombination.[2]

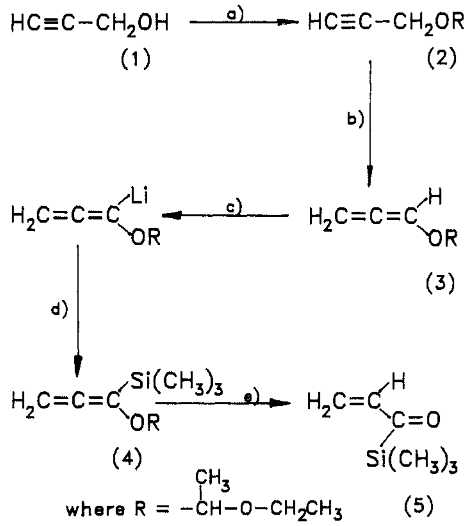
Photodegradation, both in the solid state and solution, of poly(3-methyl-3-buten-2-one) (PMIPK), poly(2-methyl-1-phenyl-2-propen-1-one), and poly(methyl methacrylate) (PMMA), all of which have methyl substituents on the carbon $\gamma$ to the carbonyl group, proceeds mainly via the type I process.[3] The same is true for the majority of polyketones containing hydrogen atoms at the $\gamma$ carbon, provided they are irradiated below their glass transition temperature ($T_g$). Although one would expect the type II process to prevail, the reduced mobility of the polymer chain in the glassy solid state makes the cyclic transition state required for the Norrish type II mechanism more difficult to attain.[1b]

The main-chain scission which attends photodegradation of these polyketones is utilized in certain practical applications, most notably as resists in the lithographic fabrication of semiconductor devices[4a] and, to a lesser extent, as photodegradable packaging materials.[4b] In general, the molar absorptivity of the carbonyl chromophore in these polymers is very low, thus necessitating long exposure times in lithographic applications. Acylsilanes ($\alpha$-silyl ketones),[5] on the other hand, exhibit molar absorptivity several times higher than that of the carbon analogues. In these compounds, the silicon atom is directly bonded to the carbonyl carbon which results in a large bathochromic shift in the electronic excitation spectrum of the carbonyl group.[5-11] The well-known n → $\pi^*$ transition of aliphatic ketones at 280 nm ($\epsilon \approx 30$) is red-shifted in the case of the acylsilanes by 100–180 nm.[6] The transition also has greater intensity ($\epsilon \approx 130$) and the absorption spectrum exhibits a well-developed vibrational structure. There has been some controversy concerning the assignment of the long-wavelength absorption band of the acylsilanes. Most authors believe it is due to the n → $\pi^*$ transition as in the case of the aliphatic ketones. Ramsey et al.,[10] on the other hand, have attributed it to the $\sigma \rightarrow \pi^*$ transition involving the $\sigma$ electrons of the Si–C bond.

The magnitude of the red shift is determined by the electronic structure of the acylsilane.[6,9,11] An increased electron delocalization in the molecule caused by the introduction of conjugation into the $\pi$-electron system, can shift the transition to as high as 540 nm.[6,12,13] These observations suggest that poly($\alpha,\beta$-unsaturated acylsilanes) might exhibit higher photosensitivity to UV radiation than their carbon analogues. The former also possess a high silicon content which would be advantageous in microlithographic applications.[14]

Although there does not appear to be any prior literature reference to these polymers, the $\alpha,\beta$-unsaturated acylsilanes themselves are known to be light and heat sensitive and can only be stored at low temperatures in the presence of free-radical scavengers.[12,15c] This instability suggested to us that polymerization of these compounds may indeed

**Scheme I**
**Synthesis of 1-(Trimethylsilyl)-2-propen-1-one (5)[a]**



[a] Reaction conditions: (a) $H_2C{=}CHOCH_2CH_3$, *p*-TsOH; (b) *t*-BuOK, 2–3 h, 60 °C; (c) *n*-BuLi, THF, −70 °C, 1–5 min; (d) $Me_3SiCl$, −70 °C; (e) THF, 0.05 M $H_2SO_4$, 40 min at room temperature.

proceed very readily and led us to investigate the polymerization of simple homologues. In this paper, we present initial results on the polymerization of 1-(trimethylsilyl)-2-propen-1-one (VTMSK) and report some properties of the novel organosilicon polymer, poly[1-(trimethylsilyl)-2-propen-1-one] (PVTMSK).

**Synthesis of VTMSK.** Although several synthetic routes to simple acylsilanes have been developed,[5,15] the preparation of conjugated $\alpha,\beta$-unsaturated acylsilanes is a more challenging task as the intermediates and the final products are quite reactive. 1-(Trimethylsilyl)-2-propen-1-one (**5**) used in this study was synthesized by a procedure outlined in Scheme I (all steps were carried out in the presence of a free-radical inhibitor).[12]

**Polymerization of VTMSK.** Most simple enones polymerize readily in the presence of free-radical initiators. Only in the case of severe steric crowding such as that present in 2,4,4-trimethyl-2-penten-3-one (isopropenyl *tert*-butyl ketone) is the free-radical polymerization prevented.[16] We found that VTMSK is also readily polymerized. In fact, pure VTMSK left for several hours at room temperature solidified into a hard, glassy, high molecular weight product ($\bar{M}_n = 2.1 \times 10^5$, $\bar{M}_w/\bar{M}_n = 4.2$).[17] Polymerization occurred even in the presence of oxygen.

Subsequent polymerizations carried out under controlled conditions confirmed the easy polymerization of this monomer. For example, monomer which had been freed of inhibitor by a room-temperature distillation into a liquid-nitrogen-cooled flask polymerized readily even in the absence of an added initiator. The yield of polymer after 24-h bulk polymerization was over 90% ($\bar{M}_n = 1.4 \times 10^5$, $\bar{M}_w/\bar{M}_n = 5.83$). In the case of free-radical-initiated solution polymerization (0.83 M solution of VTMSK in hexane, 0.2 mol % AIBN, oxygen-free conditions), the conversion after 24 h at 44 °C was 55.6% ($\bar{M}_n = 8.14 \times 10^4$, $\bar{M}_w/\bar{M}_n = 2.04$).

PVTMSK is soluble in numerous organic solvents, including hexane, but is insoluble in methanol. Precipitation conditions are tricky as many solvent–nonsolvent combinations lead to emulsions or highly swollen gels. Only methanol was successfully used as a precipitant, although the polymer precipitated in this solvent was still strongly swollen. These observations indicate the unusually high solubility of PVTMSK which is a common characteristic of many organosilicon polymers.

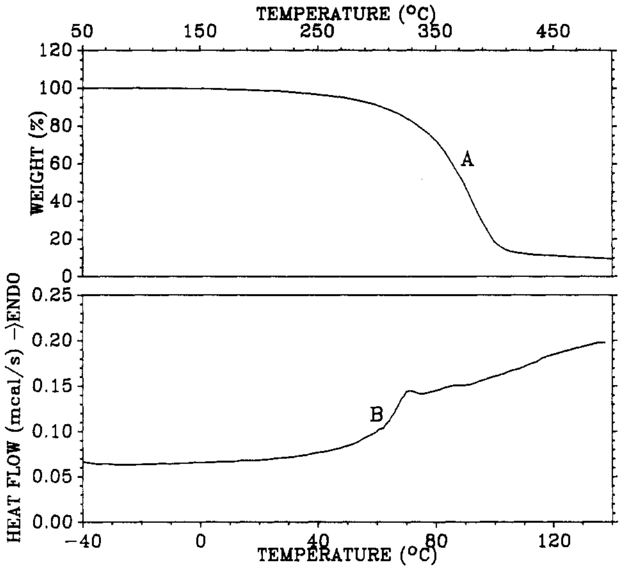


**Figure 1.** (A) Thermogravimetric analysis data for PVTMSK (heating rate 20 °C/min in air); (B) DSC curve for PVTMSK (heating rate 10 °C/min in nitrogen).

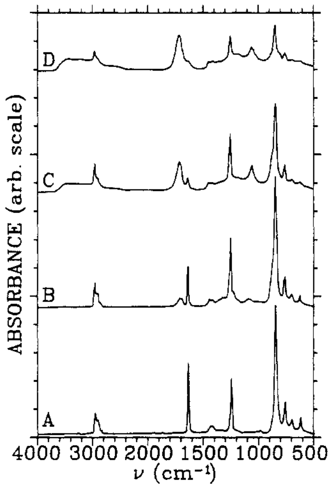


**Figure 2.** IR spectrum of a solid PVTMSK film (A). Spectra B, C, and D were recorded after exposure of the film to doses of deep-UV radiation equal to 1, 3, and 5 J/cm$^2$, respectively.

**Thermal Properties.** Thermogravimetric analysis (TGA) shows that the weight loss during heating of PVTMSK in air begins at ca. 150 °C, and the onset of thermal decomposition is at 340 °C (Figure 1, curve A). In a typical TGA experiment, ~95% of the initial weight remained at 260 °C which reduced to 15% at 400 °C. Since PVTMSK contains 21.9% Si, these data imply that volatile silicon compounds must be lost during thermal decomposition. The glass transition temperature of PVTMSK was 64 °C (Figure 1, curve B). During the DSC experiment, we observed an exothermic process at ca. 150 °C which proceeded without a significant weight change. The nature of this process is currently under investigation.

**Spectral Properties.** The strong, characteristic $\nu_{C=O}$ band in PVTMSK appears at 1636 cm$^{-1}$ (Figure 2, curve A). This is slightly shifted from the frequency observed for the conjugated monomer (1639 cm$^{-1}$) and is somewhat less than that for 1-(trimethylsilyl)-1-ethanone (acetyltrimethylsilane) (1645 cm$^{-1}$),[6,15a] which may be considered as a low molecular weight analogue of PVTMSK. The carbonyl absorption in the carbon analogue of PVTMSK, poly(vinyl *tert*-butyl ketone), appears at 1695 cm$^{-1}$. Other

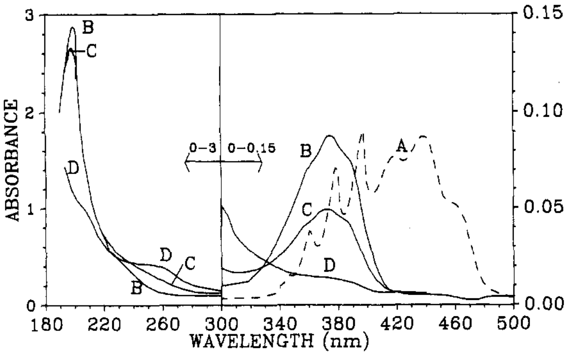


**Figure 3.** UV spectra of VTMSK (A) and PVTMSK (B) in hexane at 1.5 × $10^{-3}$ mole/L. Spectra C and D are those for solution B irradiated in deep-UV with an incident dose of 1 and 5 J/cm$^2$, respectively.

characteristic bands include $\delta_s(CH_3)$ in $H_3CSi\lessdot$ at 1249 cm$^{-1}$ and a strong band at 843 cm$^{-1}$ ($Si(CH_3)_3$).

IR spectra of a PVTMSK film before and after irradiation with mid- and deep-UV radiation[18] in air show that the $\nu_{C=O}$ band at 1636 cm$^{-1}$ disappears upon exposure (Figure 2, curves B-D) and is replaced by a broader carbonyl band at 1718 cm$^{-1}$. Two new bands also appear at 1055 and 1180 cm$^{-1}$, the former indicating possible formation of Si–O bonds. Similar spectral changes have been observed after heating the film in air at temperatures exceeding 120 °C. TGA shows no weight loss at such temperatures, thus it seems that there occurs some as-yet unspecified thermal rearrangement involving the TMS–CO– moiety.

The electronic spectra of VTMSK and its polymer are shown in Figure 3. The characteristic yellow color of the monomer caused by the absorption peak centered at 434 nm ($\epsilon$ = 96.4)[12] (Figure 3, curve A) disappeared after polymerization as the absorption band shifted to higher energies ($\lambda_{max}$ = 369 nm) (Figure 3, curve B). This blue shift is caused by an increase in the energy of the n (or $\sigma$) → $\pi^*$ transition resulting from the loss of conjugation with the vinyl group. The vibrational structure visible in the spectrum of the monomer is largely lost, although two small shoulders at ca. 350 and 385 nm can still be seen. The position of the short-wavelength $\pi \rightarrow \pi^*$ transition at 195 nm remained unchanged after polymerization, although the transition is several times weaker than in the monomer. The value of $\lambda_{max}$ is identical (195 nm) with that reported for 1-(trimethylsilyl)-1-ethanone.[6]

We found that the 369-nm band bleaches on exposure to deep- and mid-UV radiation[18] (Figure 3, curves C and D). The intensity of this band decreased both in the solid state and solution to 55% and 12% of the original value after exposure to incident doses of 1 and 5 J/cm$^2$, respectively. Concomitant with the disappearance of the 369-nm band was the appearance of a new, weaker absorption band at ca. 255 nm. Interestingly, no significant changes were observed in the UV absorption spectrum of the monomer solution after irradiation under similar conditions. This fact is rather surprising, since VTMSK has been reported to be light sensitive.

We have found that the molecular weight of PVTMSK decreases after exposure of the polymer to deep- and mid-UV radiation both in the solid state and in solution.[18] This UV-induced degradation suggests lithographic application as a positive resist. Films selectively exposed to deep- and mid-UV were developed by spraying with 2-propanol. PVTMSK in the form of a thin (0.3 $\mu$m) film on silicon or in chloroform solution also degraded after several days of exposure to fluorescent light in the laboratory.

The lithographic sensitivity of PVTMSK was relatively low, requiring UV doses in the range 300–500 mJ/cm$^2$ to remove the film completely by spraying with 2-propanol. In addition, swelling of the polymer caused some pattern distortion. Films exposed to lower doses of UV radiation became very rough and porous after attempted development. These properties are probably related to the low $T_g$ of PVTMSK and its high solubility, and/or they may indicate the occurrence of a competing cross-linking reaction.

Photodegradation of PVTMSK both in solution and in the solid state may proceed by a photochemical rearrangement previously found in the case of acylsilanes and involving the formation of reactive siloxycarbenes:[15d,19]

$$R_3Si{-}C({=}O){-}R \rightarrow [R_3Si{\cdot}C({=}O^{\cdot}){-}R]^* \rightarrow R_3Si{-}O{-}\ddot{C}{-}R$$

The appearance of the 1050-cm$^{-1}$ Si–O band in the IR spectrum of UV-irradiated PVTMSK is in agreement with this hypothesis. The photochemically generated siloxycarbenes may also react with oxygen to give the carbonyl functionality (strong band at 1718 cm$^{-1}$).

We have also found that thin films of PVTMSK are degraded after exposure to a 25-keV electron beam in vacuum. As in the case of development of the UV-exposed films, the pattern developed by spraying with 2-propanol was severely distorted as a result of swelling of the remaining film. The e-beam sensitivity of PVTMSK was comparable to that of PMMA. Microlithographic characterization of PVTMSK and other poly($\alpha,\beta$-unsaturated acylsilanes) currently being investigated in our laboratory will be published elsewhere.

**Acknowledgment.** We thank M. J. Bowden for critical reading of the manuscript, Prof. J. M. Guillet for a sample of poly(vinyl *tert*-butyl ketone), and C. Klausner, T. N. Bowmer and E. Vogel for TGA and DSC analysis.

**Registry No.** VTMSK, 51023-60-0; PVTMSK, 109088-35-9.

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(17) $^{13}$C NMR (12% w/v in $CDCl_3$, 50.1 MHz) −2.58, 28.90, 50.16, 248.63 ppm vs. internal $Me_4Si$; $^1$H NMR (1% in $CDCl_3$, 200 MHz) 0.2, 1.35, 1.85, 2.7 ppm (v br). GPC determinations were carried out using THF as a solvent at 30.0 °C. All molecular weights are given vs. polystyrene standards.

(18) Thin (~0.5 μm) films of PVTMSK were spin coated from solutions in chloroform or chlorobenzene on quartz or NaCl plates or on polished silicon wafers. They were exposed in air to deep-UV radiation from a high-pressure Xe–Hg lamp by using an Optical Associates Inc. light source. The 260 ± 20 nm band was isolated by using a pair of dichroic mirrors, and the mid-UV/vis part of the spectrum was isolated by exposing the samples through an optical-quality glass slide (λ > 300 nm). The radiation doses were measured by using silicon detectors and radiochromic films (Far West Technology).

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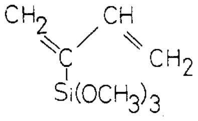
## Polymerization of Monomers Containing Functional Silyl Groups. 4. Anionic Polymerization of 2-(Trimethoxysilyl)-1,3-butadiene

**Introduction.** Anionic living polymerization is one of the most elegant tools for the preparation of polymers having well-defined chain structure.[1] Unfortunately, it is generally considered that the monomers applicable to this method have so far been limited to nonfunctional conjugated hydrocarbon monomers such as styrene and butadiene.

Recently we have found[2,3] that the anionic polymerization of para-substituted styrenes with alkoxysilyl functionality proceeds without chain transfer and termination reactions to afford stable living polymers at −78 °C. As a result, we have obtained well-defined polymers with controlled molecular weight and with narrow molecular weight distributions. In addition, the resulting polymers have an alkoxysilyl group in each monomer unit and therefore may be used for grafting onto inorganic materials as well as for cross-linking between polymer chains by hydrolysis of alkoxysilyl group and subsequent condensation of the silanols formed.

In this paper, we wish to report the anionic polymerization of 2-(trimethoxysilyl)-1,3-butadiene, which has a similar hydrolyzable alkoxysilyl functionality.

**Experimental Section.** 2-(Trimethoxysilyl)-1,3-butadiene (1) was synthesized by the reaction of 1,4-dichloro-2-(trichlorosilyl)-2-butene with methanol, followed by dechlorination with Zn powder.[4] The resulting colorless liquid was purified by fractional distillation under reduced pressure; bp 70–71 °C at 20 mmHg, yield 67% based on the chlorosilane used. $^1$H NMR 3.53 (s, 9 H, $CH_3O$); 5.10, 5.40 (2d, 2 H, $J$ = 10, 17 Hz, $CH_2{=}CH$); 5.73, 5.89 (2s, 2 H, $CH_2{=}C$); 6.44 ppm (dd, 1 H, $J$ = 10, 17 Hz, $CH_2{=}CH$). The anionic polymerization of 1 was carried out under high-vacuum conditions (~$10^{-6}$ mmHg) according to the previously described procedures.[2,3]



1

(*E*)-4-(Trimethoxysilyl)-4-octene and the *E*,*Z* mixture, which imitate the 1,4-structure of monomer unit in the polymer, were synthesized. The *E* isomer was prepared by hydrosilylation of 4-octyne with trimethoxysilane catalyzed by chloroplatimic acid.[5] The *E*,*Z* mixture was obtained by the photoisomerization of the *E* isomer.[6]

$^1$H and $^{13}$C NMR spectra were recorded with a JEOL GX-400 instrument in $CDCl_3$. Gel permeation chromatography (GPC) utilized a Toyosoda HLC-802 instrument with differential refractive index detection, THF being the elution solvent. The number-average molecular weight was measured by vapor pressure osmometry (VPO) using a CORONA 117 instrument in benzene solution.

**Result and Discussion.** Although 2-(trimethoxysilyl)-1,3-butadiene (1) and the related compounds have been recently synthesized by Sato and his co-workers[4] as new silane coupling agents, polymerization of this monomer has not been published up to now. Since we have been carrying out the anionic polymerization of styrenes with functional silyl groups,[2,3] this compound is one of the most attractive diene monomers in the series of our study.

The polymerization of 1 was carried out in THF at −78 °C with oligo(α-methylstyryl)dipotassium as initiator. The polymerization appeared to be extremely slow and to be completed after 90–160 h. Sticky polymers were obtained quantitatively by adding the polymerization mixture into a large excess of water. Alkoxysilyl groups on the polymer chain were stable throughout the anionic polymerization and the workup process. This was confirmed by $^1$H NMR analysis of the polymer.

The results of anionic polymerization of 1 are summarized in Table I. As can be seen, there is fairly good agreement between the predicted molecular weights based on the ratios of monomer to initiator and the observed values measured by VPO. For each polymer, analysis by GPC reveals a unimodal molecular weight distribution of very low polydispersity. These results are consistent with relatively rapid initiation and the absence of chain-transfer and termination reactions during the course of the polymerization of 1.

The microstructure of the resulting polymers is of considerable interest since physical properties of polydienes depend upon the structure of the repeating units. For poly(1) obtained here, we have determined the mode of polymerization (1,4, 1,2, or 3,4) and geometry of the monomer units (*E* or *Z*) by $^1$H and $^{13}$C NMR spectroscopy. Figure 1 shows the $^1$H NMR spectrum of poly(1), where signals due to methylene protons of the main chain and methoxy protons appeared at 2.2 and 3.5 ppm, respectively. In the olefinic proton region, only two individual peaks centered at 6.14 and 6.21 ppm were observed. The relative integrated intensity of this spectrum showed that the proton ratio was exactly 1 ($=$CH):4 ($-CH_2$):9 ($-OCH_3$). This strongly suggests that poly(1) prepared in this study consists of 1,4-adducts. The appearance of two peaks in the olefinic region in Figure 1 indicates that monomer units are incorporated as a mixture of geometric isomers, *E* and *Z*. These peaks were assigned by comparing their chemical shifts with those of well-defined, low molecular weight model compounds, (*E*)-4-(trimethoxysilyl)-4-octene and the *E*,*Z* mixture. The chemical shifts of olefinic protons in these model compounds are summarized in Table II. As

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