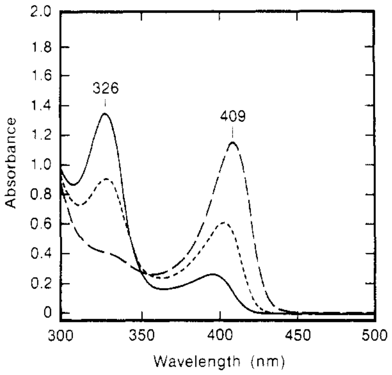

Figure 2. Thermochromism of poly(bis(*p*-*n*-butoxyphenyl)silane) in *p*-*tert*-butylbenzene: (—) 35 °C, (- - -) 75 °C, (– –) 150 °C.

2 shows the thermochromic behavior for a solution of **3** in *p*-*tert*-butylbenzene. The spectral changes observed with temperature are completely reversible. The implication from the variable temperature behavior of **3** is that backbone conformational changes are occurring and at high temperatures significantly longer planar zigzag segments of the polymer chain are present. The UV spectra of the poly(bis(*p*-alkoxyphenyl)silanes) at elevated temperatures closely resemble those previously reported for the poly(bis(*p*-alkylphenyl)silanes) at ambient temperatures, although the spectral width of the long wavelength absorption is somewhat greater for the former.

The origin of this unusual substituent effect is interesting to contemplate. It seems unlikely in nonpolar solvents that the steric demands of the *p*-alkoxy substituents are significantly greater than those of the comparable *p*-alkyl groups. Furthermore, space-filling molecular models suggest that both types of *p*-aryl substituents can be nicely accommodated into a planar zigzag backbone conformation by a slight twisting of the aromatic rings so that the plane of the ring is not exactly perpendicular to that of the polymer backbone. However, a trans coplanar backbone leads to an alignment of the *p*-alkoxy substituent dipoles on silicon atoms which are 1,3 to one another. Perhaps, it is this unfavorable dipole alignment rather than steric effects which destabilizes the planar zigzag form and causes it to twist.

If this is the case, substitution at the meta positions on the ring relative to silicon should bring some relief, since the substituent dipoles on the aromatic rings positioned 1,3 to one another could adopt a conformation where they are not in alignment. Consistent with this proposal, the UV spectrum of the meta-disubstituted derivative **4** shows a strong, narrow absorption (ϵ/SiSi 18 300, FWHH = 11 nm) at 403 nm with only a weak, barely detectable shoulder at 325 nm.

Similarly, when the symmetrical, substitution pattern of the bis(*p*-alkoxyphenyl)silane polymers was disturbed by either the formation of the 1:1 copolymer **6** or by the generation of the atactic, unsymmetrically substituted homopolymer **5**, changes were observed in the UV spectra. In this regard, the UV spectra of both **5** and **6** exhibited two absorption maxima around 322 and 400 nm, the intensities of which were comparable. These spectra were also thermochromic in the fashion described earlier. In addition, the absorption spectra of **5** and **6** were both solvent dependent. For example, for **5**, the ratio of the absorbance at 324 nm to that at 400 nm changed from a value of 1.3 when measured in hexane to ~0.38 in THF solvent. This solvatochromic behavior is also consistent with the suggestion of a delicate conformational equilibrium which is perturbed by the interaction of the polar solvent with the dipolar substituents.

In summary, the poly(bis(alkoxyphenyl)silanes) constitute another class of substituted silane polymers with interesting spectroscopic properties. The unexpected spectral effects caused by the presence of *p*-alkoxy substituents appear to be conformational in origin as suggested by their thermochromism. In addition, certain unsymmetrically substituted materials are solvatochromic due to conformational changes induced by solute–solvent interactions.

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Registry No. 1 (homopolymer), 116102-67-1; **1** (SRU), 116102-79-5; **2** (homopolymer), 116102-69-3; **2** (SRU), 116102-80-8; **3** (homopolymer), 116102-71-7; **3** (SRU), 116102-81-9; **4** (homopolymer), 116102-73-9; **4** (SRU), 116102-82-0; **5** (homopolymer), 116102-75-1; **5** (SRU), 116102-83-1; **6** (homopolymer), 116102-76-2; **7** (homopolymer), 116102-78-4; **7** (SRU), 116102-84-2.

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Preparation of Controlled Molecular Weight, Olefin-Terminated Polymers by Free Radical Methods. Chain Transfer Using Allylic Sulfides

Carbon-centered radicals react with allylic sulfides of general structure 1, to effect S_H2' displacement of the thiyl group (Scheme I).[1] The mechanism may be visualized as an initial radical addition to the olefinic center of 1 fol-

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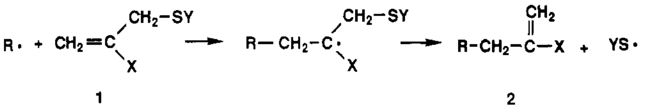
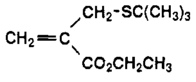
Scheme I



lowed by fragmentation to afford **2**. The process regenerates the double bond adjacent to its original position and expels a thiyl radical.

It seemed to us that this type of reaction could be utilized to effect chain transfer in free radical polymerization, provided certain criteria were met. These include the requirement that the rate constant for addition of macroradicals to the allylic sulfide be comparable in magnitude with the propagation rate constant for the polymerization and that the fragmentation step be fast and efficient to preclude copolymerization of 1 with the monomer. In addition, the expelled thiyl radical YS• must be effective in initiating further polymerization. We now report preliminary experiments which demonstrate that appropriately substituted allylic sulfides can function as ideal chain-transfer agents in free radical polymerization.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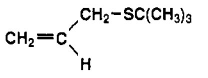
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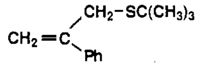
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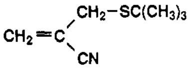
6

When samples of methyl methacrylate containing various concentrations of ethyl [(*tert*-butylthio)methyl]acrylate (**3**)[1b] (Table I, entries 1–4) were polymerized for 1 h at 60 °C with AIBN as initiator, the resultant polymers were of markedly lower molecular weight compared with those prepared in the absence of **3**. The chain-transfer constant (C_x), reflecting the relative rate constants for chain transfer versus propagation and calculated by using the Mayo equation,[2] was 0.74. The compound therefore compares favorably with the commonly used thiols for reducing molecular weight (e.g. *n*-butanethiol, $C_x = 0.67$).[3] Since the yields of polymers were not depressed to a substantial extent by the presence of **3** in the polymerization system, the lowering of molecular weight is likely to occur by a process of true chain *transfer*, rather than by simple termination of the growing polymer chains without reinitiation of new ones.

The thioether **3** was also efficient in lowering molecular weight in styrene polymerizations (Table I, entries 5–8). The chain-transfer constant (60 °C) in this case was 0.95, which is close to the ideal[4] of 1.0 and contrasts with that of a typical thiol (e.g., 1-dodecanethiol, $C_x = 15–19$).[3] Accordingly, polymers prepared at moderate conversions with **3** have a low polydispersity ($\bar{M}_w/\bar{M}_n \simeq 1.7–2.2$).

Other allylic sulfides were also examined as potential chain-transfer agents. The unsubstituted compound **4**[5] showed little activity in reducing molecular weight, presumably because of a lack of activation of the double bond toward radical addition. The styrene derivative **5**,[6] however, was effective in lowering molecular weight, having a chain-transfer constant at 60 °C of 1.24 for the polymerization of methyl methacrylate and 0.80 for the polymerization of styrene. These results are consistent with the expected higher reactivity of **5** toward the electrophilic poly(methyl methacrylyl) radical compared with the more nucleophilic polystyryl radical.

The acrylonitrile derivative **6**[6] was also found to be a useful chain-transfer agent. Its chain-transfer constants were 1.90 and 1.35 in styrene and methyl methacrylate polymerizations, respectively, at 60 °C (Table I, entries 21–27).

Table I
Polymerizations Carried Out at 60 °C in the Presence of Various Allylic Sulfides

entry	allylic sulfide	monomer[a]	10^3[allylic sulfide]/[monomer]	% convrsn	$\bar{M}_n$[b]
1	**3**	MMA	0	14.0	136 700
2	**3**	MMA	1.28	12.8	61 800
3	**3**	MMA	2.37	12.0	40 800
4	**3**	MMA	4.52	10.9	24 500
5	**3**	STY	0	9.4	103 600
6	**3**	STY	1.17	9.2	47 800
7	**3**	STY	2.46	8.7	30 600
8	**3**	STY	4.55	8.4	19 400
9	**4**	STY	0	8.0	118 000
10	**4**	STY	3.04	8.1	112 200
11	**4**	STY	6.18	8.0	124 000
12	**5**	MMA	0	10.9	205 200
13	**5**	MMA	1.17	10.4	46 100
14	**5**	MMA	2.26	10.1	27 900
15	**5**	MMA	4.07	9.4	16 800
16	**5**	MMA	8.00	8.6	9 600
17	**5**	STY	0	8.1	125 000
18	**5**	STY	1.18	8.1	61 200
19	**5**	STY	2.25	7.7	40 500
20	**5**	STY	3.43	7.3	28 900
21	**6**	MMA	0	17.6	181 400
22	**6**	MMA	1.43	14.0	35 500
23	**6**	MMA	2.71	12.5	23 800
24	**6**	MMA	5.24	12.5	12 700
25	**6**	STY	0	12.4	118 700
26	**6**	STY	1.55	11.3	29 800
27	**6**	STY	4.54	11.4	11 700

[a] Methyl methacrylate polymerizations were carried out in neat monomer for 1 h at 60 °C and were initiated with AIBN (12.1 mM); styrene polymerizations were carried out for 3 h at 60 °C in neat monomer containing AIBN (8.37 mM). [b] Number-average molecular weight determined by GPC, calibrated with polystyrene standards.

The mechanism depicted in Scheme I leads to an expectation that the low molecular weight polymer chains prepared by using **3**, **5**, or **6** would be terminated by a double bond. To test this, low molecular weight samples of polystyrene and poly(methyl methacrylate) were prepared by using these compounds and purified by repeated precipitation to remove all traces of the unreacted chain-transfer agent. In the case of poly(methyl methacrylate) prepared with **5**, the ^{1}H NMR spectrum had signals at δ 4.95 and 5.15, confirming the presence of a terminal olefin, and a signal centered at δ 7.2, indicative of a phenyl ring. Using the GPC-derived molecular weight of 3230 and the relative integrals of the above signals and the signal centered at δ 3.55 due to the poly(methyl methacrylate) ester groups, the average number of unsaturated styryl end groups per polymer chain was calculated to be 0.94.[7] A signal at δ 1.24, assigned to the *tert*-butylthio group on the end remote from the styryl group, was insufficiently separated from other signals for a meaningful integral to be obtained. The polymer was shown by elemental analysis to contain sulfur.[8] The relative integrals of the olefinic and aromatic signals showed that **5** did not copolymerize.

Evidence for the presence of unsaturated end groups in low molecular weight polystyrene ($\bar{M}_n$ = 3600) prepared with **5** was also obtained from olefinic signals in the ^{1}H NMR spectrum at δ 4.7 and at δ 5.0. Similarly, polystyrene prepared by using the acrylonitrile derivative **6** had ^{1}H NMR signals centered around δ 5.3 and 5.6 and an IR absorption at 2220 cm^{-1}, which confirms the presence of the α,β-unsaturated nitrile end group. The ^{1}H NMR spectrum of low molecular weight poly(methyl methacrylate) ($\bar{M}_n$ = 4900) prepared with **3** contained signals at δ 5.45 and 6.20, due to the double bond, and a signal centered at δ 4.15, consistent with the incorporation of the ethyl ester moiety.

Since styryl, α,β-unsaturated ester, and α,β-unsaturated nitrile end groups are potentially polymerizable, the low molecular weight polymers prepared by using **3**, **5**, and **6** are likely to possess the properties of a macromonomer. We are currently investigating both the reactivity of these polymers and the likelihood that appropriately substituted allylic sulfides will be useful for the preparation of low molecular weight mono- and di-end-functional polymers.

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Registry No. **3**, 92822-43-0; **5**, 116233-34-2; **6**, 116233-35-3; STY, 100-42-5; MMA, 80-62-6.

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(6) These compounds were prepared by reaction of the appropriate bromo compound with 2-methyl-2-propanethiolate ion. They were characterized by ^{1}H NMR and mass spectra and their purity was checked by TLC on silica gel.

(7) The ^{1}H NMR free induction decay was transformed, rephased, and carefully integrated five times. The standard deviation of the ratios determined in this way was 3%.

(8) Although the analyzed sulfur content was 0.6%, which is less than that expected (1%), if every polymer chain is initiated with a butylthio group, the precision of the determination is such that accurate quantitation at this low level is not possible. The sulfur content of polystyrene ($\bar{M}_n$ = 3600) prepared with **5** and of poly(methyl methacrylate) ($\bar{M}_n$ = 4900) prepared with **3** was found to be 0.8% and 0.6%, respectively.

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CORRECTIONS

Toshio Masuda,* Eiji Isobe, and Toshinobu Higashimura*: Polymerization of 1-(Trimethylsilyl)-1-propyne by Halides of Niobium(V) and Tantalum(V) and Polymer Properties. Vol. 18, Number 5, May 1985, p 841.

The UV–visible spectrum and the values of $\lambda_{\max}$ and $\epsilon_{\max}$ were incorrect. The $\lambda_{\max}$ and $\epsilon_{\max}$ should read 234 nm and 3400, respectively; there is no absorption above 290 nm. Similar absorptions are observed in the following analogues: $(\mathrm{MeC{\equiv}CSiMe_2}\text{-}n\text{-}\mathrm{C_6H_{13}})_n$ $\lambda_{\max}$ 235 nm, $\epsilon_{\max}$ 3480; $(\mathrm{MeC{\equiv}CSiMe_2CH_2SiMe_3})_n$ $\lambda_{\max}$ 236 nm, $\epsilon_{\max}$ 3480.