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Polymerization of Monomers Containing Functional Silyl Groups. 2. Anionic Living Polymerization of (4-Alkoxysilyl)styrenes

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ABSTRACT: Anionic polymerizations of [4-(dimethylalkoxysilyl)]-, [4-(methyldialkoxysilyl)]-, and [4-(triethoxysilyl)]styrenes were investigated at −78 °C in THF with oligo(α-methylstyryl)dilithium or -dipotassium. Under such conditions, polymerizations of these monomers proceeded as a living system except for the polymerizations of monomers with either the methoxysilyl or ethoxysilyl group initiated with oligo(α-methylstyryl)dilithium. By this method, polymers of predictable molecular weights and narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n$ = 1.04–1.16) were obtained in quantitative yields. The stability of the propagating active ends of the polymers was also investigated under various conditions: at −78 and +30 °C for 0.5 and 24 h with lithium, sodium, and potassium as the countercation.

Introduction

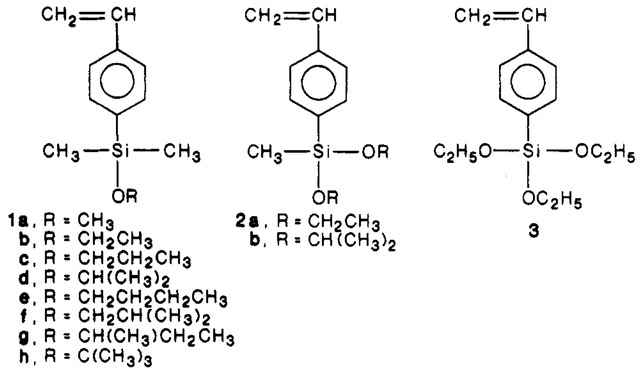
Anionic living polymerization provides a preferred method for synthesizing tailor-made polymers of nearly monodisperse distribution of molecular weight. Unfortunately, the range of vinyl monomers capable of producing persistent living polymers is generally limited to nonpolar conjugated hydrocarbon monomers such as styrene, 1,3-butadiene, and isoprene.[1]

We have recently found that styrene containing an isopropoxysilyl group with hydrolytic potential is anionically polymerized to afford a "living polymer".[2] Such polymers may be very attractive from the viewpoint of molecular design, since they have well-defined structures of predetermined molecular weights and of narrow molecular weight distributions. In addition to this advantage, they are also useful for preparing organic–inorganic composition materials because they are readily subjected to hydrolysis and thus suitable for grafting of the polymers onto silica and metal oxide surfaces.[3]

During the course of our previous study, we also found that in the polymerization of styrene with the less bulky methoxysilyl group, undesirable side reactions occurred and broadened the molecular weight distribution in the resulting polymer. Thus, the choice of alkoxysilyl substituent in the monomer may be important to the success of the living polymerization.

This work has been devoted to determining the influence of the alkoxysilyl group of the styrene derivative on the anionic polymerization. We therefore attempt here a more extensive study on the polymerization behavior of the 11 monomers 1–3 whose structures are shown in Chart I.

Chart I



Experimental Section

Materials. 4-Chlorostyrene was kindly supplied by Hokko Chemical Industry Co., Ltd. It was distilled at 52–54 °C (5 mm) over calcium hydride. α-Methylstyrene, dimethyldichlorosilane, methyltrichlorosilane, dimethyldimethoxysilane, dimethyldiethoxysilane, methyltriethoxysilane, tetraethoxysilane, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol were purified from the commercial products by distillation over calcium hydride. *n*-Pentane and benzene were refluxed over phosphorus pentoxide for 5 h and distilled under a nitrogen atmosphere. Triethylamine and pyridine were refluxed over calcium hydride for 5 h and distilled under a nitrogen atmosphere. Tetrahydrofuran (THF) was used as the solvent in all polymerization experiments. It was refluxed over sodium wire for 5 h and distilled at 65 °C from sodium naphthalide solution. Naphthalene was purified from the commercial product by sublimation. The oligo(α-methylstyryl)dilithium, -disodium, and -dipotassium were freshly prepared just prior to polymerization from the corresponding metal naphthalides and a 2–4 molar quantity of α-methylstyrene at 30 °C for 1 min and then at −78 °C for 5 min. The concentration of metal naphthalide was determined by previous titration with standard 1-octanol in a sealed reactor through break seals under vacuum.[4]

Propoxydimethylchlorosilane. To a stirred solution of dimethyldichlorosilane (22.7 g, 0.176 mol) in *n*-pentane (150 mL) were slowly added 1-propanol (10.6 g, 0.176 mol) and triethylamine (16.7 g, 0.165 mol) in *n*-pentane (150 mL) over a 1-h period at 0 °C under an atmosphere of nitrogen. After the mixture was stirred for 5 h at room temperature, it was filtered and the white solid was washed with *n*-pentane. From the combined *n*-pentane solution, the product was fractionally distilled at 45–50 °C (85 mm) to give 10.6 g (39%) of colorless, liquid propoxydimethylchlorosilane: 60-MHz ^{1}H NMR (CCl_4) δ 3.67 (2 H, t, OCH_2), 1.67–0.73 (5 H, m, CH_2CH_3), 0.40 (6 H, s, $SiCH_3$).

Similarly, the following compounds were obtained. They were colorless liquids. The yields, boiling points, and chemical shifts of the NMR spectra are listed. 2-Propoxydimethylchlorosilane: yield 34%; bp 52–54 °C (110 mm); 60-MHz ^{1}H NMR (CCl_4) δ 4.17 (1 H, m, CH), 1.20 (6 H, d, CCH_3), 0.40 (6 H, s, $SiCH_3$). Butoxydimethylchlorosilane: yield 74%; bp 81 °C (90 mm); 60-MHz ^{1}NMR (CCl_4) δ 3.67 (2 H, t, OCH_2), 1.67–0.73 (7 H, m, $CH_2CH_2CH_3$), 0.40 (6 H, s, $SiCH_3$). 2-Butoxydimethylchlorosilane: yield 59%; bp 70 °C (80 mm); 60-MHz ^{1}H NMR (CCl_4) δ 3.46 (2 H, d, OCH_2), 2.10–1.40 (1 H, m, CH), 0.90 (6 H, d, CCH_3), 0.43 (6 H, s, $SiCH_3$). (2-Methylpropoxy)dimethylchlorosilane: yield 68%; bp 68 °C (80 mm); 60-MHz ^{1}H NMR (CCl_4) δ 4.20–3.60 (1 H, m, CH), 1.73–0.67 (8 H, m, $CH_3CHCH_2CH_3$), 0.42 (6 H, s, $SiCH_3$). (1,1-Dimethylethoxy)dimethylchlorosilane: yield 69%; bp 60–64 °C (120 mm); 60-MHz ^{1}H NMR (CCl_4) δ 1.33 (9 H, s, CCH_3), 0.41 (6 H, s, $SiCH_3$).

Tri(2-propoxy)methylsilane. To a stirred solution of methyltrichlorosilane (22 g, 0.15 mol) in dry pyridine (20 mL) was slowly added 2-propanol (41 g, 0.68 mol) in dry pyridine (20 mL) over a 1- h period at 0 °C under an atmosphere of nitrogen. After the mixture was stirred for 5 h at room temperature and then

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refluxed for 5 h, it was filtered and the white solid was washed with dry benzene. From the combined solutions, the product was fractionally distilled at 102 °C (100 mm) to give 23 g (78%) of colorless, liquid tri(2-propoxy)methylsilane (lit.[5] bp 163 °C (749 mm)).

(4-Vinylphenyl)dimethylmethoxysilane (1a). A solution of dimethyldimethoxysilane (8.4 g, 70 mmol) in dry THF (50 mL) was added dropwise over a 1-h period to a solution of (4-vinylphenyl)magnesium chloride (70 mmol, prepared from 4-vinylphenyl chloride (9.7 g, 70 mmol) and magnesium (2.43 g, 100 mmol) in dry THF (100 mL)). The reaction mixture was stirred at room temperature overnight under a nitrogen atmosphere. The crude product was obtained by direct distillation from the mixture. It was purified carefully by fractional distillation at 64–65 °C (1 mm) (lit.[6] bp 70–72 °C (1 mm)) to give 9.6 g (50 mmol, 71%) of colorless, liquid **1a**: 60-MHz ^{1}H NMR (CCl_4) δ 7.50, 7.27 (4 H, 2 d, phenyl), 6.68 (1 H, 2 d, vinyl CH), 5.69, 5.19 (2 H, 2 d, J = 11, 18 Hz, vinyl CH_2), 3.37 (3 H, s, OCH_3), 0.33 (6 H, s, $SiCH_3$).

(4-Vinylphenyl)dimethylethoxysilane (1b). A reaction similar to the one above was run with dimethyldiethoxysilane (10.3 g, 70 mmol) and (4-vinylphenyl)magnesium chloride (70 mmol) in THF (150 mL). The product was distilled at 80 °C (1 mm) (lit.[6] bp 80–81 °C (1 mm)) to give 6.5 g (30 mmol, 43%) of colorless, liquid **1b**: 60-MHz ^{1}H NMR (CCl_4) δ 7.56, 7.37 (4 H, 2 d, J = 8.0 Hz, phenyl), 6.72 (1 H, 2 d, J = 10.6, 18.0 Hz, vinyl CH), 5.73, 5.21 (2 H, 2 d, J = 10.6, 18.0 Hz, vinyl CH_2), 3.78 (2 H, q, J = 7.0 Hz, OCH_2), 1.22 (3 H, t, J = 7.0 Hz, OCH_2CH_3), 0.30 (3 H, s, $SiCH_3$).

(4-Vinylphenyl)dimethylpropoxysilane (1c). A reaction similar to the one above was run with propoxydimethylchlorosilane (10.4 g, 68 mmol) and (4-vinylphenyl)magnesium chloride (71 mmol) in THF (100 mL). The product was distilled at 75–77 °C (1 mm) to give 9.5 g (43 mmol, 63%) of colorless, liquid **1c**: 60-MHz ^{1}H NMR (CCl_4) δ 7.55, 7.31 (4 H, 2 d, J = 8.0 Hz, phenyl), 6.70 (1 H, 2 d, vinyl CH), 5.73, 5.20 (2 H, 2 d, J = 11, 18 Hz, vinyl CH_2), 3.52 (2 H, t, OCH_2), 1.55 (2 H, m, CH_2), 0.87 (3 H, t, CCH_3), 0.33 (6 H, s, $SiCH_3$).

(4-Vinylphenyl)dimethyl(2-propoxy)silane (1d). A reaction similar to the one above was run with 2-propoxydimethylchlorosilane (10.4 g, 68 mmol) and (4-vinylphenyl)magnesium chloride (70 mmol) in THF (150 mL). The product was distilled at 75–78 °C (1 mm) to give 12.0 g (55 mmol, 80%) of colorless, liquid **1d** (lit.[6] bp 86 °C (0.8 mm)): 60-MHz ^{1}H NMR (CCl_4) δ 7.50, 7.27 (4 H, 2 d, phenyl), 6.65 (1 H, 2 d, vinyl CH), 5.65, 5.17 (2 H, 2 d, J = 11, 18 Hz, vinyl CH_2), 4.30–3.57 (1 H, m, methine CH), 108 (6 H, d, CCH_3), 0.30 (6 H, s, $SiCH_3$).

(4-Vinylphenyl)dimethylbutoxysilane (1e). A reaction similar to the one above was run with butoxydimethylchlorosilane (14.8 g, 89 mmol) and (4-vinylphenyl)magnesium chloride (100 mmol) in THF (160 mL). The product was distilled at 89 °C (2 mm) to give 8.0 g (34 mmol, 38%) of colorless, liquid **1e**: 60-MHz ^{1}H NMR (CCl_4) δ 7.40, 7.17 (4 H, 2 d, phenyl), 6.59 (1 H, 2 d, vinyl CH), 5.62, 5.13 (2 H, 2 d, J = 11, 18 Hz, vinyl CH_2), 3.48 (2 H, t, OCH_2), 1.60–0.53 (7 H, m, $CH_2CH_2CH_3$), 0.31 (6 H, s, $SiCH_3$).

(4-Vinylphenyl)dimethyl(2-methylpropoxy)silane (1f). A reaction similar to the one above was run with (2-methylpropoxy)dimethylchlorosilane (14.8 g, 89 mmol) and (4-vinylphenyl)magnesium chloride (100 mmol) in THF (160 mL). The product was distilled at 84 °C (2 mm) to give 14.3 g (61 mmol, 69%) of colorless, liquid **1f**: 60-MHz ^{1}H NMR (CCl_4) δ 7.49, 7.25 (4 H, 2 d, phenyl), 6.66 (1 H, 2 d, vinyl CH), 5.67, 5.19 (2 H, 2 d, J = 11, 18 Hz, vinyl CH_2), 3.29 (2 H, d, OCH_2), 2.00–1.33 (1 H, m, methine CH), 0.88 (6 H, d, CCH_3), 0.33 (6 H, s, $SiCH_3$).

(4-Vinylphenyl)dimethyl(2-butoxy)silane (1g). A reaction similar to the one above was run with 2-butoxydimethylchlorosilane (14.8 g, 89 mmol) and (4-vinylphenyl)magnesium chloride (100 mmol) in THF (160 mL). The product was distilled at 71 °C (1 mm) to give 14.2 g (61 mmol, 68%) of colorless, liquid **1g**: 60-MHz ^{1}H NMR (CCl_4) δ 5.64, 5.16 (2 H, 2 d, J = 11, 18 Hz, vinyl CH_2), 3.98–3.38 (1 H, m, methine CH), 1.68–0.61 (8 H, m, $CH_3CHCH_2CH_3$), 0.33 (6 H, s, $SiCH_3$).

(4-Vinylphenyl)dimethyl(1,1-dimethylethoxy)silane (1h). A reaction similar to the one above was run with (1,1-dimethylethoxy)dimethylchlorosilane (14.8 g, 89 mmol) and (4-vinylphenyl)magnesium chloride (100 mmol) in THF (160 mL). The product was distilled at 66 °C (1 mm) to give 11.9 g (51 mmol, 57%) of colorless, liquid **1h**: 60-MHz ^{1}H NMR (CCl_4) δ 7.50, 7.22 (4 H, 2 d, phenyl), 6.66 (1 H, 2 d, vinyl CH), 5.67, 5.17 (2 H, 2 d, J = 11, 18 Hz, vinyl CH_2), 1.22 (9 H, s, CCH_3), 0.33 (6 H, s, $SiCH_3$).

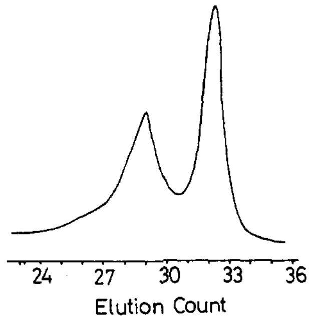


Figure 1. GPC curve for the reaction product from polystyryllithium and poly(**1a**).

(4-Vinylphenyl)methyldiethoxysilane (2a). A reaction similar to the one above was run with methyltriethoxysilane (16.6 g, 86 mmol) and (4-vinylphenyl)magnesium chloride (72 mmol) in THF (140 mL). The product was distilled at 73 °C (1 mm) (lit.[7] bp 80–81 °C (0.2 mm)) to give 5.8 g (24 mmol, 33%) of colorless, liquid **2a**: 60-MHz ^{1}H NMR (CCl_4) δ 7.59, 7.37 (4 H, 2 d, J = 8.0 Hz, phenyl), 6.72 (1 H, 2 d, vinyl CH), 5.73, 5.21 (2 H, 2 d, J = 10.6, 18.0 Hz, vinyl CH_2), 3.78 (4 H, q, J = 7.0 Hz, OCH_2), 1.22 (6 H, t, J = 7.0 Hz, CH_2CH_3), 0.30 (3 H, s, $SiCH_3$).

(4-Vinylphenyl)methyldi(2-propoxy)silane (2b). A reaction similar to the one above was run with tri(2-propoxy)methylsilane (18.9 g, 86 mmol) and (4-vinylphenyl)magnesium chloride (72 mmol) in THF (140 mL). The product was distilled at 82 °C (1 mm) to give 6.6 g (25 mmol, 29%) of colorless, liquid **2b**: 60-MHz ^{1}H NMR (CCl_4) δ 7.46, 7.23 (4 H, 2 d, J = 7.6 Nz, phenyl), 6.63 (1 H, 2 d, J = 11.0, 17.2 Hz, vinyl CH), 5.63, 5.16 (2 H, 2 d, J = 11.0, 17.2 Hz, vinyl CH_2), 4.07 (2 H, 2 q, J = 6.0 Hz, OCH), 1.11 (12 H, 2 d, J = 6.0 Hz, $OCH(CH_3)$), 0.20 (3 H, s, $SiCH_3$).

(4-Vinylphenyl)triethoxysilane (3). A reaction similar to the one above was run with tetraethoxysilane (20.8 g, 100 mmol) and (4-vinylphenyl)magnesium chloride (50 mmol) in THF (150 mL). The product was distilled at 90 °C (1 mm) (lit.[7] bp 92–93 °C (0.2 mm)) to give 13.3 g (50 mmol, 50%) of colorless, liquid **3**: 60-MHz ^{1}H NMR (CCl_4) δ 7.65, 7.35 (4 H, 2 d, phenyl), 6.73 (1 H, 2 d, J = 11, 18 Hz, vinyl CH), 5.71, 5.23 (2 H, 2 d, J = 11, 18 Hz, vinyl CH_2), 3.90 (6 H, q, J = 7.0 Hz, OCH_2), 1.26 (9 H, t, J = 7.0 Hz, CH_2CH_3). Gas chromatography showed that the purity of monomers **1**–**3** used in this study was at least 99.5% after repeated fractional distillation.

In order to remove impurities in the monomers, benzylmagnesium chloride (5 mL, 0.5 M solution in THF) was added to **1**, **2**, or **3** (5.0 g) at 0 °C under a nitrogen atmosphere, and the mixture was stirred for 10 min. It was then degassed and distilled on a vacuum line into ampules fitted with break seals. Thus the monomers distilled from THF solution were obtained and stored at 0 °C until ready for use.

Polymerization Procedure. All polymerizations were carried out at −78 °C with shaking under high-vacuum conditions ($\approx 10^{-6}$ mm) in an all-glass apparatus equipped with break seals. The monomer was added at once to the initiator solution in THF at −78 °C. The polymerizations of **1**, **2**, and **3** were usually completed within 1 min and were terminated with methanol or 1-octanol after 2–10 min. The polymers were precipitated by adding a large excess of methanol. They were redissolved in THF, precipitated into methanol two additional times, and freeze-dried.

Reaction of Polystyryllithium with Poly(1a). Polystyryllithium (1 g, $\bar{M}_n = 1 \times 10^4$), prepared from styrene (1 g, 9.62 mmol) and butyllithium (0.100 mmol) in THF (20 mL) at −78 °C for 10 min, was added to poly(**1a**) (0.192 g, 0.100 mmol of $Si(OCH_3)$ unit in the polymer, $\bar{M}_n = 1 \times 10^4$) in THF (10 mL) at −78 °C. The mixture was stirred overnight at −78 °C and then was poured into a large excess of methanol to precipitate. It was redissolved in THF, precipitated into methanol one more time, and freeze-dried. The polymer weight obtained was near quantitative based on total polymer weights (polystyrene and poly(**1a**)). The gel permeation chromatogram is shown in Figure 1. The first peak

Table I
Anionic Polymerizations of (Alkoxysilyl)styrenes with Oligo(α-methylstyryl)dipotassium in THF at −78 °C for 2–10 min[a]

monomer	monomer, mmol	potassium naphthalide, mmol	α-methylstyrene, mmol	$\bar{M}_n \times 10^4$ calcd	$\bar{M}_n \times 10^4$ obsd[b]	$\bar{M}_w/\bar{M}_n$
1a	5.50	0.0680	0.257	3.2	3.3	1.07
1b	3.57	0.0630	0.454	2.5	2.7	1.10
1c	4.40	0.0670	0.212	3.0	2.9	1.07
1d	7.14	0.0911	0.246	3.5	3.3	1.06
1e	4.13	0.106	0.285	1.9	1.9	1.04
1f	5.08	0.0681	0.196	3.6	3.4	1.06
1g	4.51	0.115	0.290	1.9	1.8	1.06
1h	3.43	0.101	0.229	1.6	1.3	1.09
2a	5.51	0.120	0.410	2.2	2.1	1.07
2b	4.19	0.168	0.376	1.3	1.3	1.07
3	3.87	0.137	0.402	1.6	1.7	1.09

[a] Yields of polymers isolated were 95–100%. Concentrations of active ends were (3.5–4.2) × 10^{-3} M. [b] $\bar{M}_n$(obs) was obtained by VPO in benzene.

(elution count = 32) in the bimodal distribution curve was found to be virtually identical with those of poly(**1a**) and the polystyrene obtained from polystyryllithium. Therefore, it is obvious that the second peak (elution count = 28.8) resulted from the reaction of polystyryllithium with poly(**1a**) to form the graft copolymer. The molecular weight of this copolymer was calculated to be 6 × 10^4 using the standard polystyrene calibration curve. On the basis of these results, we estimate that the graft copolymer is the structure of poly(**1a**) with five polystyrene arms as average.

Determination of Actual Carbanion Content by Titration. The operations were conducted under vacuum conditions by the method previously reported.[8]

Instruments for Measurements. ^{1}H NMR Spectra (60-MHz) were recorded with a JEOL PMX 60 instrument. Gel permeation chromatograms (GPC) were obtained with a Toyo Soda HLC-802 instrument with UV or refractive index detection, THF being the elution solvent. Vapor pressure osmometry (VPO) measurements for the number-average molecular weight determination were made with a Corona 117 instrument in benzene solution.

Results and Discussion

Anionic Polymerizations of 1, 2, and 3. Anionic polymerization of the (monoalkoxysilyl)styrenes **1a–h** was first carried out in THF at −78 °C using oligo(α-methylstyryl)dipotassium as an initiator. In all cases the reaction mixtures turned dark red, which seemed unchanged at −78 °C even after 24 h but disappeared immediately upon treatment with a few drops of methanol. Quantitative yields of polymers were obtained by addition of an excess of methanol to the precipitate. The results are summarized in Table I.

The GPC curves of the resulting polymers all showed single peaks with $\bar{M}_w/\bar{M}_n$ ratios ranging from 1.04 to 1.10.[9] Some representative profiles are illustrated in Figure 2. It can be seen in Table I that there is good agreement between the observed molecular weights determined by VPO and the predicted ones from the monomer to initiator ratios. These results indicate the rapidity of initiation and the lack of termination and transfer reactions in these polymerizations that are characteristic of living polymerization.

It is worthy of note that (dialkoxysilyl)- and (trialkoxysilyl)styrenes **2** and **3** have been anionically polymerized under the same conditions to afford polymers of predictable molecular weights and of narrow molecular weight distributions. The results also confirm a living character of these polymerizations. This is particularly surprising considering the high reactivities of di- and trialkoxysilyl compounds toward carbanions.

On the other hand, problems were encountered in the polymerizations of **1**, **2**, and **3** with the use of oligo(α-methylstyryl)dilithium rather than the corresponding potassium salt. For example, on mixing **1a** with the initiator solution, an immediate color change was observed from bright red to brownish orange. This color gradually faded with the passage of time. Termination was accomplished by the addition of a few drops of methanol, and the brownish orange color immediately disappeared. A quantitative yield of the polymer was precipitated by addition of an excess of methanol.[10] The GPC curve of this polymer showed a single peak but with a somewhat broad molecular weight distribution with $\bar{M}_w/\bar{M}_n$ = 1.61. The measured molecular weight was found to be higher than the value predicted from **1a**: initiator ratio, as shown in Table II. These results and the observation for the color decay with time suggest that undesirable side reactions occur during the course of the polymerization of **1a**. It is known that organolithium reagents can cleave silyl ethers in a nucleophilic way as shown in eq 1.[11] Hence, the

$$\text{Si–OR} + \text{R'Li} \rightarrow \text{Si–R'} + \text{ROLi} \qquad (1)$$

methoxysilyl groups in the monomer and possibly also in the polymer may cause termination reactions with both the initiator and the propagating chain end in a manner similar to that in eq 1, so that broadening of the molecular weight distribution may occur.[2] The occurrence of such reactions is also supported by the formation of graft copolymer from the reaction of polystyryllithium and poly(**1a**) in a separate experiment. Polystyryllithium ($\bar{M}_n$ = 1 × 10^4), prepared from butyllithium-initiated polymerization of styrene in THF, was added to poly(**1a**) ($\bar{M}_n$ = 1 × 10^4), previously isolated, in THF at −78 °C, and the mixture was stirred overnight. GPC analysis of the mixture indicated formation of the graft copolymer, which was

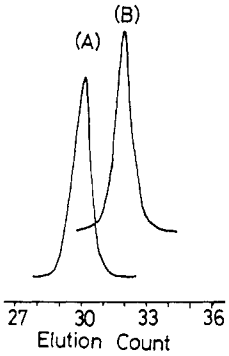


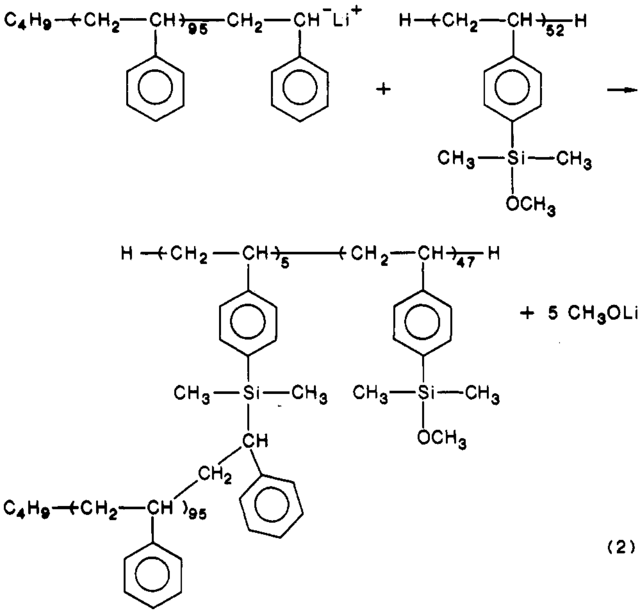
Figure 2. GPC curves for poly[(4-vinylphenyl)dimethylmethoxysilane] (A) and poly[(4-vinylphenyl)triethoxysilane] (B). Peak A: $\bar{M}_n$ (obsd) = 3.3 × 10^4, $\bar{M}_w/\bar{M}_n$ = 1.07. Peak B: $\bar{M}_n$ (obsd) = 1.7 × 10^4, $\bar{M}_w/\bar{M}_n$ = 1.09.

Table II
Anionic Polymerizations of (Alkoxysilyl)styrenes with Oligo(α-methylstyryl)dilithium in THF at -78 °C for 2-10 min[a]

monomer	monomer, mmol	lithium naphthalide, mmol	α-methylstyrene, mmol	$\bar{M}_n \times 10^4$ calcd	$\bar{M}_n \times 10^4$ obsd[b]	$\bar{M}_w/\bar{M}_n$
1a	6.48	0.129	0.427	2.0	2.7	1.61
1b	3.86	0.0931	0.387	1.8	1.8	1.21
1c	4.55	0.112	0.388	1.8	2.0	1.14
1d	3.14	0.0773	0.353	2.0	2.0	1.13
1e	4.87	0.137	0.401	1.7	1.8	1.16
1h	4.72	0.0760	0.401	3.0	2.7	1.16
2a	4.22	0.122	0.366	1.7	1.9	1.29
2b	4.96	0.168	0.439	1.6	1.2	1.09
3	3.77	0.107	0.461	2.0	2.0	1.30

[a] Yields of polymers isolated were 95-100%. Concentrations of active ends were (3.5-4.2) × 10^{-3} M. [b] $\bar{M}_n$(obsd) was obtained by VPO in benzene solution.

poly(**1a**) with an average of five polystyrene arms based on the molecular weight estimation as shown in eq 2.



(2)

With the use of ethoxysilyl derivatives **1b**, **2a**, and **3**, the termination reactions may take place to a limited extent as shown by the fact that the resulting polymers have moderately broad molecular weight distributions ($\bar{M}_w/\bar{M}_n$ = 1.21-1.30).

In contrast to those results, anionic polymerizations of (alkoxysilyl)styrenes **1c**, **1d**, **1e**, **1h**, and **2b** proceed with the apparent absence of the side reactions mentioned above. These results are summarized in Table II. The molecular weight distributions of these polymers were found to be reasonably narrow, with $\bar{M}_w/\bar{M}_n$ = 1.09-1.16. As can be seen, the observed molecular weights by VPO are in good accord with the predicted values for a bifunctional initiator. Clearly, side reactions are absent in these systems (a consequence, perhaps, of steric factors caused by the bulkiness of the alkoxy group attached to the silicon atom).

In summary, a series of (alkoxysilyl)styrenes have been polymerized by either oligo(α-methylstyryl)dilithium or -dipotassium initiators to yield "living polymers" except for the polymerizations of monomers with the less bulky alkoxy (methoxy and ethoxy) groups by oligo(α-methylstyryl)dilithium initiation. It appears that this latter initiator yields a system where side reactions may compete with the propagation step.

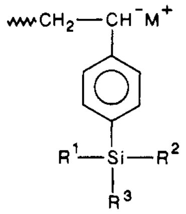
With lithium as the countercation of the living polymer, it is well-known that the stronger solvation of THF molecules to Li^+ than Na^+ and K^+ facilitates to a greater extent the separation of ion pairs to produce highly reactive solvent-separated ion pairs and the free ions.[12] Such reactive centers may react more often at the silicon atom of the methoxysilyl group to cause some terminations during the polymerization, whereas potassium is generally considered to be poorly solvated by THF and consequently the possibility of the production of such reactive forms is small. A more reasonable explanation of the observed difference is the fact that Li^+ would be more effective than K^+ in coordinating to the silyl ether oxygen in the transition state and facilitating the cleavage reaction.

Table III
Results of Stability of Carbanions 4 Derived from 1 and Oligo(α-methylstyryl)dilithium in THF at -78 °C for 30 min

oligo(α-methylstyryl)dilithium, mmol	4	4, mmol	% surviving carbanion[a]
0.135	**4a**	0.0400	30
0.131	**4b**	0.0820	63
0.111	**4c**	0.0792	71
0.118	**4d**	0.117	99
0.105	**4e**	0.0760	72
0.104	**4f**	0.0917	88
0.112	**4g**	0.105	94
0.146	**4h**	0.142	97

[a] Surviving carbanion was calculated from the [**4**]:[oligo(α-methylstyryl)dilithium] ratio. Concentrations of active ends were (3.5-4.2) × 10^{-3} M.

Stability of the Living Polymers Derived from 1, 2, and 3. As mentioned in the preceding section, the polymerizations of **1**, **2**, and **3**, except for a few cases, were found to proceed as a living system free from transfer and termination reactions. Since alkoxysilyl-substituted styryl anions (**4**) thus obtained are of novel type and include alkoxysilyl functions that are potentially attacked by anionic initiators and/or their own anions, it is of special interest to elucidate to what extent the anion may be stable under the various conditions.



4

M = Li, Na, K
R^1, R^2, R^3 = CH_3 and/or alkoxy group

The actual content of **4** in the polymerization system was determined by the direct titration of the characteristic colored solution of **4** to a colorless end point using standardized 1-octanol, since **4** with Li^+ as a counterion always

Table IV
Conditions and Percentages of Carbanions 4 Surviving[a]

conditions		percentage of carbanion surviving derived from										
temp, °C	time, h	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**	**2a**	**2b**	**3**
−78	0.5	30	63	71	99	72	88	94	97	89	103	91
−78	24		31	21	78	39	39	76	93	72	99	86
+30	0.5	8	8	9	25	7	13	18	50	14	11	10

[a] Carbanion was derived from **1**, **2**, or **3** and oligo(α-methylstyryl)dilithium in THF.

Table V
Conditions and Percentages of Carbanions 4 Surviving[a]

conditions		percentage of carbanion surviving derived from										
temp, °C	time, h	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**	**2a**	**2b**	**3**
−78	0.5	100	105	100	98	97	98	101	106	99	99	108
−78	24	89	108	100	100	96	96	95	97	99	101	97
+30	0.5	40	74	93	93	84	91	79	85	91	95	91

[a] Carbanion was derived from **1**, **2**, or **3** and oligo(α-methylstyryl)dipotassium in THF.

Table VI
Conditions and Percentages of Carbanions 4 Surviving[a]

conditions		percentage of carbanions surviving derived from							
temp, °C	time, h	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1f**
−78	0.5	91	93	101	100	93	93	95	95
−78	24	69	75	76	91	72	87	91	96
+30	0.5	10	13	21	24	23	46	38	77

[a] Carbanion was derived from **1** and oligo(α-methylstyryl)disodium in THF.

was brownish orange in THF and **4** with Na^+ or K^+ was dark red. All operations of this procedure were performed in a glass apparatus sealed under high vacuum. To minimize the influence of impurities in the monomer, the titrations were performed at a [monomer]:[initiator] ratio of about 10.

Effect of Alkoxy Group Attached to the Silicon Atom on the Stability of 4. Typical results of such titrations are shown in Table III, where a comparison is made of the initial concentration of initiator (oligo(α-methylstyryl)dilithium in this case) and the final concentration of **4** with Li^+ after 30 min of polymerization at −78 °C. The last column indicates the percentage of surviving active anion, which is calculated from the [final concentration of **4**]:[initiator] ratio. Table III covers the data for all the polymerizations of the series of **1** initiated with oligo(α-methylstyryl)dilithium.

As can be seen, a significant amount of the active anion derived from **1a** was destroyed after 30 min of polymerization, only 30% of the original anion surviving. With polymers from **1b**, **1c**, **1e**, and **1f**, losses of anions were also found to occur, although not so seriously. On the other hand, living polymers from **1d**, **1g**, and **1h** were essentially stable, 94–99% of the original anions surviving in these cases. From these results, the stability of the living polymer may be influenced by the identity of the alkoxy group attached to the silicon atom in the monomer used. This stability increased in the order $OCH_3 < OCH_2CH_3 < OCH_2CH_2CH_3 < OCH_2CH_2CH_2CH_3 < OCH_2CH(CH_3)_2 < OCH(CH_3)_2 \simeq OCH(CH_3)CH_2CH_3 \simeq OC(CH_3)_3$. Thus, the use of the more bulky alkoxy groups should suppress the loss of active center concentration.

Table IV summarizes the results of the percentages of the living anions surviving in the polymerizations of **1**, **2**, and **3** under various conditions. The effect of the alkoxy group on the stability of the living polymer was found to become more pronounced after 24 h. Interestingly, the stability of the living polymer increased with the number of ethoxy groups attached to the silicon atom in the order $Si(CH_3)_2(OCH_2CH_3) < Si(CH_3)(OCH_2CH_3)_2 < Si(OCH_2CH_3)_3$. Raising the temperature to 30 °C reduced the percentage of living anions that survived to a much greater extent in all cases. The effect of temperature was thus critical.

Table VII
Conditions and Percentages of Polystyrylanions Surviving[a]

conditions		percentage of	
temp, °C	time, h	polystyryldilithium	polystyryldipotassium
−78	24	105	100
+30	0.5	102	99

[a] Carbanion was derived from styrene and oligo(α-methylstyryl)dilithium or dipotassium in THF.

Effect of Countercation on the Stability of 4. Table V summarizes the results of the stability of living polymers with potassium as counterion. It can be seen that, compared to the results with Li^+, the active ends of polymers with K^+ are markedly stable at −78 °C, where loss of the anion cannot be detected within experimental error even after 24 h. Raising the temperature to 30 °C decreased the stability, but not greatly under such a condition. The active ends of polymers from monomers with relatively bulky alkoxy groups are stable even at 30 °C.

Table VI summarizes the results of the stability of living polymers with sodium as a counterion, where only some representative examples are listed for comparison. The data show that all the active ends of polymers with Na^+ studied here were stable at −78 °C at least for 30 min but were gradually destroyed with the passage of time. At 30 °C for 30 min, the extent of decrease in the percentage of surviving anion was apparently significant as compared with those with K^+. A comparison of the data in Tables IV–VI clearly indicates that the stability of **4** is very much influenced by the counterion and is in the order $K^+ > Na^+ > Li^+$ for each system. Particularly, the potassium countercation confers much greater stability than sodium or lithium. With **4** with Na^+ and Li^+, some side reactions that annihilate the living ends are often unavoidable even

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at −78 °C. Accordingly, the system using potassium as countercation may correctly be classified as composed of true living polymers.

As a control, we checked the stabilities of polystyryllithium and -potassium under the same conditions. The results are summarized in Table VII, where it can be seen that loss of the living ends is not observed at −78 °C for 24 h and at 30 °C for 30 min. Accordingly, living polystyrene proves to be stable under these conditions where some loss of anions was detected in the living polymers of (alkoxysilyl)styrenes studied here. This strongly suggests the participation of the alkoxysilyl group in the reactions which lead to the loss of active center concentration.

Under the polymerization conditions at −78 °C, the anionic polymerizations appear to be almost instantaneous and complete within a few minutes, whereas side reactions are slow and far from complete after 30 min even in the fastest example. It is therefore considered that the influence of such reactions may be practically negligible on propagation and the side reactions may gradually occur mainly after the conclusion of the polymerization at −78 °C. In fact, well-defined polymers were obtained in quantitative conversions in all cases except for the polymerizations of monomers with methoxy- and ethoxysilyl groups initiated with oligo(α-methylstyryl)dilithium.

Finally, the results presented in Tables IV–VI are of general chemical interest and provide much information for synthesizing block copolymers by the sequential addition method where the use of a long-lived sample of polymer is required at the first polymerization.

Registry No. **1a** (homopolymer), 98542-13-3; **1a**·2K, 105762-17-2; (**1a**)($H_2C{=}CHC_6H_5$) (graft copolymer), 105785-22-6; **1b** (homopolymer), 105785-23-7; **1b**·2K, 105762-18-3; **1c**, 105785-13-5; **1c**·2K, 105762-19-4; **1c**·2Li, 105762-21-8; **1d**·2K, 105762-20-7; **1d**·2Li, 105762-22-9; **1e**, 105785-14-6; **1e**·2K, 105762-24-1; **1e**·2Li, 105762-28-5; **1f**, 105785-15-7; **1f**·2K, 105762-25-2; **1g**, 105785-16-8; **1g**·2K, 105762-26-3; **1h**, 105785-17-9; **1h**·2K, 105762-27-4; **1h**·2Li, 105762-29-6; **2a** (homopolymer), 105785-24-8; **2a**·2K, 105762-23-0; **2b**, 105785-18-0; **2b**·2K, 105762-31-0; **2b**·2Li, 105762-32-1; **3**, 105785-25-9; **3**·2K, 105762-30-9; $H_3C(CH_2)_2OSi(CH_3)_2Cl$, 1825-70-3; $H_3C(CH_2)_3OSi(CH_3)_2Cl$, 1825-72-5; $H_3CCH_2CH(CH_3)OSi(CH_3)_2Cl$, 2725-10-2; $(H_3C)_2CHCH_2OSi(CH_3)_2Cl$, 51986-70-0; $(H_3C)_3COSi(CH_3)_2Cl$, 58566-07-7; 4-$H_2C{=}CHC_6H_4Cl$, 1073-67-2; $H_3CSi(OCH(CH_3)_2)_3$, 5581-67-9; $Cl_2Si(CH_3)_2$, 75-78-5; $HO(CH_2)_2CH_3$, 71-23-8.

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A Tetramethylene Diradical as the Initiating Species in the Spontaneous Charge-Transfer Copolymerization of *p*-Methoxystyrene with Dimethyl Cyanofumarate

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ABSTRACT: The 1:1 alternating copolymerization of *p*-methoxystyrene with dimethyl cyanofumarate proceeds spontaneously in solution at 28 °C. Partitioning of product between copolymer and a dihydropyran cycloadduct favors the small molecule upon dilution, supporting the intermediacy of a tetramethylene diradical. Propagation at the diradical is attested by the increase of molecular weight with conversion. The tetramethylene diradical can be trapped. The equilibrium constant for electron donor–acceptor (EDA) complex formation was determined by NMR spectroscopy. The rate of copolymerization is proportional to the square of the monomer concentrations for equimolar initial concentration. Under these conditions the charge-transfer complex disappears according to first-order kinetics. Comparison of the experimental data with a kinetic scheme, derived with consideration of propagation as proceeding by both free monomer and the EDA complex acting as a monomer, showed that the latter is not significant at our concentrations. These results support and extend our concept of bond-forming initiation in spontaneous charge-transfer polymerizations.

Introduction

Diradical tetramethylenes have been popular intermediates in organic chemistry.[1] They have been generated by a number of different methods, mostly photochemical cleavage of cyclopentanones and in Norrish-2 photoreactions,[2] and are also formed in thermal cycloaddition reactions of olefins. Convincing studies have been those of Bartlett, who studied the cycloadditions of poly(fluoroethylenes),[3] and Pasto, who studied the cycloadditions of alkenes.[4] Recently, captodative substituents have been found to stabilize tetramethylene diradicals.[5,6]

Trapping these diradicals has been difficult and succeeds only with the most reactive trapping reagents, including oxygen and di-*tert*-butyl selenoketone.[7,8] They are very

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