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Polymerization of Monomers Containing Functional Silyl Groups. 9. Anionic Living Polymerization of (4-Vinylphenyl)(*N*,*N*-diethylamino)dimethylsilane

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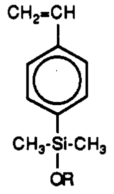
ABSTRACT: Anionic polymerization of (4-vinylphenyl)(*N*,*N*-diethylamino)dimethylsilane (4) was investigated in THF at -78 °C with oligo(α-methylstyryl)lithium, -dilithium, or -dipotassium. The reaction mixtures were always red, similar to that observed in the living polystyrene. The polymerization of 4 proceeded well to give the polymer in a quantitative yield with each of these initiators. Since the polymer of 4 obtained was very sensitive to moisture, in order to characterize the molecular weight and molecular weight distribution it was converted to the more stable poly[(4-vinylphenyl)(2-propoxy)dimethylsilane]. The resulting polymers were found to possess predictable molecular weights and narrow molecular weight distributions. This strongly suggests that the polymerization of 4 proceeds without chain transfer and termination reactions to afford a "living polymer". From the direct colorimetric titration of the colored reaction mixture, it was found that the polystyryl anion derived from 4 was stable in THF -78 °C after 24 h but gradually deactivated to lose ca. 20% of the original anion at 30 °C after 0.5 h.

Introduction

In recent years, we have been studying the anionic polymerizations of monomers having functional silyl groups.[1-5] During these studies, we found that the styrenes (1)[1,2] and 1,3-butadienes (2) with alkoxysilyl groups[3,4] and 4-dimethylsilylstyrene (3)[5] were anionically polymerized to afford "living polymers". The resulting polymers possessed predetermined molecular weights and narrow molecular weight distributions. New types of well-defined block copolymers containing monodisperse polymer sequences were also prepared by means of the anionic living polymerizations. Thus, the silicon-oxygen and silicon-hydrogen bonds are found to be unreactive and stable toward the carbanions of the living polymers if the polymerization conditions are carefully chosen.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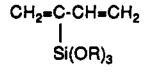
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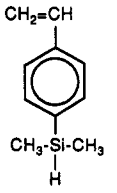
$CH_2{=}C(Si(OR)_3){-}CH{=}CH_2$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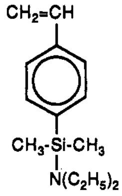
In addition to the above advantages, these polymers are attractive materials because they have reactive alkoxysilyl and hydrosilyl groups in each monomer unit which may undergo some interesting reactions. For example, alkoxysilyl groups are readily hydrolyzed to give silanols that can react with inorganic compounds such as silica and metal oxides.[6] Accordingly, poly(1) and poly(2) may be useful for the surface modification of inorganic materials and for the preparation of organic-inorganic composite materials. The silicon-hydrogen bond attached to poly(3) can add carbon-carbon multiple bonds in alkenes and alkynes to result in the formation of new silicon-carbon bonds.[7] Important and versatile speciality functions may be introduced into poly(3) by the above reactions. Graft copolymers may be synthesized by the reactions of poly(3) with polymers with terminal C=C bonds.

As part of a series of papers on the anionic polymerization of monomers with functional silyl groups, we report here the anionic polymerization of (4-vinylphenyl)(*N*,*N*-diethylamino)dimethylsilane (4), which involves a silicon-nitrogen bond that is considered to be more reactive than the silicon-oxygen bond.[8]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Experimental Section

Materials. 4-Chlorostyrene was kindly supplied by Hokko Chemical Industry Co., Ltd. It was used after fractional distillation at 52-54 °C (5 mmHg) over calcium hydride. Commercially available butyllithium and dimethyldichlorosilane were used without purification. Diethylamine was used after passing through a 1-m column packed with 4A molecular sieves. Styrene and α-methylstyrene were washed with 5% NaOH and then with water and dried over $MgSO_4$. They were distilled over calcium hydride under an atmosphere of nitrogen and then distilled together with tetrahydrofuran (THF) under high vacuum after addition of benzylmagnesium chloride in THF (1 mL of a 0.5 M solution in THF per 10 mL of monomer). They were stored at -30 °C in ampules equipped with breakseals just prior to polymerization. Pentane was washed with concentrated H_2SO_4 and then water. It was dried over $MgSO_4$, refluxed over sodium wire, and finally distilled from its butyllithium solution under a nitrogen atmosphere. Tetrahydrofuran (THF) was refluxed over sodium wire and then distilled from its green-colored sodium naphthalenide solution under a nitrogen atmosphere. Lithium and potassium naphthalenides were prepared by the reaction of naphthalene with a slight excess of freshly cut lithium or potassium metal in THF at 25 °C for 5-10 h in a reaction vessel equipped with breakseals. They were filtered to remove unreacted metals. The concentrations were determined by colorimetric titration with standardized octanol in sealed reactors from the characteristic green colors to the nearly colorless end point. Oligo(α-methylstyryl)dilithium and -dipotassium were freshly prepared just prior to polymerization from the corresponding metal naphthalenides and a 2-4 M quantity of α-methylstyrene at 25 °C for 1 min and then at -78 °C for 15 min. Benzylmagnesium chloride was prepared from benzyl chloride and a slight excess of magnesium in THF at 0 °C in the usual manner.

(*N*,*N*-Diethylamino)dimethylchlorosilane. To a stirred solution of dimethyldichlorosilane (41.0 g, 0.315 mol) in pentane (100 mL) over 1 h at 0 °C under a nitrogen atmosphere. The reaction mixture was allowed to stand overnight at room temperature. It was filtered and the white solid was washed with dry pentane under a nitrogen atmosphere. After evaporation of pentane in the filtrate, the residual oil was fractionally distilled at 77–81 °C (60 mmHg) to give 45.0 g (0.272 mol, 86% yield) of (*N*,*N*-diethylamino)dimethylchlorosilane as a colorless liquid: 90-MHz ^{1}H NMR (C_6D_6) δ 2.75 (4 H, q, NCH_2), 0.94 (6 H, t, CH_3), 0.36 (6 H, s, $SiCH_3$).

(4-Vinylphenyl)(*N*,*N*-diethylamino)dimethylsilane (4). A solution of (*N*,*N*-diethylamino)dimethylchlorosilane (25.2 g, 0.152 mol) in THF (70 mL) was added dropwise to a stirred solution of (4-vinylphenyl)magnesium chloride, prepared from 4-chlorostyrene (34.8 g, 0.251 mol) and magnesium (9.18 g, 0.378 mol) in THF (170 mL). The reaction mixture was allowed to stir for 10 h at room temperature. The crude product was obtained by direct distillation from the reaction mixture. It was purified by fractional distillation at 81–82 °C (1 mmHg) to give 17.5 g (0.0742 mol, 49% yield) of 4 as a colorless liquid: 90-MHz ^{1}H NMR (C_6D_6) δ 7.64–7.33 (4 H, m, C_6H_4), 6.69 (1 H, dd, J = 11 Hz, CH=), 5.73, 5.15 (2 H, dd, J = 18, 11 Hz, CH_2=), 2.84 (4 H, q, J = 7 Hz, NCH_2), 0.99 (6 H, t, J = 7 Hz, CH_3), 0.36 (6 H, s, $SiCH_3$); 23-MHz ^{13}C NMR (C_6D_6) δ 140.3, 138.4 (C_6H_4, C1 or C4), 137.5 (CH=), 134.3 (C_6H_4, C3), 125.9 (C_6H_4, C2), 113.8 (CH_2=), 40.5 (NCH_2), 16.0 (CH_3), −1.1 ($SiCH_3$); IR 1248 ($SiCH_3$), 925 cm^{-1} (SiN).

Special care is needed for handling monomer 4, because it is readily hydrolyzed with moisture in the air. To remove impurities in 4, phenylmagnesium chloride (5 mL, 0.25 M solution in THF) was added to 4 (7.1 g, 31 mmol) in an all-glass apparatus equipped with breakseals. The mixture was then degassed and distilled on a vacuum line into the ampules with breakseals. The 4 was diluted to 0.4–0.6 M solutions with THF and stored at 0 °C until ready for polymerization.

Polymerization Procedure. All the polymerizations were carried out at −78 °C for 0.5 h with stirring under high-vacuum conditions (10^{-6} mmHg) in an all-glass apparatus equipped with breakseals in the usual manner. The desired change of monomer in THF solutioin was added to a THF solutioin of initiator with strong stirring. Both solutions must be kept at −78 °C. The polymerization was then terminated with a slight excess of absolute 2-propanol with respect to the initiator at −78 °C after 0.5 h. The reaction mixture was carefully evaporated with a vacuum pump, and the residual polymer dissolved in dry benzene was freezed-dried. The polymer of 4 thus obtained was characterized by IR spectroscopy, ^{1}H NMR spectroscopy, and size exclusion chromatography (SEC): 90-MHz ^{1}H NMR (C_6D_6) δ 7.8–6.4 (4 H, m, C_6H_4), 2.9 (4 H, m, NCH_2), 2.6–1.3 (3 H, m, CH_2CH), 1.1 (6 H, t, CH_3), 0.5 (6 H, s, $SiCH_3$); IR 1248 ($SiCH_3$), 925 cm^{-1} (SiN). Anal. Calcd for $(C_{14}H_{23}NSi)_n$: C, 72.57; H, 9.91; N, 5.83. Found: C, 71.82; H, 9.87; N, 5.78.

Determination of Actual Carbanion Content by Direct Titration in the Polymerization System. The concentration of carbanion was determined by direct colorimetric titration of the colored solution to the colorless end point with standardized octanol in a sealed reactor through breakseals under vacuum. The operations were conducted by the method previously reported.[9]

Substitution Reaction of the *N*,*N*-Diethylamino Group to the Alkoxy Group in the Polymer of 4. The living polymer solution was terminated with a large excess of absolute 2-propanol (50–100 equiv of 2-propanol relative to the content of the (*N*,*N*-diethylamino)silyl group in the polymer). Acetic acid (10 mol % relative to the aminosilyl content) was added to the mixture, and the resulting solution was allowed to stand at 30 °C for 15 h under a nitrogen atmosphere. The polymer was isolated by precipitation in methanol and was purified by reprecipitation an additional two times from THF solution to methanol. The yield of the polymer was nearly 100% based on the form of poly[(4-vinylphenyl)(2-propoxy)dimethylsilane]. The polymer thus obtained was characterized by IR spectroscopy, ^{1}H NMR spectroscopies, and elemental analysis: 90-MHz ^{1}H NMR ($CDCl_3$) δ 7.5–6.1 (4 H, m, C_6H_4), 3.9 (1 H, m, CH), 2.3–0.6 (3 H, m, CH_2CH), 1.0 (6 H, d, CH_3), 0.3 (6 H, s, $SiCH_3$); IR 1250 ($SiCH_3$), 1027, 1019 cm^{-1} (SiOC). Anal. Calcd for $(C_{13}H_{20}OSi)_n$: C, 71.22; H, 9.15; N, 0.00. Found: C, 71.13; H, 9.36; N, 0.00.

Similarly, the substitution reaction of the *N*,*N*-diethylamino group to either the methoxy or octoxy group in the polymer of 4 was successfully achieved. Yields of polymers were quantitative in both cases. The results of IR, ^{1}H NMR, and elemental analyses were satisfactory from the viewpoint of complete substitution to alkoxy groups.

Measurements. Infrared spectra were recorded on a Jasco IR-G spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (89.6 MHz for ^{1}H and 22.53 MHz for ^{13}C) and a JEOL GSX-270 (67.80 MHz for ^{13}C) in $CDCl_3$ and C_6D_6. Chemical shifts were reported in ppm downfield relative to tetramethylsilane (δ 0) for ^{1}H NMR and to $CDCl_3$ (δ 77.1) for ^{13}C NMR as standard. Size exclusion chromatograms (SEC) for characterization of the molecular weight distribution were obtained at 40 °C with a Toyo Soda HLC-802 instrument with ultraviolet or refractive index detection. THF was the carrier solvent at a flow rate of 1.4 mL/min. Vapor pressure osmometry (VPO) measurements for number-average molecular weight determination were made with a Corona 117 instrument in benzene solution with a highly sensitive thermoelectric couple and equipment of very exact temperature control. Molecular weights to 10^5 could be determined within an analytical error of ±5%.

Results and Discussion

Anionic Polymerization of 4. A series of polymerization of 4 was carried out in THF at −78 °C for 0.5 h with either oligo(α-methylstyryl)lithium, -dilithium, or -dipotassium. Addition of the first quantity of 4 instantaneously turns the deep red initiator solution to a reddish one in the case of Li^+ or a violet-brown color in the case of K^+. The characteristic color, which remains as long as the temperature is kept below −78 °C, indicates the formation of a living anion derived from 4 in the polymerization system. The color disappeared immediately when absolute 2-propanol was added as expected.

Since the silicon–nitrogen bond is highly sensitive to moisture, the workup of the polymer of 4 is carefully carried out in absolute solvents under an atmosphere of nitrogen. The polymer solution terminated with 2-propanol was poured into a large excess of absolute methanol under a nitrogen atmosphere. The polymer precipitated was filtered, washed with absolute methanol, and freeze-dried. There arises a problem even for this treatment. It was observed that the resulting polymers always had very broad molecular weight distributions. This is probably due to the hydrolysis of the (*N*,*N*-diethylamino)silyl group by accidental moisture, followed by cross-linking between the polymer chains. Thus, broadening of the molecular weight distribution is unavoidable during the isolation and purification steps of the polymer of 4, since it is very difficult to perfectly protect the polymer from moisture during those steps.

Therefore, the polymer solution terminated with 2-propanol was carefully evaporated with a vacuum pump, and the residual polymer was directly characterized without purification. The IR and ^{1}H NMR spectra of the polymer showed the absorptions and signals of the expected structure of poly[(4-vinylphenyl)(*N*,*N*-diethylamino)dimethylsilane] obtained by conventional vinyl polymerization. The ^{1}H NMR spectrum also showed no indication that the substitution reaction from the *N*,*N*-diethylamino group to the 2-propoxy group on the silicon atom occurred in the polymer. The molecular weights and their distributions of the polymer of 4 were estimated by SEC. The results are summarized in Table I.

As can be seen, the SEC profiles show unimodal peaks and narrow distributions for all polymer samples. The values of $\bar{M}_w/\bar{M}_n$ were calculated to be around 1.1 using a standard polystyrene calibration. The $\bar{M}_n$ estimated from the same calibration are found to be in reasonable agreement with the $\bar{M}_n$ calculated from [M]/[I] ratios. Polymers of different molecular weights were thus prepared by adjusting the rations of 4 to initiator. The results

Table I
Anionic Polymerization of 4 with Various Initiators in THF at −78 °C for 0.5 h[a]

4, mmol	initiator type	initiator mmol	α-MeSt,[b] mmol	$10^{-3}\bar{M}_n$-(calc)	$10^{-3}\bar{M}_n$-(obsd)[c]	$\bar{M}_w/\bar{M}_n$[d]
5.04	K-Nap[e]	0.343	0.680	7.3	6.9	1.07
3.69	K-Nap	0.129	0.357	14	10	1.09
3.19	K-Nap	0.0655	0.331	24	19	1.13
6.97	K-Nap	0.0780	0.441	43	40	1.15
9.64	K-Nap	0.0638	0.408	72	60	1.17
6.01	Li-Nap[f]	0.229	0.351	13	12	1.12
3.74	Li-Nap	0.100	0.378	18	16	1.19
10.9	BuLi[g]	0.0529	0.247	49	44	1.08

[a] Yields of polymers were nearly quantitative in each case. [b] α-Methylstyrene. [c] $\bar{M}_n$(obsd) was estimated from the SEC curve by using the standard polystyrene calibration curve. [d] The value of $\bar{M}_w/\bar{M}_n$ was estimated from the SEC curve by using the standard polystyrene calibration curve. [e] Potassium naphthalenide. [f] Lithium naphthalenide. [g] Butyllithium.

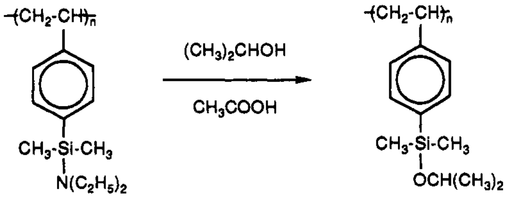
obtained by SEC indicate the anionic living polymerization of 4.

In the polymer solution terminated with 2-propanol, the polymer of 4 appears to be stable for a long time even in the presence of excess amounts of 2-propanol under a nitrogen atmosphere. However, further characterization to determine the absolute $\bar{M}_n$ could not be done in the form of the polymer of 4 because broadening of the molecular weight distribution was always encountered during the purification of the polymer.

Substitution Reaction of the *N,N*-Diethylamino Group to the Alkoxy Group in the Polymer of 4. Silylamines are known to be powerful silylating reagents of alcohols. Therefore, the Si–N bond in the polymer of 4 is possibly displaced by the much stronger Si–O bond by treatment of alcohol.

As mentioned above, the polymer of 4 was stable even in the presence of an excess of 2-propanol, and no substitution reaction from the *N,N*-diethylamino group to the 2-propoxy group in the polymer was observed. The mixture of the polymer and 2-propanol in THF was then heated to 60 °C for 15 h, but the degree of substitution was found to be still very low (<5%).

On the other hand, the addition of a little acid such as acetic acid or *p*-toluenesulfonic acid markedly facilitated the substitution reaction where the intermediate ammonium salt might play an important role as previously reported.[10,11] Complete conversion from the polymer of 4 to poly[(4-vinylphenyl)(2-propoxy)dimethylsilane] could be achieved at 30 °C by the reaction of the polymer of 4 with 2-propanol in THF with the use of 0.1 equiv of acetic acid relative to the content of the aminosilyl group in the polymer, as shown below:



The IR and ^{1}H NMR spectra of the resulting polymer showed the structure of pure poly[(4-vinylphenyl)(2-propoxy)dimethylsilane] within the analytical limits of both spectra, respectively. More reliable evidence for complete substitution was obtained by elemental analysis, which showed no nitrogen content at all. Similarly, poly[(4-vinylphenyl)methoxydimethylsilane] and poly[(4-vinylphenyl)octoxydimethylsilane] were obtained quantitatively by treating the polymer of 4 with methanol or octanol. The shapes of the SEC peaks of the resulting polymers were nearly identical with those of their parent polymers. The result indicates that neither the cross-linking between polymer chains nor undesirable side reactions occurs during the substitution reactions. Thus, the polymer of 4 can be converted to the more stable poly[(4-vinylphenyl)alkoxydimethylsilane] without problems, and hence the method appears to be suitable for preparing well-defined polymers having a variety of alkoxysilyl groups.

Table II
Molecular Weights and Molecular Weight Distributions of Poly[(4-vinylphenyl)(2-propoxy)dimethylsilane]

$10^{-3}\bar{M}_n$-(calcd)	$10^{-3}\bar{M}_n$[a]-(obsd)	$\bar{M}_w/\bar{M}_n$[b]	$10^{-3}\bar{M}_n$-(calcd)	$10^{-3}\bar{M}_n$[a]-(obsd)	$\bar{M}_w/\bar{M}_n$[b]
10	11	1.12	36	32	1.15
16	16	1.14	63	70	1.17
19	22	1.15			

[a] $\bar{M}_n$(obsd) was obtained by VPO in benzene solution. [b] The value of $\bar{M}_w/\bar{M}_n$ was estimated from the SEC curve by using the standard polystyrene calibration curve.

The use of excess acetic acid with respect to the aminosilyl group immediately caused gelation of the polymer. This is possibly due to the fact that both the aminosilyl and the resulting alkoxysilyl groups are not stable and are readily hydrolyzed in an acidic medium. Therefore, the reaction should be carried out under basic to neutral conditions where the resulting polymers are stable, although a little acid is required to promote the substitution reaction.

The resulting poly[(4-vinylphenyl)(2-propoxy)dimethylsilane] thus obtained was stable enough to be purified by repeated reprecipitation from THF solution to methanol. The molecular weights and their distributions measured by VPO and SEC are listed in Table II.

It can be seen that in all samples the observed values of $\bar{M}_n$ by VPO are in good agreement with the predicted values from [M]/[I]. The SEC charts show that each polymer possesses a narrow distribution of molecular weight, the values of $\bar{M}_w/\bar{M}_n$ being less than 1.2. The shapes of the SEC peaks obtained before and after the substitution reaction are nearly identical. All the evidence from these results confirms that 4 gives a normal anionic living polymer. Accordingly, under the polymerization conditions used in this work, the silicon–nitrogen bonds in the monomer and polymer proved unreactive toward the carbanions of both initiators and the active chains ends of the polymer. Furthermore, the narrowness of the molecular weight distribution indicates that the initiation reaction is rapid enough compared to the propagation step.

Synthesis of Block Copolymer. Since 4 polymerizes anionically to give a living polymer, synthesis of the block copolymer containing the polymer sequence of 4 is feasible by the addition of a second monomer to the living polymer of 4. When styrene as second monomer was added to the polymeric dianion of 4, originally prepared by oligo(α-methylstyryl)dilithium initiation in THF at −78 °C, the viscosity immediately increased and a quantitative yield of polymer was obtained. The resulting polymer was characterized by ^{1}H NMR, VPO, and SEC.

The resulting polymer was found to possess an $\bar{M}_n$ of 54 000, in close accord with the predicted value of 48 000. The composition of each block determined by the ^{1}H NMR spectrum was found to be nearly equal to that calculated from both monomers fed in the polymerization. The SEC analysis shows that the peak of the starting polymer of 4 sequence shifts toward the higher molecular weight side after addition of styrene. As anticipated, a narrow molecular weight distribution exists for the resulting block

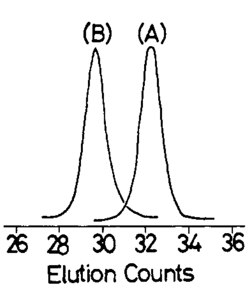


Figure 1. SEC curves of the polymer of 4 (A) and poly(styrene-*b*-4-*b*-styrene) (B). The values of $\bar{M}_w/\bar{M}_n$ were 1.12 and 1.14 for peaks A and B, respectively.

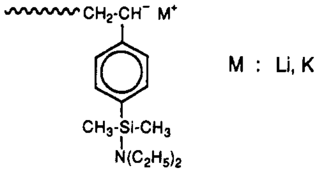
Table III
Results of Stability of 5 in THF

conditions		initiator[a]		5,	5 surviving,[b]
temp, °C	time, h	alkali metal	mmol	mmol	%
−78	0.5	K	0.106	0.108	100
−78	24	K	0.0901	0.0888	99
0	0.5	K	0.109	0.0920	85
30	0.5	K	0.0969	0.0730	75
−78	0.5	Li	0.104	0.101	98
−78	24	Li	0.0910	0.0910	100
0	0.5	Li	0.0964	0.0791	82
30	0.5	Li	0.106	0.0854	81

[a] Initiator: oligo(α-methylstyryl)di(alkali metal). [b] Percentages of 5 surviving were calculated from the ratios of [5] to [initiator].

copolymer as shown in Figure 1. These analyses clearly indicate that the polymer consists primarily of a BAB-type triblock copolymer where A and B are the polymer of 4 and polystyrene sequences, respectively. The successful synthesis of block copolymer also provides strong evidence for the living character of the anionic polymerization of 4.

Stability of the Active Propagating Chain End of Poly(4). Since the polystyryl anion 5 derived from 4, shown below, is a carbanion of novel type which involves



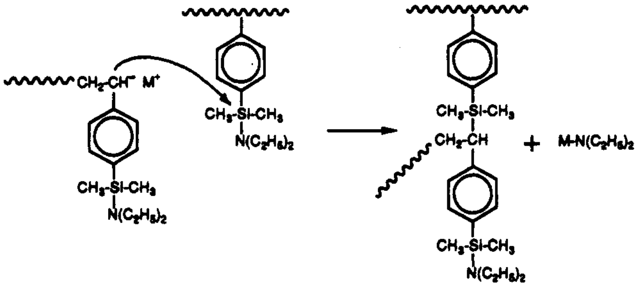
(5)

silicon–nitrogen bonds, it is of interest to evaluate what extent 5 may be stable under various conditions. We have determined the actual concentration of 5 by a direct, in situ titration of the characteristic red color of 5 to a colorless end point using a standardized octanol in THF solution in a sealed glass reactor. In this way, it is possible to estimate the actual concentration of active anion in the polymerization system and hence to discuss the stability of 5 quantitatively.

The results are summarized in Table III, where a comparison is made of the initial concentration of initiator and the final concentration of 5 for 0.5 or 24 h after mixing initiator and 4. The last column lists the calculation value from the ratio of [5] to [initiator], which suggests the percentage of surviving 5 under the conditions employed.

As can be seen, the 5 with K⁺ or with Li⁺ appears to be stable at −78 °C even after 24 h, where no loss of active end is realized within the analytical error (±3%). Although raising the temperature to 30 °C reduced the percentages of active anions, about 80% of the initial carbanions still remained after 0.5 h with both K⁺ and Li⁺ as countercations. By comparison, both polystyryldilithium and -dipotassium were titrated in a similar manner. The results indicated no loss of living ends of polystyrenes at −78 °C after 24 h and 30 °C after 0.5 h. Accordingly, the active chain ends of the polymer of 4 appear to be stable at −78 °C but less stable at 30 °C, compared to the cases of both living polystyrenes with K⁺ and Li⁺.

Although a clear explanation for the deactivation of 5 cannot be obtained at present, we presume that the following reaction occurred from the fact that polymers of very broad molecular weight distributions were always obtained in systems where anion losses were observed to a considerable extent. The reaction involves attack of 5 upon the silicon atom of another polymer in a nucleophilic way, as shown. Such a reaction is expected to broaden the molecular weight distribution.



It should be noted that such anion losses at 30 °C are not a problem in the polymerization of 4 because it is always carried out at −78 °C and appears to be complete within a few minutes even at −78 °C. Values of $\bar{M}_w/\bar{M}_n$ (Table I) close to unity and, our ability to prepare block copolymers are evidence for the stability of 5 at −78 °C.

In conclusion, we have found that the anionic polymerization of 4 proceeds without chain termination reactions to afford a living polymer of 4. The silicon–nitrogen bonds in 4 and the polymer are stable under anionic living polymerization. However, the polymer is very sensitive to moisture and difficult to purify by reprecipitation even under a nitrogen atmosphere using absolute solvents. Broadening of the molecular weight distribution of the polymer is always observed after the purification step. Therefore, we converted the polymer of 4 to the more stable poly[(4-vinylphenyl)(2-propoxy)dimethylsilane] to characterize the exact molecular weight and the distribution.

Supplementary Material Available: ^{1}H and IR spectra of poly[(4-vinylphenyl)(*N*,*N*-diethylamino)dimethylsilane] and poly[(4-vinylphenyl)(2-propoxy)dimethylsilane] (2 pages). Ordering information is given on any current masthead page.

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