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(33) CHN analytical data for two typical polymers are as follows. (a) Anal. Calcd for $[NP(OPh)_{1.7}(OC_6H_4Me\text{-}p)_{0.3}]_n$: C, 63.1; H, 4.1; N, 5.9. Found: C, 63.2; H, 5.0; N, 6.1. (b) Anal. Calcd for $[NP(OPh)_{0.4}(OC_6H_4Me\text{-}p)_{1.6}]_n$: C, 65.2; H, 5.3; N, 5.6. Found: C, 65.1; H, 5.2; N, 6.0.
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Polymerization of Monomers Containing Functional Silyl Groups. 3. Anionic Living Polymerization of (4-Vinylphenyl)dimethylsilane

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ABSTRACT: Anionic polymerization of (4-vinylphenyl)dimethylsilane was investigated at −78 °C in THF or THF–pentane mixture with oligo(α-methylstyryl)dilithium, -disodium, or -dipotassium. Under such conditions, the polymerization of this monomer proceeded as a living system. Polymers of predictable molecular weights and of narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n$ = 1.08–1.19) were obtained in quantitative yields. The living polymer thus obtained can initiate further polymerization of styrene to afford a new type of block copolymer, poly[styrene-*b*-(4-vinylphenyl)dimethylsilane-*b*-styrene].

Introduction

It is well-known that silicon hydrides add to olefins, acetylenes, and carbonyl compounds in the presence of either radical initiators or, more commonly, certain transition metals and their complexes.[1] The hydrogens of silicon hydrides can readily be displaced by both electrophiles and nucleophiles.[2] Many of these reactions are of great value in organic synthesis. The preparation of a silicon hydride containing polymer has attracted special interest in this regard, because the silicon hydride on the polymer may undergo a wide variety of the above-mentioned reactions by which important and versatile specialty functions may be introduced into the polymer.

Extensive studies have appeared on the synthesis and application of poly(methylsiloxanes) and their copolymers with dimethylsiloxane units where the Si–H bonds are present in the main chains. It was reported mostly in patents that they were prepared either by the hydrolysis of CH_3SiHCl_2 or by the ring-opening polymerization of cyclic oligomers of $-\overline{[CH_3Si(H)O]_n}-$.

In contrast, the polymers having silicon hydrides in the side chains are less widely known. In the presence of transition metals, the polymerizations of vinyldialkyl- and vinyldiarylsilanes proceeded via polyaddition mechanism in preference to the occurrence of vinyl polymerization. As a result, linear polymers represented as $-(SiR_1R_2CH_2CH_2)_n-$ with no SiH groups were obtained.[3,4] On the other hand, it was reported that radical and VCl_3–$Al(C_2H_5)_3$-initiated polymerizations of vinylsilanes and 4-substituted styrenes with SiH group resulted in the polymers with polyvinylic structures assigned on the basis of their IR and NMR spectra.[5,6] The vinyl reactivity of (4-vinylphenyl)dimethylsilane was also discussed from its radical polymerization behavior.[7] In these systems, however, there are still some possibilities that the addition of the SiH group to the vinyl bond might occur, because radical initiators used in the polymerization also play a role as hydrosilylation catalysts.[1] Accordingly, a linear polymer

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Table I
Anionic Polymerization of 1 with Organopotassium Compounds in THF at -78 °C for 5-10 min[a]

	initiator			$10^{-4}\bar{M}_n$		
1, mmol	type	mmol	α-methylstyrene, mmol	calcd	obsd[b]	$\bar{M}_w/\bar{M}_n$
3.04	K-Nap[c]	0.131		0.75	0.74	1.08[d]
7.70	K-Nap	0.301	1.10	0.92	0.98	1.18
3.96	K-Nap	0.119		1.1	1.0	1.10
6.47	K-Nap	0.194	0.436	1.1	1.2	1.10
5.37	cumyl K[e]	0.0754		1.2	1.5	1.10
3.88	K-Nap	0.0986	0.398	1.4	1.3	1.08[d]
6.96	K-Nap	0.0688	0.251	2.9	3.1	1.15
6.86	K-Nap	0.0466	0.232	4.9	4.5	1.10
12.87	K-Nap	0.0381	0.140	11	14	1.29

[a] Yields of polymers isolated were 90–100%. [b] $\bar{M}_n$(obsd) was obtained by VPO in benzene solution. [c] Potassium naphthalenide. [d] Polymerization was carried out in THF–pentane mixture (6/4, v/v). [e] Cumyl potassium.

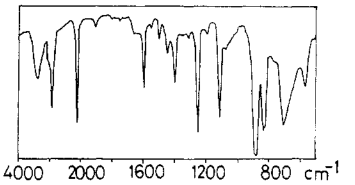


Figure 1. IR spectrum of poly[(4-vinylphenyl)dimethylsilane].

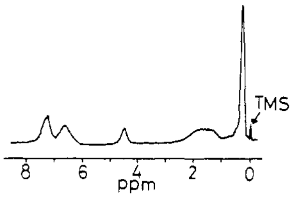


Figure 2. ^{1}H NMR spectrum of poly[(4-vinylphenyl)dimethylsilane].

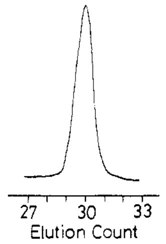
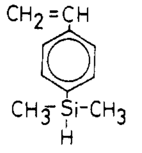


Figure 3. GPC curve for poly[(4-vinylphenyl)dimethylsilane]: $\bar{M}_n$(obsd) = 4.5 × 10^4; $\bar{M}_w/\bar{M}_n$ = 1.10.

with SiH group in each monomer unit may be difficult to prepare by means of the above polymerizations.

We wish to report here the preparation of a linear, well-defined poly[(4-vinylphenyl)dimethylsilane] by the anionic living polymerization of (4-vinylphenyl)dimethylsilane (1).



(1)

Results and Discussion

Silicon hydrides are known to react easily with reactive nucleophiles such as alkali-metals and organolithium compounds which are often used as anionic initiators.[8,9] Therefore, it might have been considered that such reactions cause serious problems in the anionic polymerization of monomer containing SiH group. However, in 1971, Haussmann and Greber briefly demonstrated the possibility of anionic polymerization of [4-(2-propenyl)-phenyl]dimethylsilane.[10] This monomer underwent anionic initiation with sodium naphthalenide in tetrahydrofuran (THF) at −78 °C to afford an oligomer (molecular weight was about 2600) in 92% yield. Although more detailed information is not available from their experiment, the result obtained encourages us to try the polymerization of the styrene analogue, (4-vinylphenyl)-dimethylsilane, 1, under anionic conditions.

Anionic Polymerization of 1 with Organopotassium Compounds. The anionic polymerization of 1 was carried out with potassium naphthalenide, 2-phenyl-2-propylpotassium (cumylpotassium), or oligo(α-methylstyryl)dipotassium in THF at −78 °C. Upon addition of 1 to the potassium naphthalenide in THF, an immediate color change from green to bright red occurred, whereas appreciable color change was not observed in the cases of cumylpotassium and oligo(α-methylstyryl)dipotassium as initiators because they were similarly red. The red apparently remained unchanged at −78 °C for 24 h but disappeared immediately by adding methyl iodide through the breakseal under vacuum conditions. The polymer was then precipitated by pouring the mixture into a large amount of methanol, giving an almost quantitative yield.

As shown in Figure 1, the IR spectrum of the polymer has strong absorptions at 2100 and 880 cm^{-1} corresponding to the Si–H group. The ^{1}H NMR spectrum of the polymer showed the signals of the expected structure of poly[(4-vinylphenyl)dimethylsilane] (Figure 2). The signals for the $SiCH_2CH_2$ group were not observed in the spectrum. Furthermore, it was found that the integral ratio of SiH to C_6H_4 was 1:4 as expected. These results indicate that there was no occurrence of SiH addition to vinyl double bond at least within the detectable limit of our ^{1}H NMR spectrum.

The polymer thus obtained is a white solid, soluble in a wide variety of solvents such as pentane, hexane, cyclohexane, benzene, toluene, carbon tetrachloride, dichloromethane, chloroform, diethyl ether, 1,4-dioxane, THF, acetone, methyl ethyl ketone, triethylamine, pyridine, carbon disulfide, ethyl acetate, *N,N*-dimethylformamide, *tert*-butyl alcohol, and 1-octanol. It is insoluble in water, methanol, ethanol, acetonitrile, and nitromethane.

The molecular weights and the distributions for this series of polymers are listed in Table I. The predictable molecular weights based on the mole ratio of monomer to initiator agreed well with the measured values obtained by vapor-pressure osmometry (VPO). The analysis of gel permeation chromatography (GPC) indicated that the resulting polymers possessed narrow molecular weight distributions and that the values of $\bar{M}_w/\bar{M}_n$ were calculated to be around 1.1.[11] A representative GPC profile is illustrated in Figure 3. Accordingly, these results clearly indicate that the anionic polymerization of 1 proceeds without chain transfer and termination reactions under

Table II
Anionic Polymerization of 1 with Oligo(α-methylstyryl)dilithium or Oligo(α-methylstyryl)disodium in THF at −78 °C for 5–10 min[a]

	initiator			$10^{-4}\bar{M}_n$		
1, mmol	type	mmol	α-methylstyrene, mmol	calcd	obsd[b]	$\bar{M}_w/\bar{M}_n$
6.43	Li-Nap[c]	0.203	0.366	1.1	1.1	1.54
9.72	Li-Nap	0.192	1.02	1.8	1.6	1.55
9.55	Li-Nap	0.0948	0.504	3.4	3.4	1.75
7.94	Na-Nap[d]	0.291	1.13	0.98	1.1	1.81
5.22	Na-Nap	0.145	0.421	1.2	1.3	1.46
9.55	Na-Nap	0.0454	0.176	6.9	6.7	1.80

[a] Yields of polymers isolated were 90–100%. [b] $\bar{M}_n$(obsd) was obtained by VPO in benzene solution. [c] Lithium naphthalenide. [d] Sodium naphthalenide.

Table III
Anionic Polymerization of 1 with Oligo(α-methylstyryl)dilithium or Oligo(α-methylstyryl)disodium at −78 °C in THF–Pentane Mixture[a]

	initiator			$10^{-4}\bar{M}_n$		
1, mmol	type	mmol	α-methylstyrene, mmol	calcd	obsd[b]	$\bar{M}_w/\bar{M}_n$
3.74	Li-Nap[c]	0.113	0.379	1.2	1.3	1.15
4.92	Li-Nap	0.111	0.216	1.5	1.5	1.19
3.96	Na-Nap[d]	0.144	0.432	0.96	0.98	1.18
6.02	Na-Nap	0.163	0.326	1.2	1.4	1.19

[a] Polymerizations were carried out in THF–pentane mixture (7/3–6/4, v/v). Yields of polymers isolated were 93–98%. [b] $\bar{M}_n$ (obsd) was obtained by VPO in benzene solution. [c] Lithium naphthalenide. [d] Sodium naphthalenide.

the above conditions. Furthermore, rapid initiation may be evidenced by the fact that the polymers have narrow molecular weight distributions. The results also suggest that the presence of the SiH function does not interfer the anionic polymerization of 1 at all.

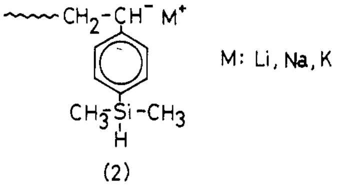
It should be noted that at a high ratio of monomer to initiator ([M]/[I] = 338), there was some deviation between the calculated and the observed values of molecular weight. The molecular weight distribution was found to be relatively broad ($\bar{M}_w/\bar{M}_n = 1.29$). This is probably due to partial destruction of the initiator and/or the active propagating end of the polymer by impurities in 1 during the course of the polymerization. Therefore, more careful purification of 1 should be needed to obtain the polymer of a higher molecular weight than 10^5 and of a narrow molecular weight distribution.

Anionic Polymerization of 1 with Oligo(α-methylstyryl)dilithium and -disodium. The polymerization of 1 with oligo(α-methylstyryl)dilithium or -disodium in THF at −78 °C appeared similar to that with the corresponding potassium salt as mentioned above. The reaction mixture showed a characteristic bright red color in every case. Termination was accomplished by the addition of a few drops of methyl iodide, and the red immediately disappeared. The yields of polymers obtained were near quantitative. The results are summarized in Table II.

Contrary to the results with the potassium salts, the polymers with these initiators had relatively broad molecular weight distributions, the $\bar{M}_w/\bar{M}_n$ values of which were in the range from 1.4 to 1.8. There is, however, quite good agreement between the values of molecular weights calculated and measured by VPO. As will be described in detail in the next section, we have observed no loss of active propagating end of the polymer at the conclusion of the polymerization. Therefore, the reason for the broad distribution is not due to any destruction of either initiator or active propagating end of the polymer. The most likely explanation would be due to the simultaneous existence of initiation and propagation reactions during a considerable period of the polymerization.

More satisfactory results were obtained when the polymerization of 1 was carried out at −78 °C in a THF-pentane mixture. They are summarized in Table III. As can be seen, the polymers of predictable molecular weights were obtained in quantitative yields. Under these conditions, a noticeable point is that the molecular weight distribution could be made narrow ($\bar{M}_w/\bar{M}_n$ = 1.15–1.19). Although the reason is not clear at the present time, it is likely that the propagation step would become relatively slow compared to the initiation step by changing the polarity of the system. To our knowledge, there has not been a similar observation in the previous studies.

Stability of Active Propagating End of the Polymer. Morton and co-workers previously developed a colorimetric titration technique by which the actual concentration of living polystyryl anion could be determined.[12] This was accomplished by a direct, in situ titration of the characteristic red polystyryl anion to a colorless end point by standarized 1-butanol–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 quantitatively. Since poly[4-(dimethylsilyl)styryl] anion (2) is a carbanion of novel type and includes SiH groups which may potentially be attacked with its own carbanion in a nucleophilic way, it is of interest to evaluate to what extent 2 may be stable under various conditions.



(2)

By the application of the above titration method to our system with some modification using the standardized methyl iodide as a titration reagent instead of 1-butanol, the actual concentration of 2 could be determined, since the 2 with Li^+ was always a reddish orange and the 2 with Na^+ or K^+ was dark red, similar to those observed in living polystyryl anions with these counterions. To minimize the influence of impurity in 1, titrations were taken at a ratio [1]/[initiator] of about 10.

The results are summarized in Table IV where a comparison is made of the initial concentration of initiator and

Table IV
Results of Stability of Carbanions 2 in THF

conditions		initiator[b]			
temp, °C	time, h	alkali metal	mmol	2, mmol	% 2 survived[a]
−78	0.5	K	0.114	0.119	100
−78	24	K	0.118	0.114	97
30	0.5	K	0.114	0.111	93
−78	0.5	Na	0.0990	0.0939	95
−78	24	Na	0.111	0.0989	89
30	0.5	Na	0.117	0.0537	46
−78	0.5	Li	0.118	0.117	99
−78	24	Li	0.100	0.0830	83
30	0.5	Li	0.0971	0.0322	33

[a] Percentages of 2 survived were calculated from the ratio of [2] to [initiator]. Analytical error of these titrations was usually within ±3%. [b] Initiator, oligo(α-methylstyryl)dialkali-metal salt.

Table V
Block Copolymerization of 1 with Styrene or Isoprene at −78 °C in THF with Oligo(α-methylstyryl)dipotassium

block copolymer type	A monomer	B monomer	block copolymer[a] $10^{-4}\bar{M}_n$ (calcd)	(homopolymer)[b] $10^{-4}\bar{M}_n$ (obsd)[c]
B–A–B	1	styrene	2.5 (0.72)	2.4 (0.73)
A–B–A	1	styrene	5.7 (0.62)	5.2 (0.60)
A–B–A	1	isoprene	5.1 (1.5)	5.2 (2.0)

[a] Yields of polymers were 95–100%. Values of $\bar{M}_w/\bar{M}_n$ were 1.10–1.18. [b] Homopolymers were obtained at the first polymerization. [c] $\bar{M}_n$(obsd) was obtained by VPO.

the final concentration of 2 after the conclusion of the polymerization (almost instantaneous in all cases examined here). The last column lists the calculation value from the ratio of [2] to [initiator] which may imply the percentage of surviving 2 under the conditions.

As can be seen, the 2 with K^+ appears to be stable at −78 °C even after 24 h where no loss of active end is realized within analytical error (±3%). Surprisingly, more than 90% of the initial carbanion remained at 30 °C after 30 min. In the cases of the 2 with Li^+ and Na^+, almost all the active ends had survived at −78 °C at least after 30 min but were slowly destroyed with time. Raising the temperature to 30 °C reduced the percentages of active anions survived to a much greater extent, only 33% and 46% of the original anions having survived for the 2 with Li^+ and Na^+, respectively. Thus, the effect of the counterion to the stability of 2 seems to be critical. Such anion losses are not a problem in practice for the polymerization of 1 because it was always carried out at −78 °C and appears to be complete within a few seconds. Further evidence for the stability of 2 is provided by successful preparation of block copolymer which will be described in the next section.

Block Copolymerization. The lack of a termination reaction and the remaining activity of 2 have been demonstrated in the preceding section. It is possible that the utilization of this polymeric anion as an initiator of polymerization of second monomer results in the preparation of new block copolymers containing poly[(4-vinylphenyl)dimethylsilane] sequences.

Thus, living polymer of 1 was prepared and used to initiate styrene or isoprene as a second monomer. When styrene was added to the living polymeric dianion of 1, originally prepared by oligo(α-methylstyryl)dipotassium initiation in THF at −78 °C, the viscosity increased and a quantitative yield of polymer was obtained. The results are summarized in Table V.

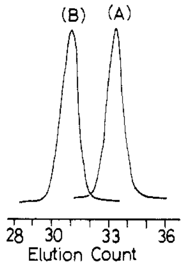


Figure 4. GPC curves for poly[(4-vinylphenyl)dimethylsilane] (A) and for poly[styrene-*b*-(4-vinylphenyl)dimethylsilane-*b*-styrene]: peak A, $\bar{M}_n$(obsd) = 7.3×10^3, $\bar{M}_w/\bar{M}_n$ = 1.08; peak B, $\bar{M}_n$(obsd) = 2.4×10^4, $\bar{M}_w/\bar{M}_n$ = 1.15.

The GPC analysis showed that the peak of the starting polymer from 1 shifted completely toward the higher molecular weight side after addition of styrene. The resulting polymer possessed a single peak without shoulder and had a narrow molecular weight distribution as illustrated in Figure 4. The observed value of $\bar{M}_n$ of the final polymer was in reasonable agreement with that calculated from the monomer-to-initiator ratio. The ^1H NMR spectra showed the presence of each block at the expected molar ratio in the resulting polymer. These results clearly indicate that the starting polymeric dianion of 1 is capable of initiating the polymerization of styrene to form a B–A–B-type triblock copolymer where A and B represent poly(1) and polystyrene units, respectively. The result also provides strong evidence for the living character of anionic polymerization of 1.

The block copolymers of A–B–A type could be successfully obtained by the opposite sequence of monomer addition (first styrene or isoprene and then 1) under the same conditions. The GPC, VPO, and ^1H NMR analyses of the resulting polymers supported the formation of the expected block copolymers. Thus, from the results of the experiments in Table V, it appears that tailored block copolymers which contain poly[(4-vinylphenyl)dimethylsilane] blocks can be prepared by this method.

Experimental Section

Materials. 4-Chlorostyrene was kindly supplied by Hokko Chemical Industry Co., Ltd. It was distilled at 52–54 °C (5 mmHg) over calcium hydride. Commercial dimethylchlorosilane was used without purification. Styrene and α-methylstyrene were washed with 5% NaOH and then with water. They were dried over $MgSO_4$ and distilled over calcium hydride under the nitrogen atmosphere. Isoprene was distilled over calcium hydride under nitrogen atmosphere. Pentane was washed with concentrated H_2SO_4 and then with water. It was dried over $MgSO_4$ and distilled over calcium hydride. Then it was distilled from its butyllithium solution under nitrogen atmosphere. Tetrahydrofuran (THF) was refluxed over sodium wire for 5 h and distilled from its sodium naphthalenide solution. Methyl iodide was washed with 5% $Na_2S_2O_3$ and then with water. It was distilled over calcium hydride under nitrogen atmosphere. 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 naphthalenides and a 2–4 M quantity of α-methylstyrene at 30 °C for 1 min and then at −78 °C for 5 min. The concentration of metal naphthalenide was determined by previous titration with standard methyl iodide in a sealed reactor through breakseals under vacuum.[13] Cumylpotassium was prepared from cumyl methyl ether and potassium–sodium alloy.[14]

(4-Vinylphenyl)dimethylsilane (1). 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)) was added dropwise over a 1-h period to a solution of dimethylchlorosilane (6.18 g, 66 mmol) in dry THF (50 mL). The reaction mixture was stirred at room temperature overnight under a nitrogen atmosphere. The magnesium chloride precipitated was filtered under a nitrogen at-

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mosphere. The crude product was obtained by distillation under a reduced pressure. It was purified carefully by fractional distillation at 58 °C (2 mmHg) [lit.[15] 61 °C (0.3 mmHg)] to give 8.9 g (55 mmol, 83%) of colorless liquid **1**: ^{1}H NMR (60-Hz, CCl_4) δ 7.58, 7.17 (4 H, m, phenyl), 6.67 (1 H, 2d, vinyl CH), 5.69, 5.19 (2 H, 2d, J = 11, 18 Hz, vinyl CH_2), 4.40 (1 H, m, SiH), 0.33 (6 H, d, $SiCH_3$).

In order to remove impurities in monomers, benzylmagnesium chloride (5 mL, 0.5 M solution in THF) was added to **1** (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 the vacuum line into the ampules fitted with breakseals. Thus, **1** distilled from THF solution was obtained and stored at 0 °C until ready for use. Similarly, styrene, α-methylstyrene, and isoprene were purified and stored in the ampules with breakseals.

Polymerization Procedure. All the polymerizations were carried out at −78 °C with shaking under high vacuum conditions ($\sim 10^{-6}$ mmHg) in an all-glass apparatus equipped with breakseals. The polymerization of **1** was usually completed within less than 5 min and was terminated with methyl iodide after 5–10 min of the polymerization. The polymers were precipitated by adding a large excess of methanol. They were redissolved in THF, precipitated into methanol 2 additional times, and freeze-dried.

Block copolymerizations and the treatment of the resulting copolymers were also performed in a similar manner as above.

Determination of Actual Anion Content by Titration. The concentration of **2** was determined by colorimetric titration with the standardized methyl iodide in a sealed reactor through breakseals under vacuum. The operations were conducted by the method as previously reported.[13]

Instruments for Measurements. ^{1}H NMR (60-MHz) spectra 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. IR spectra were run with a Jasco IR-G spectrophotometer.

Registry No. **1**, 4556-72-3; **1** (homopolymer), 28851-90-3; (**1**)(styrene) (block copolymer), 107985-72-8; (**1**)(isoprene) (block copolymer), 107985-71-7; 4-$H_2C{=}CHC_6H_4MgCl$, 7459-73-6; $(H_3C)_2SiHCl$, 1066-35-9; oligo(α-methylstyryl)dilithium, 57486-16-5; oligo(α-methylstyryl)disodium, 37244-89-6; oligo(α-methylstyryl)dipotassium, 52219-57-5.

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Oligomerization of Vinyl Monomers. 22. Oligomerization and Polymerization of Vinyl Phenyl Sulfoxide via Stereospecific and Stereoelective Vinyl Addition Reactions

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ABSTRACT: The oligomerization and polymerization of racemic and highly optically enriched vinyl phenyl sulfoxide (**3**) were carried out in THF at −78 °C. Dimer and trimer stereochemistry was consistent with the stereospecific addition of **3** to an ion pair epimer of 1-lithio(phenylsulfinyl)ethane (**2**) or 1-lithio-1,3-bis(phenylsulfinyl)butane (**4**), where the stereoelectivity for one enantiomer of **3** over the other was large. The polymerization of racemic **3** resulted in the formation of an apparently atactic polymer. In contrast, the polymerization of highly optically enriched **3** resulted in the formation of an apparently highly stereoregular polymer. These results are shown to be consistent with a process where many chain-end epimers may participate in the polymerization and each epimer undergoes vinyl addition stereospecifically and stereoelectively. However, the formation of a stereoregular polymer from optically active monomer requires that the chirality of the ion pair influence the stereoelectivity.

Introduction

In the anionic polymerization of vinyl monomers of the structure $CH_2C(R)C(Y){=}X$, where X = O or N, Y = O, N, or C and R = H or alkyl stereoregulation is often observed.[1] This has been attributed in some cases to intramolecular chelation of the counterion by the penultimate group[2] as shown in Figure 1 for the case of the living dimer of 2-vinylpyridine. For this reason the polymerization of vinyl sulfoxides is interesting. The sulfur–oxygen bond is strongly polar with a bond moment of 4.76 D[3] and coordinates strongly with metal ions. Furthermore the sulfinyl group is chiral and the reactions of lithio-α-sulfinyl carbanions with electrophiles tend to be stereoselective.[4]

We have prepared oligomers and polymers from vinyl phenyl sulfoxide (**3**) using 1-lithio-1-(phenylsulfinyl)ethane (**2**) as the initiator in THF at −78 °C. With extensively purified **3**, complete conversion of monomer to polymer was possible.[5] Optically active polymer was prepared from optically active monomer. This was possible since sulfoxides are configurationally stable under neutral and basic conditions.[6] Because **3** is configurationally stable under the polymerization conditions a stereoelective[7] polymerization is possible.

Recently we have reported the formation of the dimer of **3**.[8] Stereoelective addition of S_S-**3** to R_S-**2**[9] with the stereoselective formation of an S chiral carbon was ob-

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