Anionic Polymerization of Monomers Containing Functional Groups. 7. Anionic Polymerizations of *N*-Alkyl-*N*-(4-vinylbenzylidene)amines[1]

Takashi Ishizone, Nobuyuki Sueyasu, Kenji Sugiyama, Akira Hirao,* and Seiichi Nakahama*

Department of Polymer Chemistry, Faculty of Engineering, Tokyo Institute of Technology, Ohokayama, Meguro-ku, Tokyo 152, Japan

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ABSTRACT: The anionic polymerizations of seven styrene derivatives *para*-substituted with *N*-alkylimino groups where the alkyls varied from methyl (1), ethyl (2), isopropyl (3), cyclohexyl (4), to *tert*-butyl (5), as well as *meta* (6) and *ortho* (7) isomers of the cyclohexyl derivatives, were carried out in THF at −78 °C with oligo(α-methylstyryl)dipotassium as an initiator. The monomers 3–5 underwent anionic polymerizations quantitatively to produce stable living polymers even at room temperature. They possessed $\bar{M}_n$'s controllable by [M] to [I] ratios and narrow molecular weight distributions, the $\bar{M}_w/\bar{M}_n$ values being less than 1.1 A living polymer was also obtained from 2, but appeared stable at temperatures lower than −33 °C. On the other hand, significant side reactions occurred in the polymerizations of 1, 6, and 7. Polymers with broad molecular weight distributions or cross-linked insoluble polymers were obtained in the cases of 1 and 6. No appreciable polymerization took place with 7. Thus, the steric demand of the *N*-substituent and the substituted position of the CH═N—R group were found to be crucial to achieve the anionic living polymerizations of styrenes substituted with *N*-alkylimino groups. Some well-defined novel block copolymers with poly(4) segments were synthesized by a sequential polymerization of 4 and comonomers such as isoprene, styrene, and 2-vinylpyridine. Furthermore, both the reactivities of 4 and the resulting living polymer from 4 could be estimated from the results of block copolymerization. The polymers from 2–5 were transformed cleanly into the poly(4-formylstyrene)s with highly controlled chain structures by acid hydrolyses of the polymers.

Introduction

We have recently found that novel anionic living polymers are produced from styrene derivatives *para*-substituted with electron-withdrawing groups[2] such as (*N,N*-dialkylamino)carbonyl,[3] (trimethylsilyl)ethynyl,[4] *N*-cyclohexylimino,[5] oxazoline,[6] *tert*-butyl ester,[7] (*N,N*-dialkylamino)sulfonyl,[8] and cyano.[9] Although these groups are susceptible to react with the anionic initiators and the carbanions at the growing chain end, the polymerizations of all the above monomers proceed well to give polymers possessing highly controlled chain lengths. Our explanation for these successful living polymerizations is that the electron densities of the carbanions at the growing chain ends are reduced considerably to lower the nucleophilicities of the carbanions themselves by the electron-withdrawing effects of these groups. Moreover, the extension of π-conjugated systems from the terminal benzylic carbanions to the electron-withdrawing groups may also contribute to stabilize the carbanions to a great extent.

In the preceding paper,[5] we have already demonstrated the anionic living polymerization of 4-(*N*-cyclohexylimino)-styrene (4). The resulting poly(4) could be transformed into the poly(4-formylstyrene) which still retained a predicted molecular weight and a narrow molecular weight distribution (MWD). Thus, the living polymerization of 4 followed by the deprotection reaction of the polymer is an excellent method for the synthesis of poly(4-formylstyrene) with a well-defined chain structure.

By contrast, the anionic polymerization of structurally similar 4-(*N*-phenylimino)styrene was not successful under identical conditions.[5] Virtually no polymeric material was obtained at all. Hence, it is obvious that the *N*-substituents strongly affect the polymerization behavior of styrene derivatives bearing the imino moiety. At the present time, the ability of 4 to undergo polymerization is believed to result from the presence of the bulky *N*-cyclohexyl group, which prevents attack of the CH═N bond by the carbanions of either the initiator or the growing active end as a most likely side reaction. On the other hand, the phenyl group may not protect the CH═N moiety from such a side reaction.

These contrasting results prompted us to study the influence of other *N*-substituents on polymerization. We therefore examine the possibility of anionic living polymerizations of 4-(*N*-alkylimino)styrenes where the *N*-alkyl groups vary from methyl (1), ethyl (2), isopropyl (3), to *tert*-butyl (5) groups as shown in Scheme I. Furthermore, the anionic polymerizations of two positional isomers of 4, *meta* (6) and *ortho* (7) substituted derivatives (Chart I), are also carried out to clarify the positional effect of the substituent on these polymerizations. The objective of this work is to understand fully the effects of the *N*-alkyl group and substitution patterns on anionic living polymerization of styrene derivatives substituted with *N*-alkylimino functions.

Results and Discussion

All the *N*-alkylimino-substituted styrenes used in this study were synthesized by the dehydration reaction of primary amine and the corresponding formylstyrenes. Most reactions proceeded rapidly and exothermically to yield the monomers in good to quantitative yields. The ^{1}H and ^{13}C NMR spectra of these monomers presented one iminyl signal at the expected region, indicating that the imino groups may consist of one configuration, a presumably anti configuration on the basis of previous reports concerning the stereochemistry of the –CH═N– linkage.[10]

Evaluation of the Electron-Withdrawing Effect of the *N*-Alkylimino Groups. It is very interesting to

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Scheme I

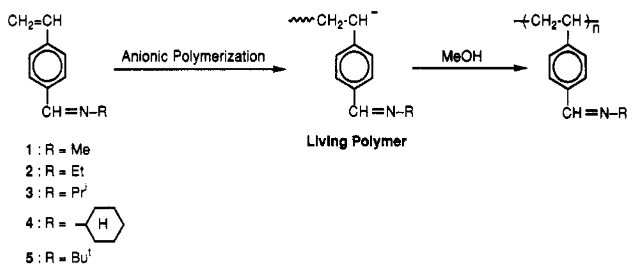
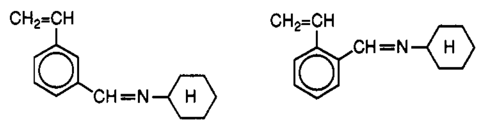


Chart I



6 7

predict the electron-withdrawing character of *N*-alkylimino groups of the monomers, since the character will strongly affect the polymerization behaviors of these monomers. The Hammett σ value is especially useful for quantitative discussion of the character. The value of the *N*-phenylimino moiety has been reported to be 0.42,[11] and it clearly shows the electron-withdrawing character of the group comparable to either ester (σ_p = 0.45) or acetyl (σ_p = 0.50) functionalities.

Interestingly, Reynolds and his co-workers have reported that the character of the substituent of 4-substituted styrene derivatives can also be evaluated from the chemical shifts of the vinyl β-carbon in ^{13}C NMR spectra of the monomers.[12] The β-carbon chemical shifts of **1**–**5** were 115.1, 114.9, 114.9, 114.9, and 114.7 ppm, respectively. The values shifted apparently toward lower field than that of the parent styrene (113.8 ppm), while there was little difference in the chemical shifts of the vinyl β-carbons among the five monomers. These values indicate the electron-withdrawing character of the *N*-alkylimino functionalities and that the five 4-substituted styrene monomers **1**–**5** may possibly provide similar reactivities under anionic conditions. Therefore, the effect of the steric factor of their *N*-alkyl substituents may be more important and should be considered in the polymerization reaction of **1**–**5**. In addition, the new Hammett σ_p values of *N*-alkylimino groups can actually be determined by their chemical shifts to be in the range of 0.19–0.25 for **1**–**5** according to the method reported by Reynolds.[12]

The substituent position of styrene monomers can also certainly affect the polymerization behavior, since the electron-withdrawing character as well as the π-resonance stabilization of the terminal propagating carbanion is considered to be different for each substituent position, e.g., *ortho*-, *meta*-, or *para*-position. The polymerizations of **4**, **6**, and **7** are of interest in this regard.

Anionic Polymerizations of *N*-Alkyl-*N*-(4-vinylbenzylidene)amines 1–5. The polymerizations of **1**–**5** were first carried out in THF at −78 °C for 10 min with oligo(α-methylstyryl)dipotassium. When these monomers were added to the initiator solution, the color of the reaction system immediately changed from red to the characteristic dark red of the polystyryl anions from **1**–**5**, indicating that the initiation step was rapid in each run. After 10 min, a small amount of methanol was added to terminate the polymerization reaction, and the red coloration immediately disappeared. In each case, gas chromatography (GC) analyses of the reaction mixtures indicated that the polymers were obtained essentially quantitatively as unreacted monomers were not detected. The resulting polymers were purified by reprecipitations and freeze-drying from benzene and then characterized by ^{1}H and ^{13}C NMR and IR spectra. From these analyses, it was observed that the signals and absorptions due to vinyl groups of the monomers completely disappeared. In the ^{1}H NMR spectra of the polymers, the characteristic signals at around 8.2 ppm for the CH=N protons were clearly observed at reasonable integral ratios to other signals. The ^{1}H and ^{13}C NMR analysis data of the polymers were consistent with the assigned structures of poly[4-(*N*-alkylimino)styrene]s obtained exclusively by the vinyl polymerizations of **1**–**5**. The results for their $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values are summarized in Table I.

At first, size exclusion chromatography (SEC) analysis of the polymer from **1** indicated that the MWD is relatively narrow, the polydispersity index shown by $\bar{M}_w/\bar{M}_n$ being 1.19. There is, however, a small shoulder on the higher molecular weight side in addition to the sharp SEC chromatographic peak, as can be seen in Figure 1A. Since this suggested that the undesirable side reaction probably occurred between the polymer chains after polymerization, we attempted to allow the reaction mixture to stand for a longer reaction time, 30 min, at −78 °C. The phenomenon thereupon became more distinguished, and the chromatogram of the polymer sample became multimodal as shown in Figure 1B. The estimated molecular weight from SEC analysis was significantly higher than the calculated value. When the reaction mixture was allowed to stand for an even longer time, 90 min, the mixture was completely immobile and became a red-colored jellylike material including the whole solvent of the system. No soluble poly(**1**) was recovered, and alternatively an insoluble gel was obtained in nearly quantitative yield after Soxhlet extraction using benzene as an extract, which indicated that appreciable cross-linking had taken place at this stage. Similar gelation was immediately caused at room temperature on addition of **1** to the initiator solution. In this case, the conversion of **1** was again observed to be quantitative after 10 min. Instead, with use of oligo(α-methylstyryl)dilithium as an initiator, the polymer, having a very broad and multimodal MWD, was produced in 66% yield after 30 min at −78 °C.

These observations suggest that serious side reactions occur to a considerable extent during the polymerization of **1**, presumably after the complete consumption of the monomer. The most likely reactions might be both inter- and intramolecular nucleophilic attacks of the carbanion at both growing chains on the carbon–nitrogen double bond of the CH=N—CH_3 group in the produced poly(**1**) as shown in Scheme II. The intermolecular reaction finally led to the gelation because of the cross-linking reaction between the polymer chains. Steric hindrance of the methyl group of **1** and/or the resulting poly(**1**) seems to be insufficient to protect the imino moiety from the nucleophilic attack of the carbanion.

We next tried to polymerize an alternative monomer, **2**, having an *N*-ethyl group on the nitrogen atom. Monomer **2** was polymerized quantitatively at −78 °C for 10 min with oligo(α-methylstyryl)dipotassium in THF. In marked contrast to the case of **1**, a soluble polymer was obtained at −78 °C even after 24 h. The SEC analyses of both the polymers obtained after 10 min and 24 h show that they possess unimodal and narrow MWDs. The SEC chromatogram of the poly(**2**) obtained after 24 h of reaction is shown in Figure 2. There is good agreement between the calculated molecular weights from [M]/[I] and the observed values by vapor pressure osmometry (VPO). These results reveal that **2** undergoes anionic living

Table I. Anionic Polymerizations of 1–5 in THF

run	monomer	monomer amt, mmol	temp, °C	time, min	initiator	initiator amt, mmol	α-MeSt[a] amt, mmol	yield, %	$10^{-3}\bar{M}_n$ calcd[b]	$10^{-3}\bar{M}_n$ obsd[c]	$\bar{M}_w/\bar{M}_n$[d]
1	1	4.02	−78	10	K–Naph[e]	0.113	0.243	100	11	7.6[f]	1.19
2	1	2.75	−78	30	K–Naph	0.0890	0.265	95	9.7	13[f]	2.75
3	1	3.33	−78	90	K–Naph	0.0943	0.280	100	11	*g*	
4	1	3.20	rt	10	K–Naph	0.0932	0.241	100	11	*g*	
5	1	3.46	−78	30	Li–Naph[h]	0.105	0.212	66	10	*i*	
6	2	3.61	−78	10	K–Naph	0.126	0.217	99	9.3	9.5	1.08
7	2	2.37	−78	90	K–Naph	0.0730	0.225	99	11	9.7	1.05
8	2	2.91	−78	24 h	K–Naph	0.0600	0.332	100	17	14	1.05
9	2	2.74	−33	10	K–Naph	0.0805	0.126	100	11	11	1.08
10	2	3.15	rt	10	K–Naph	0.109	0.191	100	9.6	*g*	
11	2	3.30	−78	30	Li–Naph	0.0955	0.193	15	1.7	1.8	1.09
12	2	2.36	−78	24 h	Li–Naph	0.0639	0.398	100	13	13	1.12
13	3	2.03	−78	10	K–Naph	0.0798	0.284	95	9.7	10	1.04
14	3	4.45	−78	20	K–Naph	0.0821	0.337	99	22	24	1.06
15	3	4.09	rt	10	K–Naph	0.141	0.324	100	11	11	1.10
16	3	3.15	−78	10	Li–Naph	0.113	0.289	44	4.5	6.0	1.09
17	3	3.06	−78	24 h	Li–Naph	0.109	0.275	80	8.3	9.1	1.08
18	3	6.15	−78	57 h	Li–Naph	0.164	0.372	100	14	16	1.10
19	4	2.81	−78	15	K–Naph	0.0764	0.130	100	16	15	1.07
20	4	3.24	−78	20	Bz–K[j]	0.0345	0.0501[k]	100	20	20	1.07
21	4	5.03	−78	10	K–Naph	0.0680	0.313	100	33	29	1.07
22	4	2.62	0	10	K–Naph	0.0863	0.396	100	14	12	1.07
23	4	2.47	rt	10	K–Naph	0.0929	0.502	100	13	13	1.12
24	4	3.40	−78	20	*n*-BuLi	0.0402	0.156[k]	50	9.0	9.2	1.09
25	4	2.46	−78	4 h	Li–Naph	0.131	0.286	100	9.1	8.5	1.09
26	5	3.32	−78	10	K–Naph	0.147	0.494	100	9.2	7.9	1.05
27	5	2.16	rt	10	K–Naph	0.0776	0.262	100	11	9.1	1.07
28	5	2.35	−78	10	Li–Naph	0.0783	0.126	73	8.8	7.5	1.10
29	5	3.59	−78	4 h	Li–Naph	0.138	0.258	100	10	9.4	1.09

[a] α-Methylstyrene. [b] $\bar{M}_n$(calcd) = [monomer] × (MW of monomer) × yield × f/[initiator] + (MW of initiator); f = 1 or 2, corresponding to the functionality of the initiator. [c] $\bar{M}_n$(obsd) was obtained by VPO measurement in benzene. [d] $\bar{M}_w/\bar{M}_n$ was obtained by SEC analysis in THF solution. [e] Potassium naphthalenide. [f] M_n(obsd) was obtained by SEC calibration of standard polystyrenes in THF. [g] The reaction mixture became insoluble probably due to the cross-linking of the polymer. [h] Lithium naphthalenide. [i] Multimodal and broad MWD. [j] Benzylpotassium. [k] 1,1-Diphenylethylene was used as a capping reagent instead of α-methylstyrene.

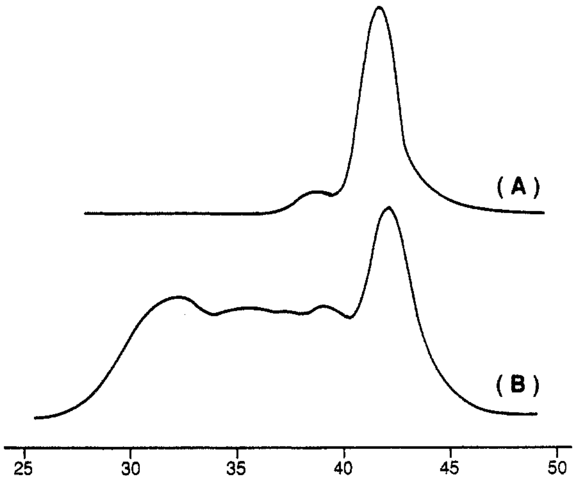


Figure 1. SEC curves of poly(1)s obtained at −78 °C: (A) after 10 min, $\bar{M}_w/\bar{M}_n$ = 1.19 (Table I, run 1); (B) after 30 min, $\bar{M}_w/\bar{M}_n$ = 2.75 (Table I, run 2).

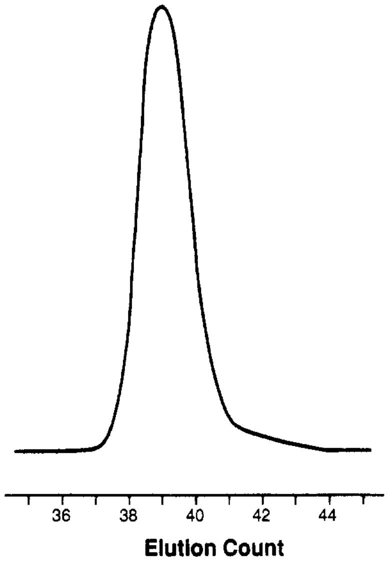
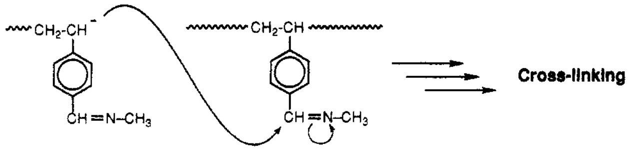


Figure 2. SEC curve of poly(2) obtained at −78 °C after 24 h of reaction, $\bar{M}_w/\bar{M}_n$ = 1.05 (Table I, run 8).

Scheme II



polymerization, giving polymers with well-defined chain structures. Thus, by changing the *N*-alkyl substituent from methyl to ethyl, we can succeed to completely protect the CH═N bond from the attack of carbanion. A stable living polymer from 2 was obtained at −78 °C. The polymer yielded at −33 °C after 10 min of polymerization also had the predicted $\bar{M}_n$ and narrow MWD as well as those produced at −78 °C. However, the growing active end of the polymer appears unstable at room temperature to result in quantitative formation of an insoluble polymer after 10 min.

The polymerization of 2 with oligo(α-methylstyryl)dilithium proceeded very slowly at −78 °C in THF. For example, the yield of the polymer was only 15% after 30 min, although 100% conversion of 2 could be attained after 24 h. The polymers obtained by the lithium initiators also possessed controllable molecular weights and narrow MWDs. Careful examination revealed that, in the SEC curve of the polymer obtained after 24 h (run 12), there was a very small shoulder on the higher molecular weight side which suggested that the side reaction occurred to a small extent after the polymerization. Therefore, further optimization will be needed on the polymerization time and yield of the polymer to obtain a polymer of narrow MWD without the shoulder.

The results obtained here clearly demonstrated that the polymerization of 2 proceeds ideally to give a living polymer under the appropriate conditions including reaction temperature and countercation of the initiators used. It is obvious that the *N*-alkyl substituent provides a means for a subtle control of polymerization of the styrene bearing an alkylimino group. An advantage of using 2 is thus apparent from the viewpoint of anionic living polymerization.

Although we have found a significant improvement of the polymerization by changing the *N*-substituent from methyl to ethyl, the living polymer yielded from 2 appears still unstable at room temperature. Therefore, the anionic polymerization of 3 with a bulkier isopropyl group rather than an ethyl group was attempted. The complete consumption of the monomer was achieved within 10 min in each run using the initiator bearing K^+ since 3 was no longer detected by GLC measurement. The polymers were obtained quantitatively in all cases. It is noteworthy that a soluble polymer is quanitatively obtained by polymerization at room temperature (run 15). All the $\bar{M}_w/\bar{M}_n$ values of the resulting polymers were in the range of 1.04–1.10, indicating narrow MWDs of the polymers. Moreover, the observed $\bar{M}_n$s agreed fairly well with those predicted from the molar ratios of monomer to initiator. A satisfactory result was shown with respect to $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values of the polymer obtained at room temperature. Thus, the *N*-substitution by an isopropyl group was very effective in maintaining the living the nature of the polymerization at room temperature. In other words, the *N*-isopropylimino group is stable and can coexist with the carbanion at the growing chain end derived from 3 at an elevated temperature (room temperature).

Similar results were obtained for polymerizations using lithium initiators. Good agreement between the values of $\bar{M}_n$ calculated and observed as well as narrow MWDs also confirms the living polymerization of 3 under these conditions. In the SEC curves, there were no shoulders at all, implying that the contribution of a possible side reaction is negligible, which was observed in the polymerization of 2 as mentioned before. The polymerization was again found to proceed slowly at −78 °C with the initiator containing Li^+ and afforded a polymer quantitatively after 57 h.

To ascertain the interesting finding that the living polymer is stable even at room temperature in the polymerization of 3, we have carried out the anionic polymerizations of 4 and 5 having more sterically hindered cyclohexyl and *tert*-butyl substituents. The yields of the polymers were quantitative. With use of both initiators bearing K^+ and Li^+, the results with respect to the values of $\bar{M}_n$ observed and calculated and $\bar{M}_w/\bar{M}_n$ indicate that both the reaction systems of 4 and 5 possess the characteristics of living polymerization. As expected, 4 and 5 undergo living polymerizations without difficulty at room temperature. A typical SEC chromatogram of the poly(5) produced at room temperature is shown in Figure 3. It can be concluded from the results that the polymerizations of 4 and 5 behave similarly to that of 3 under the reaction conditions employed here.

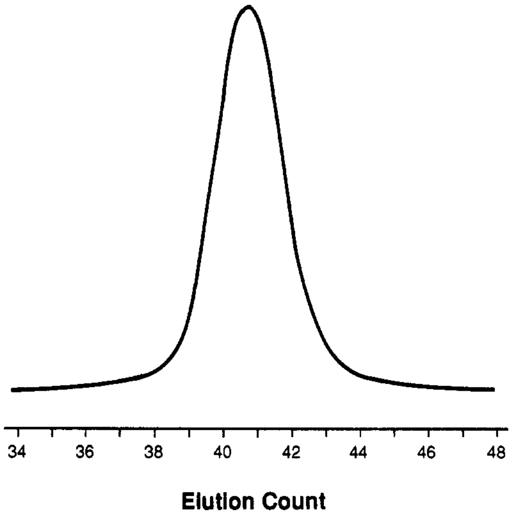


Figure 3. SEC curve of poly(5) obtained at room temperature after 10 min of reaction, $\bar{M}_w/\bar{M}_n = 1.07$ (Table I, run 27).

In summary, we have found in the polymerizations of 1–5 that the bulkiness of the *N*-alkyl group seriously affects their polymerization reactions. The polymerization of 1 with a methyl substituent competed with the side reaction even at −78 °C to afford an insoluble polymer quantitatively after 1.5 h. 2 substituted with an ethyl group tolerated the anionic living polymerization at −78 to −33 °C, while the polymerization system was not stable at room temperature. We have demonstrated that the possible side reaction such as the nucleophilic attack on the *N*-alkylimino moiety is suppressed even at room temperature by using sterically hindered isopropyl, cyclohexyl, and *tert*-butyl groups as *N*-substituents. In these polymerization reactions, the *N*-alkylimino groups coexist with the carbanions at the growing ends of the polymers from 3–5 to afford stable anionic living polymers. Consequently, polymers with narrow MWDs and the predicted molecular weight could be obtained at a wide variety of temperatures from −78 °C to room temperature. Accordingly, besides the electron-withdrawing nature and the resonance effect of an extended π-conjugated system, the steric hindrance of *N*-alkyl substituents is shown to be an essential factor for the success of anionic living polymerization of the 4-(*N*-alkylimino)styrenes.

Anionic Polymerizations of *N*-Cyclohexyl-*N*-(3-vinylbenzylidene)amine (6) and *N*-Cyclohexyl-*N*-(2-vinylbenzylidene)amine (7). The position of the substituent on the styrene monomer may certainly influence the behavior of polymerization,[13] since electronic and resonance effects and steric demand are considerably dependent on the position of the substituent. However, very few attempts to thoroughly investigate this influence on anionic living polymerization have been reported. We have recently observed that the three positional isomers (*ortho*, *meta*, and *para*) cyanostyrene[9] behave quite differently in their anionic polymerizations. It is of interest, in this regard, to investigate the polymerization behaviors of the styrenes substituted with *N*-alkylimino groups not only at the *para*-position but also at the *meta*- and *ortho*-positions. For this purpose, we examine here the anionic polymerizations of 6 and 7 which are the *meta* and *ortho* isomers of 4 with an *N*-cyclohexyl group to clarify the positional effect on the polymerization. The polymerization results of 6 and 7 are summarized in Table II.

As mentioned in the preceding section, the *para*-substituted styrene monomer of 4 was found to undergo anionic living polymerization without difficulty even at room temperature.

Table II. Anionic Polymerizations of 6 and 7 in THF

run	monomer	monomer amt, mmol	temp, °C	time, min	initiator	initiator amt, mmol	α-MeSt amt, mmol	yield, %	$10^{-3}\bar{M}_n$ calcd[a]	$10^{-3}\bar{M}_n$ obsd[b]	$\bar{M}_w/\bar{M}_n$[b]
30	6	3.07	−78	5	K-Naph	0.110	0.368	48	5.8	6.3	1.36
31	6	2.76	−78	30	K-Naph	0.0943	0.311	100	12	13	3.38
32	6	2.61	−95	30	K-Naph	0.838	0.294	54	7.0	15	2.99
33	6	3.14	−78	5	Li-Naph	0.0902	0.328	11	1.7	5.1	3.53
34	7	2.78	−78	24 h	K-Naph	0.107	0.449	trace			
35	7	2.86	−78	24 h	Li-Naph	0.106	0.346	trace			

[a] $\bar{M}_n$(calcd) = [monomer] × (MW of monomer) × yield × 2/[initiator] + (MW of initiator). [b] $\bar{M}_n$(obsd) and $\bar{M}_w/\bar{M}_n$ were obtained by SEC calibration of standard polystyrenes in THF solution.

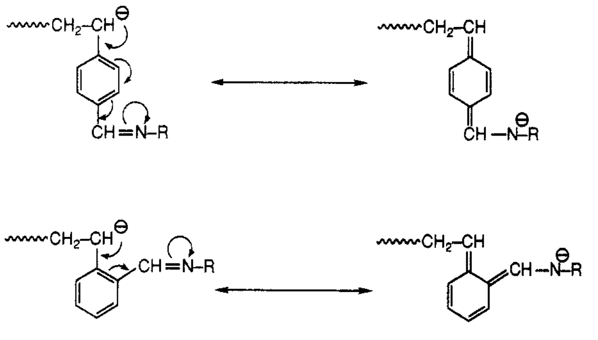
We next attempted the polymerization of the *meta* isomer of **6** under identical conditions. An immediate color change was observed from red to dark red at −78 °C on the addition of **6** to oligo(α-methylstyryl)dipotassium in THF, similar to the cases of **1**–**5**. Under these conditions, the yields of the polymer were 48% after 5 min and quantitative after 30 min. The chemical structure of the resulting polymer was ascertained by ^{1}H NMR and IR spectra as poly(**6**) produced by vinyl polymerization within the range of our measurement. Unfortunately, the polymer obtained after 30 min was found to have a broad and multimodal MWD by SEC measurement. The attempts of low-temperature polymerization at −95 °C (run 32) and with use of the initiators bearing Li$^+$ (run 33) were not satisfactory, giving polymers with very broad MWDs in low yields. These results obviously indicate that undesirable side reactions occur seriously during the course of polymerization of **6** under the conditions where the living polymerization of **4** is realized.

The polymerization of the *ortho* isomer of **7** was carried out under the same conditions. On mixing **7** and either oligo(α-methylstyryl)dipotassium or -dilithium in THF at −78 °C, the reaction mixture always exhibited a blue-violet color at first but afterward changed to a brown color within a few minutes. The unreacted **7** was recovered in nearly quantitative yields in both polymerization systems after 24 h. Only trace amounts of methanol-insoluble products were also obtained, but no attempts of the characterization could be made. Hence, no appreciable polymerization of the *ortho*-substituted monomer appeared to proceed under these polymerization conditions.

Thus, the polymerization results of **4**, **6**, and **7** clearly show that the position of the *N*-cyclohexylimino substituent strongly affects their polymerization behaviors. We could achieve the anionic living polymerization of only the *para*-substituted styrene to afford quantitatively well-defined polymers having both controllable molecular weights and narrow MWDs. By contrast, both the polymerizations of *meta* and *ortho* isomers failed with respect to living polymerization, although the polymer was obtained quantitatively in the polymerization of **6**, the *meta* isomer.

From the results of block copolymerization of **4** as mentioned later, the propagating carbanion derived from **4** is undoubtedly stabilized considerably by substituting the electron-withdrawing *N*-cyclohexylimino group at the *para*-position. Similar stabilization of the carbanion of the growing chain end will be expected in the polymerization of the *ortho* isomer (**7**) because both resonance and inductive effects of the substituent would promote similarly in the case of **4**. As can be seen in Scheme III, the *N*-alkylimino moieties of **4** and **7** can possibly accept negative charge and conjugate with the yielded benzylic carbanions through π-electron resonance. This resonance effect may play a key role in the stabilization of the propagating benzylic carbanion in addition to the inductive effect of the electron-withdrawing imino group. However, in the case of **7**, we could not obtain any polymeric products capable of identification from the reaction mixture. For this reason, we estimate that the *ortho*-substituted imino group may be suitably located near the terminal carbanion to allow the nucleophilic addition. Even if the initiation reaction of **7** occurs once, the intramolecular nucleophilic attack of the active chain end on the imino functionality may take place at the initial stage of polymerization. Thus, no polymer was obtained by the polymerization of **7**.

Scheme III



In the polymerization of the *meta* isomer (**6**), the MWDs of the resulting polymers were multimodal, although the polymer yields were quantitative under the appropriate conditions. We can speculate in this case that multimodal distribution is probably caused by the intermolecular nucleophilic attack of the propagating carbanion on the imino group of the polymer side chain. The resulting terminal carbanion derived from **6** cannot conjugate with the *meta*-substituted imino functionality through π-resonance. It therefore seems that the stabilization of the propagating carbanion is not sufficient enough for the achievement of living polymerization of **6** only by the contribution of the inductive effect of the CH=N—R moiety. Hence, the undersirable nucleophilic attack on the imino carbon could not be suppressed during the course of the polymerizations of **6** to result in polymers having broad MWDs.

Block Copolymerization of 4 with Isoprene, Styrene, 2-Vinylpyridine, and *N,N*-Diethyl-4-vinylbenzamide. As pointed out in the preceding section, we have demonstrated the anionic polymerizations of **2**–**5** in which stable living polymers with *N*-alkylimino functions can be produced. Novel types of well-defined block copolymers may possibly be synthesized by using these living polymerization systems. We here select **4** as a representative monomer for the block copolymerization and explore the synthetic possibility of block copolymers of **4** and isoprene, styrene, 2-vinylpyridine (2VP), and *N,N*-diethyl-4-vinylbenzamide[3b] (StCONEt$_2$). The reasons to select the latter four monomers are that they have different Alfrey–Price *e* values[14] and are amenable to the anionic living polymerization mechanism under the conditions employed here. Besides the synthetic possiblity of a block copolymer, another important aspect of block copolym-

Table III. Block Copolymerization of 4 with Isoprene, Styrene, 2-Vinylpyridine (2VP), and *N*,*N*-Diethyl-4-vinylbenzamide ($StCONEt_2$) at −78 °C in THF

					block copolymer (homopolymer[b])		
run	countercation	block sequence	A monomer	B monomer	$10^{-3}\bar{M}_n$(calcd)[c]	$10^{-3}\bar{M}_n$(obsd)[d]	$\bar{M}_w/\bar{M}_n$[e]
36	Li^+	B–A–B	4	2VP	20 (7.7)	19 (9.6)	1.26 (1.14)
37	K^+	B–A–B	4	$StCONEt_2$	16 (7.7)	16 (8.2)	1.10 (1.10)
38	K^+	A–B–A	4	isoprene	22 (11)	19 (14)	1.08 (1.08)
39	K^+	A–B–A	4	styrene	23 (12)	25 (13)	1.11 (1.06)
40	Li^+	A–B–A	4	2VP	18 (9.1)	15 (6.7)	1.15 (1.13)
41	K^+	A–B–A	4	$StCONEt_2$	17 (7.4)	15 (5.5)	1.12 (1.10)

[a] The yields of the polymers were nearly quantitative in each case. Difunctional initiators were used in all block copolymerizations. [b] Homopolymers were obtained at the first-stage polymerization. [c] $\bar{M}_n$(calcd) = [monomer] × (MW of monomer) × 2/[initiator] + (MW of initiator). [d] The molecular weights of the block copolymers were determined by using the molecular weights of the homopolymers and the molar ratios of monomer units in the block copolymer analyzed by ^{1}H NMR. [e] $\bar{M}_w/\bar{M}_n$ was obtained by SEC calibration using standard polystyrene.

erization is the ability to estimate the reactivities of both the monomer and the resulting living polymer by the efficiency of block copolymerization.

We have carried out the block copolymerizations by the sequential addition of 4 at first and then isoprene, styrene, 2VP, or $StCONEt_2$. In order to synthesize the block copolymer of 4 with isoprene, isoprene was added in THF at −78 °C to difunctional living poly(4) prepared with oligo-(α-methylstyryl)dipotassium. However, the homopolymer of 4 was quantitatively recovered from the reaction mixture with isoprene after 4 h. This means that the living poly(4) cannot initiate the polymerization of isoprene at all under these conditions. By contrast, styrene was quantitatively polymerized with the living poly(4). The SEC trace showed that the copolymerization product possessed a bimodal MWD. The first peak was exactly the same as that of poly(4), and the second peak was eluted at a much higher molecular weight region than that predicted. This suggests that the polymer is a mixture of virtual homopoly(4) and the block copolymer containing a polystyrene segment of very high molecular weight. In this block copolymerization, it can therefore be concluded that only a portion of the living polymer of 4 reacts with styrene to polymerize rapidly, while most of the living polymer remains unreacted. The initiation efficiency of the second polymerization was roughly estimated to be 5% from the SEC and ^{1}H NMR analyses of the products. These low reactivities of the living poly(4) toward isoprene and styrene are accounted for by the stabilization of the active chain end due to the electron-withdrawing effect of the *N*-cyclohexylimino group along with the extension of the π-conjugated system at the terminal benzylic carbanion as discussed in the preceding section.

In contrast to the cases with isoprene and styrene, both the polymerizations of more anionically reactive 2VP and $StCONEt_2$[3b,14] estimated from their *e* values were quantitatively initiated with living poly(4) to result in the formation of block copolymers. Their predictable M_n values and block segment lengths and relatively narrow MWDs were confirmed by ^{1}H NMR and SEC analyses as shown in Table III (runs 36 and 37). This results also indicates that the propagating carbanion of poly(4) is stable at −78 °C in THF at least for 30 min.

Thus, the living polymer derived from 4 does not react with isoprene but reacts slowly with styrene. It reacts quantitatively with 2VP and $StCONEt_2$, thereby suggesting the reactivity of living poly(4) is much less than those of the living polymers from isoprene and styrene and probably lies around those of the living polymers from 2VP and $StCONEt_2$.[15]

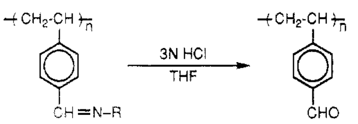
Next, we carried out the block copolymerizations by the reverse addition of two monomers. Actually, 4 was added to the difunctional living polymer of either isoprene or styrene in THF at −78 °C. In both cases, the polymerizations of 4 readily proceeded to yield the copolymers quantitatively. The contents of the poly(4) segment in the resulting copolymers analyzed by ^{1}H NMR were nearly equal to the calculated values based on the molar ratios of both monomers. The SEC chromatograms of the polymers obtained after the second polymerization exhibited unimodal peaks showing their narrow MWDs. All the results shown again in Table III strongly support that the resulting polymers are unequivocally the expected ABA-type triblock copolymers having predetermined architectures such as compositions and controllable molecular weights.

Both the living polymers from 2VP and $StCONEt_2$ also initiate quantitatively the polymerization of 4. The well-defined structures of these block copolymers were confirmed by SEC and ^{1}H and ^{13}C NMR analyses. The results are of particular interest considering the fact that the living polymers from 2VP and $StCONEt_2$ have no ability to initiate the polymerization of isoprene and react slowly with styrene.[15] This suggests that 4 is more reactive than isoprene and styrene and at least comparable to 2VP and $StCONEt_2$.

We have successfully synthesized novel block copolymers by the sequential addition of 4 and isoprene, styrene, 2VP, or $StCONEt_2$, although the order of addition of the comonomers is restricted to a few combinations. These block copolymers contain one or two blocks that have reactive *N*-cyclohexylimino groups in all monomer units. As mentioned later, this group can be transformed cleanly into the more reactive formyl function. From the results, we can also estimate the reactivities of 4 and the living polymer. They imply that 4 is anionically more reactive than styrene, but the resulting living polymer is less reactive than living polystyrene. Thus, the introduction of the *N*-cyclohexylimino group at the *para*-position of the styrene framework affects to a great extent the reactivities of the monomer and the living polymer derived. We have already found similar phenomena through studies concerning the anionic polymerizations of *para*-substituted styrenes having various electron-withdrawing groups.[2–4,6–9,15] The stabilization of their propagating chain ends has been similarly observed in the crossover reaction (block copolymerization) between their propagating species and the various monomers.[15]

Deprotection of the *N*-Alkylimino Protecting Groups from the Polymers. We previously reported that the hydrolysis reaction of poly(4) completely proceeded in 1,4-dioxane by treatment with 0.5 N HCl at 25 °C for 5–15 h.[5] It should be mentioned that this reaction condition was suitable for the hydrolysis of poly(4) having a molecular weight below 10 000, but it was somewhat insufficient for the deprotection of higher molecular weight

Scheme IV



polymers. Repeating the reaction under similar conditions was actually necessary for the complete deprotection of the *N*-cyclohexyl group from the poly(**4**) having a molecular weight higher than 10 000.

The deprotections of *N*-alkylimino groups from the other three polymers of **2**, **3**, and **5** were carried out in THF with 3 N HCl at room temperature as shown in Scheme IV. Polymers were obtained by pouring the reaction mixtures into water. After filtration, the yields of the polymers were nearly quantitative by assuming the complete deprotection of the protective groups. In each ^{1}H NMR spectrum of the polymer obtained after the deprotection reaction, the signal of the $\mathrm{CH{=}N}$ moiety near 8.2 ppm completely disappeared and alternatively the new signal corresponding to the formyl proton appeared at 9.9 ppm. In the infrared spectrum of the polymer, a new characteristic strong absorption of 1701 cm^{-1} due to the carbonyl group of aldehyde appeared and the absorption of 1640–50 cm^{-1} characteristic for the $\mathrm{CH{=}N}$ bonding no longer existed. These spectroscopic analyses strongly indicate that the complete deprotection of the polymer proceeds to form the poly(4-formylstyrene) in each case as expected. The SEC chromatograms of the resulting poly(4-formylstyrene)s were unimodal and showed sharp peaks as well as those of the parent polymers before deprotection. This SEC analysis suggests that both degradation and cross-linking of the polymer main chains do not occur during the deprotection reactions. Therefore, we can here conclude that the poly(4-formylstyrene) having a tailored molecular structure is obtained by the deprotection of the polymers of **2**–**5**, keeping the characteristics of the parent polymers.

Poly(**1**–**5**)s were white powders and could be cast into a transparent and brittle film from their solutions. The solubilities of all the polymers and poly(4-formylstyrene) obtained by the hydrolysis of these polymer samples are summarized in Table IV. The polymers of **1**–**5** are soluble in a wide range of organic solvents and particularly soluble in methanol and ethanol except for poly(**4**). Interestingly, the poly(**5**) is soluble even in pentane and hexane, in which polystyrene is insoluble. After the deprotection of these polymers, the solubilities significantly changed. The resulting poly(4-formylstyrene) is soluble in chloroform, acetone, 1,4-dioxane, THF, and *N*,*N*-dimethylformamide but insoluble in pentane, hexane, benzene, carbon tetrachloride, diethyl ether, ethyl acetate, methanol, ethanol, and water.

The glass transition temperatures (T_g's) of the polymers having $\bar{M}_n$'s in the range of 10000–30000 were measured by differential scanning calorimetry (DSC). The T_g's of poly(**1**), poly(**2**), poly(**3**), poly(**4**), and poly(**5**) were 114, 98, 105, 144, and 112 °C, respectively. These T_g values are nearly comparable with that of polystyrene (T_g = 100 °C), except for the poly(**4**).

Conclusion

In this study, we demonstrated that the bulkiness and the substitutional position of the *N*-alkylimino groups were essential to obtain stable living polymers in the anionic polymerization of *N*-alkylimino-substituted styrenes. It was also found that the electron-withdrawing imino groups of the resulting living polymers played an important role in the stabilization of the propagating carbanion to avoid the side reactions from the results of block copolymerization. Finally, well-defined poly(4-formylstyrene) was possible to obtain by the complete deprotection of the $\mathrm{CH{=}N{-}R}$ functions from the resulting poly(**2**–**5**).

Experimental Section

Materials. 4-Formyl-, 3-formyl-, and 2-formylstyrenes were prepared according to our previous report.[9b] Isoprene, styrene, and α-methylstyrene were distilled over calcium hydride and finally distilled from benzylmagnesium chloride under vacuum. 2-Vinylpyridine was first dried over potassium hydroxide and then distilled from calcium hydride on a vacuum line. 1,1-Diphenylethylene (DPE) was purified by fractional distillation and finally distilled from *n*-BuLi under vacuum. *N*,*N*-Diethyl-4-vinylbenzamide ($StCONEt_2$) was synthesized as previously reported.[3b] THF used as a polymerization solvent was refluxed over sodium wire for 5 h, distilled from lithium aluminum hydride, and finally distilled through a vacuum line from sodium naphthalenide solution.

Initiators. Commercially available *n*-butyllithium (1.6 M hexane solution) was diluted with heptane and used for the anionic polymerization. Potassium naphthalenide and lithium naphthalenide were prepared by the reactions of a small excess amount of naphthalene with the corresponding alkali metal in THF. Benzylpotassium was prepared by the reaction of benzyl methyl ether with sodium–potassium alloy in THF.[16] Oligo(α-methylstyryl)dilithium and -dipotassium were freshly prepared just prior to the polymerizations from the corresponding metal naphthalenides and a 2–4 M quantity of α-methylstyrene at 20 °C for 1 min and then at −78 °C for 10 min. These initiators were stored at −30 °C in ampules equipped with breakseals. The concentration of initiators was determined by calorimetric titration with standardized 1-octanol in a sealed reactor under vacuum.[17]

***N*-Methyl-*N*-(4-vinylbenzylidene)amine (1).** To 7.07 g of 4-formylstyrene (53.5 mmol)[9b] was added dropwise under ice bath cooling a water solution of methylamine (40 wt %, 6.18 g, 79.5 mmol). After the addition, the reaction mixture was stirred for 2 h at room temperature. The reaction mixture was diluted with diethyl ether and dried over $MgSO_4$. After evaporation of the solvent, distillation gave 6.94 g (47.8 mmol, 89%) of **1** as a colorless liquid at 52–53 °C (0.5 mmHg) from calcium hydride: ^{1}H NMR (90 MHz, $CDCl_3$) δ 3.49 and 3.51 (d, 3H, ^4J = 1.5 Hz, NCH_3), 5.29 and 5.79 (2d, 2H, J = 11 and 18 Hz, $CH_2{=}$), 6.73 (dd, 1H, $-CH{=}$), 7.38–7.71 (m, 4H, Ar), 8.23 and 8.25 (d, 1H, ^4J = 1.5 Hz, $\mathrm{CH{=}N}$); ^{13}C NMR (23 MHz, $CDCl_3$) δ 48.3 (NCH_3), 115.1 (vinyl, $CH_2{=}$), 126.5 (Ar, C3), 128.1 (Ar, C2), 135.8 (Ar, C4), 136.4 (vinyl, $-CH{=}$), 139.8 (Ar, C1), 162.1 ($\mathrm{CH{=}N}$); IR (KBr, cm^{-1}) 1649 ($\mathrm{CH{=}N}$), 1606, 1562, 1509, 1426, 1406, 1301, 1174, 1001, 991, 911, 839. Anal. Calcd for $C_{10}H_{11}N$: C, 82.72; H, 7.64; N, 9.65. Found: C, 82.34; H, 8.00; N, 9.68.

***N*-Ethyl-*N*-(4-vinylbenzylidene)amine (2).** To 6.88 g of 4-formylstyrene (52.1 mmol) was added dropwise under ice bath cooling a water solution of ethylamine (70 wt %, 5.03 g, 78.2 mmol). After the addition, the reaction mixture was stirred for 2 h at room temperature. The reaction mixture was diluted with diethyl ether and dried over $MgSO_4$. After evaporation of the solvent, distillation gave 7.42 g (46.6 mmol, 89%) of **2** as a colorless liquid at 59–63 °C (0.5 mmHg) from calcium hydride: ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.30 (t, 3H, J = 7 Hz, $-CH_3$), 3.64 (q, 2H, NCH_2, 5.30 and 5.79 (2d, 2H, J = 11 and 18 Hz, $CH_2{=}$), 6.73 (dd, 1H, $-CH{=}$), 7.38–7.73 (m, 4H, Ar), 8.26 (s, 1H, $\mathrm{CH{=}N}$); ^{13}C NMR (23 MHz, $CDCl_3$) δ 16.3 ($-CH_3$), 55.8 (NCH_2), 114.9 (vinyl, $CH_2{=}$), 126.3 (Ar, C3), 128.2 (Ar, C2), 135.9 (Ar, C4), 136.3 (vinyl, $-CH{=}$), 139.6 (Ar, C1), 159.9 ($\mathrm{CH{=}N}$); IR (KBr, cm^{-1}) 1646 ($\mathrm{CH{=}N}$), 1606, 1562, 1509, 1448, 1378, 1334, 1301, 1094, 990, 909, 841. Anal. Calcd for $C_{11}H_{13}N$: C, 82.98; H, 8.23; N, 8.80. Found: C, 82.88; H, 8.22; N, 8.79.

***N*-Isopropyl-*N*-(4-vinylbenzylidene)amine (3).** To 10.50 g of 4-formylstyrene (79.4 mmol) was added dropwise under ice bath cooling 10.21 g of isopropylamine (173 mmol). After the addition, the reaction mixture was stirred for 1.5 h at room temperature. The reaction mixture was diluted with diethyl ether and dried over $MgSO_4$. After evaporation of the solvent, distillation gave 13.00 g (75.5 mmol, 95%) of **3** as a colorless

Table IV. Solubilities of Poly(1–5)s, Poly(4-formylstyrene), and Polystyrene[a]

solvent	solubility						
	poly(1)	poly(2)	poly(3)	poly(4)	poly(5)	poly(4-formylstyrene)	polystyrene
pentane	I	I	I	I	S	I	I
hexane	I	I	I	Sw	S	I	I
benzene	S	S	S	S	S	I	S
carbon tetrachloride	I	S	S	S	S	I	S
diethyl ether	I	S	S	S	S	I	S
ethyl acetate	S	S	S	S	S	I	S
chloroform	S	S	S	S	S	S	S
acetone	S	S	S	S	S	S	S
1,4-dioxane	S	S	S	S	S	S	S
tetrahydrofuran	S	S	S	S	S	S	S
N,*N*-dimethylformamide	S	S	S	Sw	S	S	S
ethanol	S	S	S	I	S	I	I
methanol	S	S	S	I	S	I	I
water	I	I	I	I	I	I	I

[a] Key: I, insoluble; S, soluble; Sw, swelling.

liquid at 64–68 °C (0.5 mmHg) from calcium hydride: ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$) δ 1.26 (d, 6H, *J* = 6 Hz, $\mathrm{-CH_3}$), 3.45–3.59 (m, 1H, ═NCH), 5.28 and 5.77 (2d, 2H, *J* = 11 and 18 Hz, $\mathrm{CH_2}$═), 6.72 (dd, 1H, –CH═), 7.37–7.73 (m, 4H, Ar), 8.26 (s, 1H, CH═N); ^{13}C NMR (23 MHz, $\mathrm{CDCl_3}$) δ 24.2 ($\mathrm{-CH_3}$), 61.7 (NCH), 114.9 (vinyl, $\mathrm{CH_2}$═), 126.4 (Ar, C3), 128.3 (Ar, C2), 136.1 (Ar, C4), 136.5 (vinyl, –CH═), 139.6 (Ar, C1), 157.8 (CH═N); IR (KBr, cm^{-1}) 1646 (CH═N), 1610, 1563, 1510, 1381, 1298, 1142, 990, 910, 841. Anal. Calcd for $\mathrm{C_{12}H_{15}N}$: C, 83.19; H, 8.73; N, 8.09. Found: C, 83.13; H, 8.83; N, 7.95.

***N*-Cyclohexyl-*N*-(4-vinylbenzylidene)amine (4).**[5] To a mixture of 4-formylstyrene (10.05 g, 66.1 mmol), cyclohexylamine (8.14 g, 82.2 mmol), and *tert*-butylcatecohol (10 mg) was added 150 mL of benzene. The reaction mixture was heated for 5 h under reflux with axeotropic separation of water by means of a Dean-Stark water trap. The reaction mixture was diluted with diethyl ether and dried over $\mathrm{MgSO_4}$. After evaporation of the solvent, distillation gave 13.17 g (61.8 mmol, 94%) of 4 as a colorless liquid at 99–101 °C (0.5 mmHg) from calcium hydride: ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$) δ 1.17–1.70 (m, 10H, $\mathrm{-CH_2CH_2CH_2CH_2CH_2-}$), 3.18–3.28 (m, 1H, ═NCH), 5.29 and 5.79 (2d, 2H, *J* = 11 and 18 Hz, $\mathrm{CH_2}$═), 6.73 (dd, 1H, –CH═), 7.37–7.73 (m, 4H, A), 8.28 (s, 1H, CH═N); ^{13}C NMR (23 MHz, $\mathrm{CDCl_3}$) δ 24.9, 25.8, 34.5 (cyclohexyl, $\mathrm{-CH_2}$), 70.0 (NCH), 114.9 (vinyl, $\mathrm{CH_2}$═), 126.4 (Ar, C3), 128.3 (Ar, C2), 136.2 (Ar, C4), 136.5 (vinyl, –CH═), 139.6 (Ar, C1), 158.1 (CH═N); IR (KBr, cm^{-1}) 1641 (CH═N), 1606, 1563, 1509, 1450, 1298, 1076, 993, 888, 838. Anal. Calcd for $\mathrm{C_{15}H_{19}N}$: C, 84.46; H, 8.98; N, 6.57. Found: C, 84.40; H, 9.01; N, 6.60.

***N*-*tert*-Butyl-*N*-(4-vinylbenzylidene)amine (5).** A mixture of 4-formylstyrene (10.10 g, 76.4 mmol), *tert*-butylamine (8.31 g, 114 mmol), and *p*-toluenesulfonic acid (20 mg) was heated for 6 h under reflux. The reaction mixture was diluted with diethyl ether and dried over $\mathrm{MgSO_4}$. After evaporation of the ether, distillation gave 13.40 g (71.6 mmol, 94%) of 5 as a colorless liquid at 73–75 °C (0.5 mmHg) from calcium hydride: ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$) δ 1.29 (s, 9H, $\mathrm{-CH_3}$), 5.28 and 5.78 (2d, 2H, *J* = 11 and 18 Hz, $\mathrm{CH_2}$═), 6.73 (dd, 1H, –CH═), 7.37–7.75 (m, 4H, Ar), 8.25 (s, 1H, CH═N); ^{13}C NMR (23 MHz, $\mathrm{CDCl_3}$) δ 29.8 ($\mathrm{-CH_3}$), 57.3 ($\mathrm{NCCH_3}$), 114.7 (vinyl, $\mathrm{CH_2}$═), 126.3 (Ar, C3), 128.1 (Ar, C2), 136.5 (vinyl, –CH═), 136.8 (Ar, C4), 139.4 (Ar, C1), 154.6 (CH═N); IR (KBr, cm^{-1}) 1641 (CH═N), 1606, 1371, 1226, 1206, 1170, 990, 909, 841. Anal. Calcd for $\mathrm{C_{13}H_{17}N}$: C, 83.37; H, 9.15; N, 7.48. Found: C, 83.20; H, 9.11; N, 7.65.

***N*-Cyclohexyl-*N*-(3-vinylbenzylidene)amine (6).** To a mixture of 3-formylstyrene (3.71 g, 28.1 mmol),[9b] cyclohexylamine (3.20 g, 32.3 mmol), and *tert*-butylcatecohol (10 mg) was added 100 mL of benzene. The reaction mixture was heated for 5 h under reflux with azeotropic separation of water by means of a Dean-Stark water trap. After cooling, the reaction mixture was dried over $\mathrm{MgSO_4}$. After evaporation of the solvent, distillation gave 3.98 g (18.7 mmol, 66%) of 6 as a colorless liquid at 101–103 °C (0.5 mmHg) from calcium hydride: ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$) δ 1.18–1.92 (m, 10H, $\mathrm{-CH_2CH_2CH_2CH_2CH_2-}$), 3.19–3.28 (m, 1H, ═NCH), 5.27 and 5.78 (2d, 2H, *J* = 11 and 18 Hz, $\mathrm{CH_2}$═), 6.78 (dd, 1H, –CH═), 7.26–7.77 (m, 4H, Ar), 8.31 (s, 1H, CH═N); ^{13}C NMR (23 MHz, $\mathrm{CDCl_3}$) δ 24.9, 25.7, 34.4 (cyclohexyl, $\mathrm{-CH_2}$), 69.9 (NCH), 114.5 (vinyl, $\mathrm{CH_2}$═), 125.8 (Ar, C2), 127.7 (Ar, C5), 128.0 (Ar, C4), 128.7 (Ar, C6), 136.5 (vinyl, –CH═), 137.0 (Ar, C3), 138.0 (Ar, C1), 158.4 (CH═N); IR (KBr, cm^{-1}) 2930, 2850, 1645 (CH═N), 1155, 989, 908. Anal. Calcd for $\mathrm{C_{15}H_{19}N}$: C, 84.46; H, 8.98; N, 6.57. Found: C, 84.15; H, 9.16; N, 6.47.

***N*-Cyclohexyl-*N*-(2-vinylbenzylidene)amine (7).** To a mixture of 2-formylstyrene (4.00 g, 30.3 mmol),[9b] cyclohexylamine (4.09 g, 41.2 mmol), and *tert*-butylcatecohol (10 mg) was added 100 mL of benzene. The reaction mixture was heated for 5 h under reflux with azeotropic separation of water by means of a Dean-Stark water trap. After cooling, the reaction mixture was dried over $\mathrm{MgSO_4}$. After evaporation of the solvent, distillation gave 3.05 g (14.3 mmol, 47%) of 7 as a colorless liquid at 97–98 °C (0.5 mmHg) from calcium hydride: ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$) δ 0.9–2.1 (br, 10H, $\mathrm{-CH_2CH_2CH_2CH_2CH_2-}$), 3.0–3.4 (br, 1H, ═NCH), 5.39 and 5.61 (2d, 2H, *J* = 11 and 18 Hz, $\mathrm{CH_2}$═), 7.07–7.91 (m, 5H, –CH═ and Ar), 8.66 (s, 1H, CH═N); ^{13}C NMR (23 MHz, $\mathrm{CDCl_3}$) δ 24.8, 25.8, 34.5 (cyclohexyl, $\mathrm{-CH_2}$), 70.3 (NCH), 117.5 (vinyl, $\mathrm{CH_2}$═), 126.6, 127.8, 130.0, 133.6, 134.2, 138.0, 141.3, 157.0 (CH═N); IR (KBr, cm^{-1}) 1636 (CH═N), 1599, 1450, 965, 917, 771. Anal. Calcd for $\mathrm{C_{15}H_{19}N}$: C, 84.46; H, 8.98; N, 6.57. Found: C, 83.85; H, 8.97; N, 6.69.

Monomer Purification. After careful fractional distillation, the purified monomers were sealed off under a degassed condition in an apparatus equiped with a breakseal in the presence of $\mathrm{CaH_2}$. The monomer was stirred for 24 h at ambient temperature and then distilled from $\mathrm{CaH_2}$ on a vacuum line into ampules fitted with breakseals. Next, to remove impurities in the monomer, phenylmagnesium chloride (5.0 mL, 0.20 M solution in THF) was added to the monomer (ca. 30 mmol) at –78 °C under vacuum (10^{-6} mmHg) and the mixture was stirred for 30 min at ambient temperature. It was distilled again under vacuum into the apparatus equipped with a breakseal and diluted with dry THF. The resulting monomer solutions (0.3–0.5 M in THF), were stored at –30 °C until ready to use for the anionic polymerization.

Polymerization Procedures. All polymerizations were carried out with shaking under high-vacuum conditions in the all-glass apparatus equipped with breakseals as previously reported.[17] The polymerization reaction was quenched with methanol, and the reaction mixture was then poured into a large excess of water to precipitate a polymer. Polymers collected by filtration were purified by reprecipitation twice with the water–THF system. The polymers thus obtained were characterized by ^{1}H and ^{13}C NMR and IR spectroscopies and elemental analysis. The following is the full list.

Data for Poly(1): ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$) δ 0.8–2.4 (m, 3H, $\mathrm{-CH_2CH-}$), 3.5 (s, 3H, $\mathrm{-NCH_3}$), 6.1–7.6 (m, 4H, Ar), 8.2 (s, 1H, –CH═N); ^{13}C NMR (23 MHz, $\mathrm{CDCl_3}$) δ 39–46 ($\mathrm{-CH_2CH-}$), 48.1 ($\mathrm{-NCH_3}$), 127.8 (Ar, C2 and C3), 134.1 (Ar, C1), 147.1 (Ar, C4) 162.2 (–CH═N); IR (KBr, cm^{-1}) 1651, 1607, 1571, 1453, 1401, 1303, 1001, 826.

Data for Poly(2): ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$) δ 0.8–2.3 (m, 6H, $\mathrm{-CH_2CH-}$ and $\mathrm{-CH_3}$), 3.6 (s, 2H, $\mathrm{-NCH_2}$), 6.1–7.6 (m, 4H, Ar), 8.2 (s, 1H, –CH═N); ^{13}C NMR (23 MHz, $\mathrm{CDCl_3}$) δ 16.3 ($\mathrm{-CH_3}$), 39–46 ($\mathrm{-CH_2CH-}$), 55.7 (═$\mathrm{NCH_2}$), 127.8 (Ar, C2 and

C3), 134.1 (Ar, C1), 147.2 (Ar, C4) 160.1 ($-CH{=}N$); IR (KBr, cm^{-1}) 1646, 1609, 1571, 1508, 1448, 1333, 1303, 1095, 1038, 828.

Data for Poly(3): ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.7–2.1 (m, 9H, $-CH_2CH-$, $-CH_3$), 6.2–7.6 (m, 4H, Ar), 8.2 (s, 1H, $-CH{=}N$); ^{13}C NMR (23 MHz, $CDCl_3$) δ 24.3 ($-CH_3$), 39–46 ($-CH_2CH-$), 61.6 ($=NCH$), 128.0 (Ar, C2 and C3), 134.5 (Ar, C1), 147.3 (Ar, C4), 158.3 ($-CH{=}N$); IR (KBr, cm^{-1}) 1646, 1608, 1572, 1381, 1300, 1142, 826.

Data for Poly(4): ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.7–2.6 (m, 13H, $-CH_2CH-$ and $-CH_2CH_2CH_2CH_2CH_2-$), 3.2 (s, 1H, $=NCH-$), 6.2–7.8 (m, 4H, Ar), 8.2 (s, 1H, $-CH{=}N$); ^{13}C NMR (23 MHz, $CDCl_3$) 25.0, 25.8, 34.6 (cyclohexyl, CH_2), 40–46 ($-CH_2$-$CH-$), 70.0 ($=NCH$), 128.0 (Ar, C2 and C3), 134.5 (Ar, C1), 147.1 (Ar, C4) 158.6 ($-CH{=}N$); IR (KBr, cm^{-1}) 1646, 1607, 1496, 1450, 1074, 826.

Data for Poly(5): ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.9–2.1 (m, 12H, $-CH_2CH-$ and CH_3), 6.3–7.6 (m, 4H, Ar), 8.2 (s, 1H, $-CH{=}N$); ^{13}C NMR (23 MHz, $CDCl_3$) δ 29.9 ($-CH_3$), 39–46 ($-CH_2$-$CH-$), 57.1 ($-NCCH_3$), 127.9 (Ar, C2 and C3), 135.1 (Ar, C1), 147.1 (Ar, C4) 155.1 ($-CH{=}N$); IR (KBr, cm^{-1}) 1641, 1607, 1356, 1205, 1174, 909, 828.

Data for Poly(6): ^{1}H NMR (90 MHz, C_6D_6) δ 0.7–2.8 (m, 13H, $-CH_2CH-$ and $-CH_2CH_2CH_2CH_2CH_2-$), 3.35 (s, 1H, $=NCH-$), 6.5–8.1 (m, 4H, Ar), 8.2 (s, 1H, $-CH{=}N$); ^{13}C NMR (23 MHz, $CDCl_3$) δ 24.9, 25.7, 34.5 (cyclohexyl, CH_2), 40–44 ($-CH_2$-$CH-$), 69.8 ($=NCH$), 125.3, 127.5, 128.3, 129.6, 136.5, (Ar, C1, C2, C4, C5, and C6), 145.2 (Ar, C3), 158.8 ($-CH{=}N$); IR (KBr, cm^{-1}) 1646, 1584, 1603, 1449, 1382, 1346, 1073, 967, 795.

Block Copolymerization. In the all-glass apparatus equipped with breakseals in vacuo, first-stage polymerization of styrene was carried out with potassium naphthalenide as an initiator in THF at −78 °C for 10 min. After sampling to determine the characteristics of homopolystyrene, to the residual polymerization system at −78 °C was added 4 the mixture reacted for 30 min to complete the second-stage polymerization. After quenching with methanol, both homopolystyrene and the block copolymer of styrene and 4 were quantitatively obtained. The characteristics of the copolymerization product were analyzed by ^{1}H NMR spectroscopy and SEC chromatography. Both polymers possessed narrow MWDs and predictable molecular weights as shown in Table III (run 39). Other block copolymerizations of 4 and comonomers were performed in a similar manner.

Typical Procedure of Deprotection. Poly(5) (0.30 g) was dissolved in THF (20 mL) containing 12 N HCl (5 mL), and then the reaction mixture was stirred for 18 h at room temperature. After pouring the reaction mixture into water, the solution was neutralized with potassium hydroxide and the yielded polymer was filtered. The resulting polymer was again dissolved in THF (20 mL) containing 12 N HCl (5 mL), and the reaction mixture was stirred for 20 h at room temperature. The polymer was recovered by filtration after pouring the reaction mixture into water containing an excess of potassium hydroxide. The polymer was redissolved in THF and precipitated into hexane. Then it was freeze-dried from 1,4-dioxane solution. The polymer (0.15 g) was identified as poly(4-formylstyrene) by IR and ^{1}H NMR spectroscopies as previously reported.[5] The deprotection reactions of poly(2–5) were carried out to afford the poly(4-formylstyrene) in a similar manner: ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.5–2.6 (m, 3H, $-CH_2CH-$), 6.2–8.0 (m, 4H, Ar), 9.9 (s, 1H, $-CH{=}N$); IR (KBr, cm^{-1}) 1701, 1604, 1574, 1448, 1427, 1306, 1212, 1166, 841, 828.

Measurements. Infrared spectra (KBr disk) were recorded on a JEOL JIR-AQS20M FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (89.6 MHz, ^{1}H; 22.53 MHz, ^{13}C) in $CDCl_3$. Chemical shifts were reported in parts per million downfield relative to tetramethylsilane (δ 0.00) for ^{1}H NMR and to $CDCl_3$ (δ 77.1) for ^{13}C NMR as standards. Vapor pressure osmometry (VPO) measurements for number-average molecular weight determinations were made with a Corona 117 instrument in benzene solution. Size exclusion chromatograms (SEC) for MWD determinations of polymers were obtained at 40 °C with a TOSOH HLC-8020 instrument equipped with three polystyrene gel columns (TOSOH G5000H$_{XL}$, G4000H$_{XL}$, and G3000H$_{XL}$) with ultraviolet (254 nm) or refractive index detection. THF was a carrier solvent at a flow rate of 1.0 mL min^{-1}. The glass transition temperatures of the polymers were measured by differential scanning calorimetry using a Seiko Instrument DSC220 apparatus and analyzed by a SSC 5200TA station. The samples were first heated to 240 °C, cooled rapidly to −20 °C, and then scanned again at a rate of 20 °C min^{-1}.

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References and Notes

(1) 4-(*N*-Alkylimino)styrenes.

(2) Nakahama, S.; Ishizone, T.; Hirao, A. *Makromol. Chem., Macromol. Symp.* **1993**, *67*, 223.

(3) (a) Hirao, A.; Nakahama, S. *Polymer* **1986**, *27*, 309. (b) Ishizone, T.; Wakabayashi, S.; Hirao, A.; Nakahama, S. *Macromolecules* **1991**, *24*, 5015.

(4) (a) Ishizone, T.; Hirao, A.; Nakahama, S.; Kakuchi, T.; Yokota, K.; Tsuda, K. *Macromolecules* **1991**, *24*, 5230. (b) Tsuda, K.; Ishizone, T.; Hirao, A.; Nakahama, S.; Kakuchi, T.; Yokota, K. *Macromolecules*, in press.

(5) Hirao, A.; Nakahama, S. *Macromolecules* **1987**, *21*, 2968.

(6) (a) Ishino, Y.; Hirao, A.; Nakahama, S. *Macromolecules* **1986**, *19*, 2307. (b) Hirao, A.; Ishino, Y.; Nakahama, S. *Macromolecules* **1988**, *21*, 561.

(7) Ishizone, T.; Hirao, A.; Nakahama, S. *Macromolecules* **1989**, *22*, 2895.

(8) Ishizone, T.; Tsuchiya, J.; Hirao, A.; Nakahama, S. *Macromolecules* **1992**, *25*, 4840.

(9) (a) Ishizone, T.; Hirao, A.; Nakahama, S. *Macromolecules* **1991**, *24*, 625. (b) Ishizone, T.; Sugiyama, K.; Hirao, A.; Nakahama, S. *Macromolecules* **1993**, *26*, 3009.

(10) (a) Minkin, V. I.; Osipov, O. A.; Zhdanov, Y. A. *Dipole Moments in Organic Chemistry*; Plenum: New York, 1970; pp 136–138. (b) Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy*, 3rd ed.; VCH: Weinheim, 1987; p 240. (c) Burgi, H. B.; Dunitz, J. D. *Chem. Commun.* **1969**, 472. *Helv. Chim. Acta* **1970**, *53*, 1747. (d) Morgan, P. W.; Kwolek, S. L.; Pletcher, T. C. *Macromolecules* **1987**, *20*, 729.

(11) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

(12) Reynolds, W. F.; Hamer, G. K.; Bassindale, A. R. *J. Chem. Soc., Perkin Trans. 2* **1977**, 971.

(13) For examples, see: (a) Walling, C.; Briggs, E. R.; Wolfstirn, K. B.; Mayo, F. R. *J. Am. Chem. Soc.* **1948**, *70*, 1537. (b) Gey, V. E. *J. Prakt. Chem.* **1971**, *313*, 1155.

(14) (a) The Alfrey–Price *Q* and *e* values of isoprene, styrene, and 2-vinylpyridine are reported to be 1.99 and −0.55, isoprene; 1.00 and −0.80, styrene; and 1.41 and −0.42, 2-vinylpyridine. Brandrup, J.; Immergut, E. H. In *Polymer Handbook*, 3rd ed.; Greenley, R. Z., Ed.; Wiley: New York, 1989; Vol. II, p 267. (b) From the results of free radical copolymerization of $StCONEt_2$ and styrene, the *Q* and *e* values for $StCONEt_2$ are estimated to be 1.49 and 0.16, respectively. The positive *e* value of $StCONEt_2$ strongly indicates the high reactivity of this monomer under anionic conditions. Wakabayashi, S.; Ishizone, T.; Hirao, A.; Nakahama, S. Unpublished results.

(15) Ishizone, T.; Hirao, A.; Nakahama, S. *Macromolecules*, in press.

(16) Vanermen, G.; Toppet, S.; Van Beylen, M.; Geerlings, P. *J. Chem. Soc., Perkin Trans. 2* **1986**, 699.

(17) Hirao, A.; Takenaka, K.; Packirisamy, S.; Yamaguchi, K.; Nakahama, S. *Makromol. Chem.* **1985**, *186*, 1157.