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Anionic Polymerization of Monomers Containing Functional Groups. 10. Anionic Polymerizations of *N*-Aryl-*N*-(4-vinylbenzylidene)amines[1]

Takashi Ishizone, Tomohiro Utaka, Yoshiaki Ishino, 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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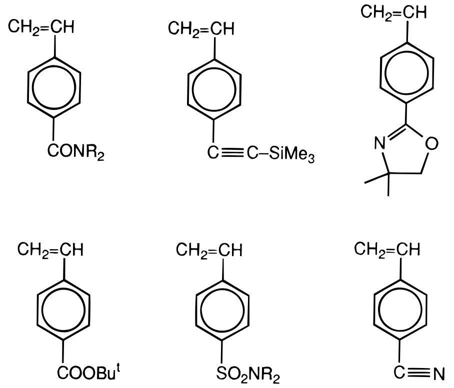
ABSTRACT: Anionic polymerizations of seven styrenes *para*-substituted with *N*-arylimino groups were carried out in THF at −78 °C with oligo(α-methylstyryl)dipotassium and -dilithium as the initiators. The *N*-aryl functionalities contained phenyl (**1**), 2-(*tert*-butyl)phenyl (**2**), 2,6-dimethylphenyl (**3**), 2,6-diethylphenyl (**4**), 2,6-diisopropylphenyl (**5**), 4-cyanophenyl (**6**), and 2,3,4,5,6-pentafluorophenyl (**7**) groups. The monomers **3**−**5** underwent anionic polymerization quantitatively to produce the polymers having predicted molecular weights based on molar ratios of monomers to initiators and narrow molecular weight distributions, the M_w/M_n values being around 1.1. On the other hand, no polymeric products were obtained from the polymerization mixture of **1**, **2**, **6**, and **7** under identical conditions. The bulkiness of the two *ortho* alkyl substituents on the *N*-aryl moiety was necessary to achieve the anionic living polymerization of styrenes bearing *N*-arylimino groups. Well-defined new block copolymers having poly(**5**) segments were synthesized by the sequential addition of **5** and styrene or *tert*-butyl methacrylate. The resulting poly(**3**−**5**) could be quantitatively transformed into the poly(4-formylstyrene) having tailored chain structures by the acid hydrolysis of *N*-arylimino moieties.

Introduction

The attempt for the anionic living polymerization of styrene derivatives with functional groups commonly encounters many difficulties,[2] because most of the functional groups are not compatible with highly reactive carbanions of the propagating chain ends. As a solution to overcome such difficulties, we have utilized the deliberate introduction of an appropriate electron-withdrawing group on the styrene framework as a means to achieve the anionic living polymerization of functional styrenes.[3] The electron-withdrawing character played an important role to stabilize the propagating carbanion derived from those styrenes to prevent the side reactions between the carbanion and the electron-withdrawing functional groups. The successful examples of the introduced electron-withdrawing groups are *N*,*N*-dialkylamide,[4] (trimethylsilyl)ethynyl,[5] oxazoline,[6] *tert*-butyl ester,[7] *N*,*N*-dialkylsulfonamide,[8] and cyano[9] groups (Chart 1). All the anionic polymerizations of styrenes *para*-substituted with these groups quantitatively proceed to give the living polymers having well-controlled molecular weights and narrow molecular weight distributions (MWDs) without great difficulties. In these polymerizations, the extended π-conjugation system including the terminal benzylic carbanion and the electron-withdrawing groups also contributes to stabilizing the propagating carbanion.[10]

Chart 1



In our previous papers,[11,12] the introduction of an electron-withdrawing *N*-alkylimino group on the styrene framework was also found to be effective for realizing the anionic living polymerization. Throughout this study, we have found that the size of the *N*-alkyl substituent is critical for the polymerization and a certain bulkiness of the alkyl substituent is required to obtain stable living polymers. For example, the anionic living polymer of 4-[(*N*-ethylimino)methyl]styrene existed only at temperatures lower than −33 °C in THF and was unstable, resulting in an insoluble gel at the elevated temperature, possibly due to the cross-linking between the polymers by the intermolecular side reaction of the propagating carbanion with the *N*-ethylimino group. More critically, the propagating carbanion derived from the *N*-methyl derivative appeared considerably unstable and the polymer became insoluble within 1.5 h even at −78 °C, although the anionic polymerization proceeded quantitatively. In marked contrast to these results, stable living polymers are always produced by the anionic polymerization of 4-[(*N*-alkylimino)methyl]styrenes with bulkier *N*-alkyl substituents such as isopropyl, cyclohexyl, and *tert*-butyl ones. Surprisingly, they are observed to be stable even at room temperature. Thus, steric requirements should be considered in addition to the electron-withdrawing character when an *N*-alkylimino substituent is employed.

In the same study,[11] we also attempted to anionically polymerize 4-[(*N*-phenylimino)methyl]styrene (**1**), the *N*-phenylimino counterpart. No appreciable polymerization occurred at all under similar conditions. Polymeric product was virtually not obtained in this case. It seems likely that the plane phenyl group could not protect the CH=N moiety toward the carbanion of either initiator or the propagating chain end if produced. The

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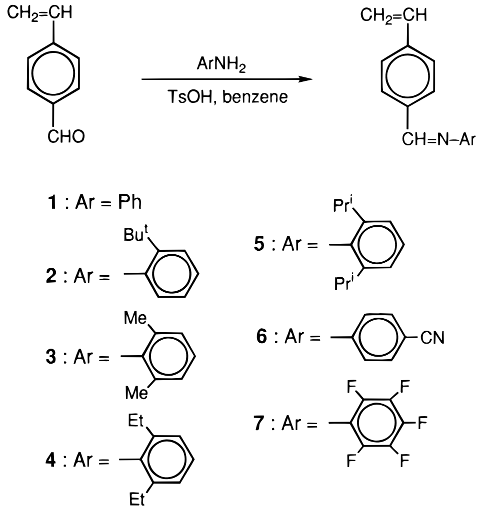
Scheme 1



N-phenyl substituent seems thus not bulky enough for our purpose, while the π-conjugation system including the CH=NPh moiety is remarkably extended. Provided the *N*-phenyl substituent could be modified to be more sterically crowded, the reaction between the carbanion and the modified imino group would be suppressed. Therefore, we newly synthesize the following four 4-[(*N*-arylimino)methyl]styrenes (**2**−**5**) whose *N*-aryl groups are more sterically hindered than **1** (Scheme 1), with a hope that these monomers undergo the anionic living polymerization. Furthermore, 4-[(*N*-(4-cyanophenyl)-imino)methyl]styrene (**6**) and 4-[(*N*-(2,3,4,5,6-pentafluorophenyl)imino)methyl]styrene (**7**) are also synthesized for changing both steric and electronic effects. The overall objective of this work is to clarify the steric and electronic demands of the *N*-aryl substituent for success of the anionic living polymerization of new 4-[(*N*-arylimino)methyl]styrene derivatives.

Results and Discussion

Evaluation of the Electron-Withdrawing Effect of the *N*-Arylimino Groups. Before the anionic polymerization of **1**−**7**, we would like to estimate both anionic polymerizabilities of these monomers and the reactivities of their living polymers if produced. We have recently found that the anionic polymerizability of styrenes bearing *N*-alkylimino groups is higher than that of styrene because of the electron-withdrawing effect of the groups.[12] The *para*-substituted *N*-arylimino groups of **1**−**7** constitute the extended π-conjugation system[13] compared with those of 4-[(*N*-alkylimimo)-methyl]styrenes. The reported Hammett σ_p value for the *N*-phenylimino group is 0.42,[14] supporting the strong electron-withdrawing character of the group comparable to either ester ($\sigma_p = 0.45$) or acetyl ($\sigma_p = 0.50$) functionalities.

As another approach, we have succeeded in the correlation of the reactivities of the *para*-substituted styrenes bearing the electron-withdrawing groups and their living polymers with the ^{13}C NMR chemical shifts of the β-carbon of the vinyl groups.[15] It is demonstrated that the introduction of the electron-withdrawing groups induces the downfield shifts of the vinyl β-carbons and affords the enhanced anionic polymerizability of the monomers and the low nucleophilic propagating carbanion of the living polymers. From the chemical shifts, the anionic polymerizability of the monomers can be evaluated and ranked in order of reactivity successfully. The styrenes *para*-substituted with *N*,*N*-dialkylamido, *N*-alkylimino, (trimethylsilyl)ethynyl, and oxazolinyl groups are the monomers showing the chemical shifts between 114.8 and 115.3 ppm and exhibit anionic polymerizabilities similar to that of 2-vinylpyridine. The chemical shifts of styrenes having *tert*-butyl ester, *N*,*N*-dialkylsulfonamido, and cyano groups are found to be further downshifted between 116.0 and 117.6 ppm. They are much more enhanced and comparable to methyl methacrylate on their anionic polymerizabilities, although they are systematically styrene derivatives. It is also observed that the reactivities of living polymers derived from two series of styrenes are similar to those of living poly(2-vinylpyridine) and living poly(methyl methacrylate), respectively, and lower than that of living polystyrene.

The observed values of β-carbon chemical shift for **1**−**5** were 115.7, 115.5, 115.7, 115.7, and 115.7 ppm, respectively. They are almost equal to each other and actually located between two series of the styrenes. It should be noted here that the values were more downshifted than those of *N*-alkylimino counterparts.[16] This strongly indicates that the anionic polymerizabilities of **1**−**5** would be higher than those of 4-[(*N*-alkylimino)-methyl]styrenes. On the other hand, their living polymers, if produced, can be estimated to be less reactive than the living polymers derived from the *N*-alkyl derivatives.

More interestingly, the values of the vinyl β-carbons of **6** and **7** were further downshifted to 116.3 and 116.8 ppm, respectively, showing the additional electron-withdrawing effects by cyano and fluorine substituents on the aryl moieties. This suggests that both **6** and **7** are more reactive than **1**−**5** in the anionic polymerization.

Anionic Polymerization of 1−**7.** The polymerization of **1** has been reported once before,[11] but its polymerization does not seem to have been fully explored. In this study, we used less nucleophilic and bulkier initiators including lithium and potassium naphthalenides capped with either α-methylstyrene or 1,1-diphenylethylene and benzylmagnesium chloride. Prolonged polymerization times were employed. The results are listed in Table 1. While the reaction mixtures always became red on mixing **1** with each of initiators except for benzylmagnesium chloride, no polymeric product was obtained for longer reaction times of 24−40 h. The starting **1** was recovered nearly quantitatively in each case. When **1** was allowed to react with benzylmagnesium chloride of a typical Grignard reagent in THF at −78 °C for 24 h, again no polymer was produced at all. The results obtained here were in accordance with our previous one.[11] Thus, no improvement can be achieved by changing the polymerization conditions. The inability of **1** to polymerize may possibly be attributed to nucleophilic reaction of the CH=N bond with either the initiator or the propagating chain end.[17] Accordingly, the contribution of *N*-phenyl substituent to steric hindrance might be insufficient to prevent the side reaction, although the electronic demand estimated by the NMR chemical shift of β-carbon is well satisfied.

As described in the Introduction, we then synthesized four alternative monomers bearing 2-monoalkyl-substituted (**2**) and 2,6-dialkyl-substituted phenylimino groups (**3**−**5**) that were purposefully designed to protect sterically the CH=N linkages from nucleophilic attack of both the initiators and the propagating carbanions.

Table 1. Anionic Polymerization of 1−7 in THF at −78 °C

	monomer		initiator				$10^{-3}M_n$		
run	type	mmol	type	mmol	time, h	yield, %	calcd[a]	obsd[b]	M_w/M_n[c]
1	**1**	2.90	K-Naph[d]/α-MeSt[e]	0.0994/0.333	24	0			
2	**1**	2.33	K-Naph/DPE[f]	0.0868/0.157	24	0			
3	**1**	2.46	Li-Naph[g]/α-MeSt	0.101/0.293	24	0			
4	**1**	3.11	Li-Naph/DPE	0.142/0.184	40	0			
5	**1**	3.12	$PhCH_2MgCl$[h]	0.166	24	0			
6	**2**	2.44	K-Naph/α-MeSt	0.111/0.347	0.5	0			
7	**2**	2.10	K-Naph/α-MeSt	0.0946/0.289	48	0			
8	**2**	2.87	Li-Naph/α-MeSt	0.139/0.419	0.5	0			
9	**3**	2.61	K-Naph/α-MeSt	0.101/0.300	0.5	100	13	13	1.20
10[i]	**3**	2.67	K-Naph/α-MeSt	0.140/0.294	0.5	100	9.5	8.9	1.14
11	**3**	2.06	K-Naph/DPE	0.0952/0.159	48	100	11	10	1.13
12	**3**	2.20	Ph_2CHK[j]	0.0601	0.5	100	8.8	8.7	1.12
13	**3**	1.77	Li-Naph/α-MeSt	0.102/0.241	0.5	27	2.4	3.9	1.13
14	**3**	1.82	Li-Naph/α-MeSt	0.104/0.330	50	90	9.0	11	1.22
15	**4**	2.32	K-Naph/α-MeSt	0.118/0.228	0.5	100	11	10	1.13
16[i]	**4**	2.55	K-Naph/α-MeSt	0.114/0.386	0.5	100	13	10	1.12
17	**4**	2.65	K-Naph/DPE	0.106/0.174	48	100	12	11	1.10
18	**4**	2.70	Ph_2CHK	0.0861	0.5	100	8.9	8.6	1.11
19	**4**	2.66	Li-Naph/α-MeSt	0.113/0.375	0.5	74	9.8	8.9	1.12
20	**4**	2.59	Li-Naph/α-MeSt	0.126/0.361	24	100	11	9.6	1.16
21	**5**	1.75	K-Naph/α-MeSt	0.0923/0.270	10 min	100	12	11	1.06
22	**5**	2.75	K-Naph/α-MeSt	0.0924/0.228	0.5	100	18	16	1.11
23[i]	**5**	1.88	K-Naph/α-MeSt	0.0999/0.246	0.5	100	12	12	1.16
24	**5**	2.43	K-Naph/DPE	0.121/0.207	48	100	12	12	1.09
25	**5**	5.60	Ph_2CHK	0.0593	0.5	100	28	29[k]	1.04
26	**5**	3.08	Ph_2CHK	0.0178	1	100	51	71[l]	1.09
27	**5**	1.02	Ph_3CK[m]	0.0314	0.5	100	9.6	15	1.26
28	**5**	3.34	Li-Naph/α-MeSt	0.131/0.336	0.5	76	11	11	1.10
29	**5**	1.90	Li-Naph/α-MeSt	0.0949/0.266	2	100	12	11	1.11
30	**5**	2.31	Li-Naph/DPE	0.126/0.155	16	100	11	10	1.11
31	**6**	0.963	K-Naph/α-MeSt	0.0877/0.272	24	0			
32	**6**	0.944	Li-Naph/α-MeSt	0.0894/0.306	24	0			
33	**7**	2.94	K-Naph/α-MeSt	0.220/0.567	24	0			
34	**7**	2.72	K-Naph/DPE	0.159/0.210	24	0			

[a] M_n(calcd) = [monomer] × yield × f/[initiator] + (MW of initiator): $f = 1$ or 2, corresponding to the functionality of the initiator. [b] M_n(obsd) was obtained by VPO measurement in benzene. [c] M_w/M_n was obtained by SEC analysis in THF solution. [d] Potassium naphthalenide. [e] α-Methylstyrene. [f] 1,1-Diphenylethylene. [g] Lithium naphthalenide. [h] Benzylmagnesium chloride. [i] At 0 °C. [j] (Diphenylmethyl)potassium. [k] M_w was determined to be 30 000 by light scattering in benzene. [l] M_w was determined to be 77 000 by light scattering in benzene. [m] (Triphenylmethyl)potassium.

The anionic polymerization of **2** was carried out in THF at −78 °C for 0.5 or 48 h. It was again observed that no appreciable polymerization occurred with each of the cases, as shown in Table 1. The protection by *ortho*-monosubstitution of the bulky *tert*-butyl group thus failed.

By contrast, 4-[(*N*-(2,6-diisopropylphenyl)imino)methyl]styrene (**5**) has been found to undergo successfully anionic living polymerization under identical conditions. The polymerization mixture exhibited the characteristic red color, which resembled that of the anionic living polystyrene during the course of the polymerization. The red color remained in THF at −78 °C even after 48 h but disappeared instantaneously upon addition of methanol to terminate the reaction. This indicates the presence of the benzylic type of propagating carbanion in the reaction mixture of **5**. For example, the polymerization proceeded quantitatively with oligo(α-methylstyryl)dipotassium in THF at −78 °C for 10 min (Table 1, run 21). The molecular weight (M_n = 11 000) measured by vapor pressure osmometry (VPO) agreed well with the calculated value (12 000) based on a molar ratio of monomer to initiator. The size exclusion chromatography (SEC) curve was unimodal without any shoulders, the polydispersity index, M_w/M_n, being 1.06, indicating a narrow MWD of the poly(**5**). Similarly, each of the various initiators listed in Table 1 was effective for the controlled polymerization of **5** with respect to the molecular weight and MWD except for (triphenylmethyl)potassium.[18] The molecular weights of the resulting poly(**5**)s could be controlled in the range of 10 000 to 30 000 even when the polymerization was carried out at 0 °C. There was, however, a slight deviation in the sample aimed at a higher M_n of 51 000, although the MWD was fairly narrow. The M_n and M_w values of the sample (run 26) were determined independently to be 71 000 and 77 000, by the VPO and light scattering measurements, respectively. In this case, a trace amount of impurities in the monomer might deactivate the initiator at the initiation step to give a poly(**5**) having a M_n value higher than expected. Even when the reaction mixture was allowed to stand for an additional 48 h at −78 °C (run 24), the resulting polymer possessed a predicted molecular weight and a narrow MWD. This strongly indicates that the CH=N bond is not attacked by the carbanion of the propagating chain end after 48 h at −78 °C. Thus, the protection is successful by introducing two isopropyl groups at both *ortho* positions of the *N*-phenyl group.

Interestingly, both **3** and **4** with less sterically hindered two methyl and ethyl groups also undergo anionic polymerization under the same conditions. The polymers were obtained quantitatively and possessed predicted values of M_n and unimodal SEC peaks with narrow distributions. The poly(**3**) and poly(**4**) having well-regulated chain lengths yielded quantitatively even at 0 °C. They had narrow MWDs (M_w/M_n = 1.14 and 1.12) similar to those of the samples obtained at −78

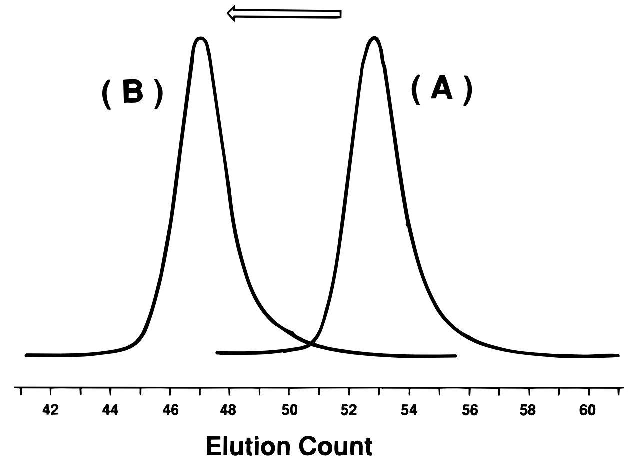


Figure 1. SEC curves of poly(**5**) at the first-stage polymerization (A) and of poly(tBMA-*b*-**5**-*b*-tBMA) obtained at −78 °C (B): peak A, M_n(obsd) = 10 000, M_w/M_n = 1.07; peak B, M_n(obsd) = 26 000, M_w/M_n = 1.08. The second monomer was added 30 min after the first-stage polymerization.

°C. These results indicate the living character of the polymerizations of **3** and **4** under the employed polymerization conditions.

Finally, the polymerizations of two other monomers, **6** and **7**, were examined. Their arylimino groups were modified to have more electron-withdrawing character by introducing cyano and pentafluoro groups into the *N*-aryl group, as mentioned before. Unfortunately, neither **6** nor **7** was observed to undergo anionic polymerization. Thus, such additional electronic modification of the monomers was not effective for their polymerizations.

In summary, among the monomers employed here, the anionic polymerizations of **3**−**5** successfully afford the polymers quantitatively. Based on the results of the tailored molecular weights and the narrow MWDs of the resulting polymers, the living character of their polymerizations is strongly suggested. Apparently, the protection of the CH═N linkage by the steric bulkiness of two *ortho*-substituting alkyl groups of the *N*-arylimino moiety is important in the anionic polymerization of 4-[(*N*-arylimino)methyl]styrene derivatives.

Block Copolymerization of 3−5 with Styrene and *tert*-Butyl Methacrylate (tBMA). The success of the controlled anionic polymerizations of **3**−**5** strongly stimulates us to synthesize the well-defined block copolymers containing poly[((*N*-arylimino)methyl)styrene] segments by the sequential copolymerization. In addition to the synthetic viewpoint, we have already used the sequential copolymerization in order to estimate the stability of the propagating carbanion and to evaluate the reactivities of monomers and the resulting living polymers.[15] The anionic block copolymerization of **5** with either styrene or *tert*-butyl methacrylate (tBMA) was carried out by the sequential addition of two different comonomers. The first-stage polymerization of **5** was performed in THF at −78 °C for 0.5 h, and then styrene was added to the polymerization mixture. In this case, no block copolymer was obtained at all, whereas the starting homopolymer of **5** and styrene monomer were recovered quantitatively. The propagating carbanion derived from **5** could not initiate the polymerization of styrene.

On the other hand, the second-stage polymerization of tBMA, more reactive than styrene under anionic conditions, occurred quantitatively from the difunctional propagating carbanion of poly(**5**). The SEC (Figure 1) and ^{1}H NMR analyses clearly showed that the resulting polymer was a desired triblock copolymer of poly(tBMA-*b*-**5**-*b*-tBMA) with a narrow MWD, as shown in Table 2. In addition to the successful preparation of block copolymer, this result provides direct evidence that a stable living polymer is formed by the polymerization of **5**. Furthermore, the results of two sequential copolymerizations also indicate that the reactivity of the propagating carbanion derived from **5** is lowered by an electron-withdrawing nature of an imino group, as expected.

Table 2. Block Copolymerization of 3−5 with Styrene and *tert*-Butyl Methacrylate in THF at −78 °C[a]

			block copolymer (homopolymer[b])		
			$10^{-3}M_n$		
run	first monomer	second monomer	calcd[c]	obsd[d]	M_w/M_n[e]
35	**3**	tBMA	26 (8.8)	27[f] (8.7)	1.35[f] (1.12)
36	**4**	tBMA	31 (8.9)	28[f] (8.6)	1.33[f] (1.11)
37	**5**	tBMA	28 (9.2)	26 (10)	1.08 (1.07)
38[g]	**5**	styrene	43 (14)	12 (12)	1.09 (1.09)
39	styrene	**5**	36 (12)	38 (12)	1.10 (1.08)
40	tBMA	**5**	36 (14)	39 (15)	1.16 (1.10)

[a] Yields of polymers were always quantitative except for run 38. [b] Homopolymer was obtained at the first-stage polymerization. [c] M_n(calcd) = [monomer] × (MW of monomer)/[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] M_w/M_n was obtained by SEC calibration using standard polystyrenes in THF solution. [f] A mixture of homopolymer and block copolymer of undesired structure was obtained due to the partial deactivation of the propagating chain end. [g] No second-stage polymerization proceeded. Homopoly(**5**) was recovered quantitatively.

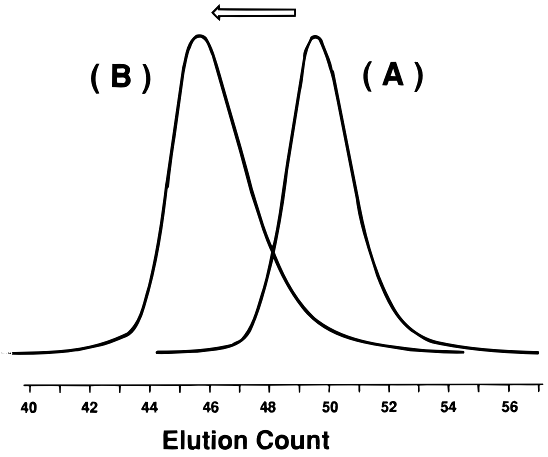


Figure 2. SEC curves of poly(tBMA) at the first-stage polymerization (A) and of poly(**1**-*b*-tBMA-*b*-**1**) obtained at −78 °C (B): peak A, M_n(obsd) = 15 000, M_w/M_n = 1.10; peak B, M_n(obsd) = 39 000, M_w/M_n = 1.16. The second monomer was added 2 h after the first-stage polymerization.

We next attempted the block copolymerization in the reversed addition mode. Namely, **5** was added to the living polymer of either styrene or tBMA under the same conditions. It was found that **5** could be polymerized in quantitative efficiency not only with anionic living polystyrene but also with living poly(tBMA). The SEC and ^{1}H NMR analyses revealed that both resulting polymers possessed the predicted molecular weights and the tailored segment compositions. For example, Figure 2 shows that the SEC curve of the resulting copolymer shifts toward a higher molecular weight region after the addition of **5** to the living poly(tBMA). Thus, well-defined block copolymers with styrene and tBMA were prepared in quantitative yield by this sequential addition order. It is obvious that the anionic polymerizability of **5** is greatly enhanced compared with that of styrene, since it is known that styrene cannot be initiated with living poly(tBMA).

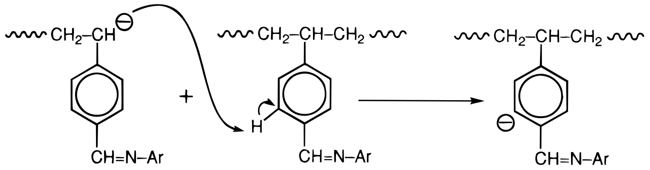
Importantly, **5** and its living polymer show reactivities different from those of the 4-[(*N*-cyclohexylimino)methyl]styrene, *N*-alkylimino derivative, and its living polymer. For example, the living poly[4-((*N*-cyclohexylimino)methyl]styrene] could initiate the polymerization of styrene in 5% efficiency,[15] while no initiation of styrene occurred at all with the living poly(**5**) under identical conditions. Looking at the monomer side, **5** was quantitatively polymerized with low nucleophilic living poly(tBMA), but the addition of 4-[(*N*-cyclohexylimino)methyl]styrene to living poly(tBMA) gave a mixture of the starting homopolymer of tBMA and the block copolymer of an unexpected chain structure.[15] The efficiency was estimated to be 60%. Thus, **5** is obviously more electrophilic than the *N*-cyclohexyl analog and, on the other hand, the living polymer of **5** is less nucleophilic than that of the *N*-cyclohexyl one. Hence, change of the cyclohexyl group to the 2,6-diisopropylphenyl one apparently changes reactivities of both the monomer and the living polymer produced. The observed reactivity of **5** and the living poly(**5**) is classified into a series of styrenes such as *tert*-butyl ester, *N*,*N*-dialkylsulfonamido, and nitrile, showing the similar reactivity of alkyl methacrylates.[15] This can be actually explained by the difference between ^{13}C NMR chemical shifts of their vinyl carbons for **5** (115.7 ppm) and 4-[(*N*-cyclohexylimino)methyl]styrene (114.9 ppm), as mentioned above.

As a conclusion, the anionic polymerizability of *N*-arylimino derivatives are dramatically raised by only changing the *N*-alkyl substituents to the *N*-aryl substituents. This molecular design is really the synthetic advantage of **5**, because this enables us to use the low nucleophilic initiators such as living poly(alkyl methacrylate)s in order to synthesize the new block copolymers having various sequences.

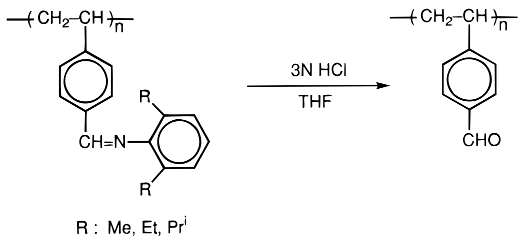
Stability of Propagating Carbanions Derived from 3, 4, and 5. As mentioned above, the propagating carbanion of poly(**5**) could quantitatively initiate the polymerization of tBMA at −78 °C to afford a well-defined block copolymer. It is therefore clearly demonstrated that all the active chain ends of poly(**5**) are stable at −78 °C for at least 0.5 h. Similarly, sequential block copolymerization of either **3** or **4** with tBMA was attempted under the identical conditions. It was, however, observed from the SEC measurements on these experiments that the resulting polymers always contained the starting homopolymers considerably in addition to their block copolymers. The results of homopolymerization of **3** and **4** strongly support that their polymerizations proceed in a living manner because the resulting polymers possess predicted molecular weights and narrow MWDs. Accordingly, their propagating carbanions derived from **3** and **4** must be significantly deactivated, particularly after the monomers are completely consumed. On the basis of SEC peak areas of these homopolymers, percentages of the deactivated chain ends were estimated to be 50 and 40% for the polymers of **3** and **4**, respectively. These results indicate that the propagating carbanions derived from **3** and **4** are already deactivated before the addition of tBMA.

The most probable deactivation reaction is the nucleophilic attack of the propagating carbanion toward the CH=N linkage of the polymer side chain, as was already confirmed in the anionic polymerizations of 4-[(*N*-alkylimino)methyl]styrenes.[12] If this reaction had occurred with time intermolecularly, the increase of the molecular weights and the apparent broadening of MWDs would be observed. However, the SEC curves of homopoly(**3**−**4**)s obtained at −78 °C for 0.5 h were unimodal and maintained the narrow MWDs. Furthermore, even the polymers of **3** and **4** obtained at −78 °C for 48 h and at 0 °C for 0.5 h still possessed narrow SEC peaks without any shoulders with keeping the predicted molecular weights. Therefore, another possibility must be considered. One possible candidate would be that the aromatic proton abstraction of the resulting polymers occurred either intramolecularly or intermolecularly (Scheme 2), which is previously reported as the *ortho*-metalation reaction of the aromatics bearing an *N*-alkylimino moiety.[19] Although the process of the deactivation is still moot, it should be noted that the introduced dimethyl and diethyl groups to the arylimino moiety attained the controlled anionic polymerization of **3** and **4** but they were not bulky enough to suppress the apparent deactivation of the terminal carbanion, especially after the polymerization. Considering from the fact that the living polymer of **5** is stable enough under the same conditions, the size of dialkyl substituents on the arylimino moiety is critical to maintaining the stability of the propagating carbanion.

Scheme 2



Scheme 3



Deprotection of the *N*-Arylimino Protecting Groups from Poly(3−5). We previously reported that the acid hydrolysis reaction of poly[4-((*N*-alkylimino)methyl)styrene]s quantitatively proceeded to afford a poly(4-formylstyrene) with controlled chain structures.[11,12] Deprotection of the *N*-arylimino functionality for poly(**3**−**5**) was similarly carried out at room temperature in THF with 3 N HCl, as shown in Scheme 3.

For example, complete deprotection of poly(**5**) bearing the bulkiest *N*-arylimino group was confirmed by the spectroscopic analyses as follows. In the ^{1}H NMR spectrum of the polymer after reaction, the signals corresponding to methyl (1.1 ppm) and methine (2.9 ppm) protons of the two isopropyl groups, aromatic protons (7.1 ppm) of the *N*-aryl moiety, and the methine proton of the imino linkage at 8.1 ppm completely disappeared and the new proton due to a formyl group appeared at 9.8 ppm. The integral ratio of the CHO proton to aromatic protons and CH_2CH protons of the polymer main chain was virtually 1:4:3, as expected, indicating the quantitative deprotection of the arylimino group. Figure 3 shows the ^{13}C NMR spectra of poly(**5**)

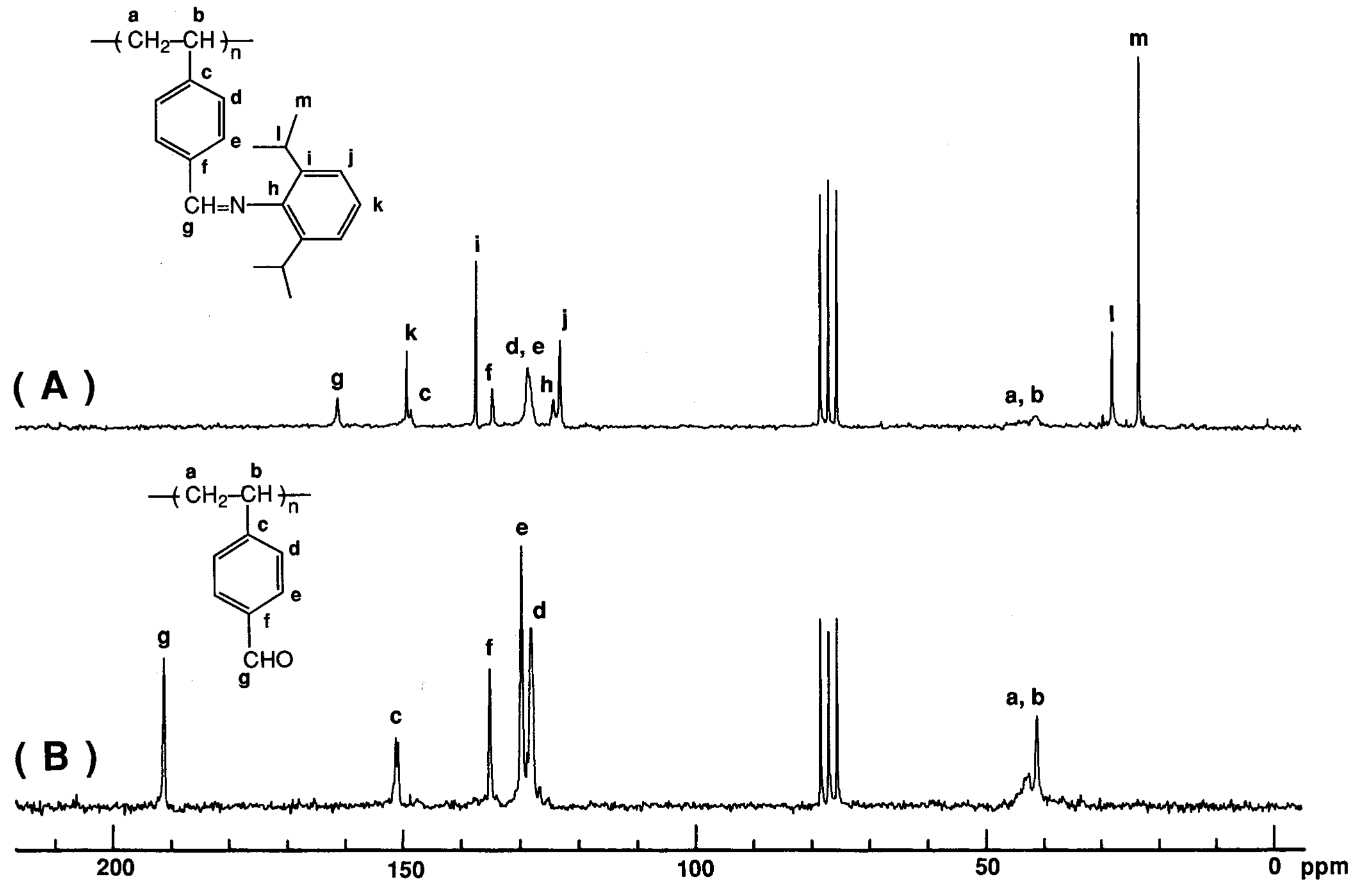


Figure 3. ^{13}C NMR spectra of poly(**5**) (A) and of poly(4-formylstyrene) obtained after the acid hydrolysis (B) in $CDCl_3$.

before and after acid hydrolysis. After the reaction, the carbon signals of the isopropyl moiety at 24 ppm (CH_3) and 28 ppm (CH), four aromatic carbons of the *N*-aryl group, and the CH=N carbon at 162 ppm no longer exist and a new characteristic carbonyl carbon of the CHO group is clearly observed at 191 ppm. In the infrared spectrum, a new characteristic strong absorption at 1701 cm^{-1} corresponding to the C=O group of the aldehyde was newly observed and the absorption at 1641 cm^{-1} due to the CH=N bonding completely disappeared. These spectroscopic observations clearly support the complete removal of the *N*-arylimino protecting group of poly(**5**). Similarly, the acid hydrolysis reactions of poly(**3**) and poly(**4**) quantitatively proceeded. The SEC curves of all the polymers after deprotections were found to be unimodal and narrow, indicating the absence of the cross-linking and chain scission of the polymers during the course of hydrolyses. It is therefore evident that the acid hydrolyses of poly(**3**–**5**) afford a well-defined poly(4-formylstyrene) in quantitative yield, keeping the favorable characteristics of the living polymers.

We can thus establish the third synthetic method to afford a tailored poly(4-formylstyrene) through the living anionic polymerization of 4-[(*N*-arylimino)methyl]-styrene and the subsequent deprotection of the resulting polymer. The other two successful examples reported previously are the use of protecting groups such as 1,3-dimethyl-2-(4-vinylphenyl)imidazolidine[20] and 4-[(*N*-alkylimino)methyl]styrenes,[11,12] where the formyl group was protected with an aminal linkage and alkylimine moiety, respectively. The advantages of the present method are the predominantly enhanced anionic polymerizability of the monomer and the stability of the *N*-arylimino protecting groups during the storage of the polymers. These enable us to employ the low nucleophilic initiators such as living poly(methacrylate) to produce a new sequential copolymer and to store the protected polymer for a long period without decomposition.

Solubility of the Polymers. The poly(**3**–**5**) obtained in this study were off-white powders and stable in air at least for several months. The solubility of the resulting polymers are shown in Table 3. The poly(**3**–**5**) were soluble in benzene, carbon tetrachloride, chloroform, dichloromethane, ethyl acetate, THF, 1,4-dioxane, and DMF, but insoluble in hexane, dimethyl sulfoxide, ethanol, methanol, and water. The three poly[4-((*N*-arylimino)methyl)styrene]s exhibit almost similar solubilities, which also resemble that of polystyrene. The only difference observed was that poly(**3**) swelled in ether but poly(**4**) and poly(**5**) were soluble in ether. After the deprotection of the polymers, the solubility of the resulting poly(4-formylstyrene) remarkably changed. It became insoluble in benzene, carbon tetrachloride, ethyl acetate, and ether and soluble in dimethyl sulfoxide.

The glass transition temperatures (T_g's) of poly(**3**), poly(**4**), and poly(**5**), measured by differential scanning calorimetry (DSC), were 134, 130, and 144 °C, respectively. The values were apparently higher than that of polystyrene ($T_g = 100$ °C), suggesting the substitution effect of the *N*-arylimino groups.

In conclusion, we have succeeded in the controlled anionic polymerization of 4-[(*N*-(2,6-dialkylphenyl)imino)methyl]styrenes, **3**–**5**, to afford well-defined polymers possessing narrow MWDs and tailored molecular weights. The persistency of the propagating chain end of living poly(**5**) is clearly demonstrated by the quantitative efficiency in the block copolymerization, while

Table 3. Solubilities of Poly(3), Poly(4), Poly(5), Poly(4-formylstyrene), and Polystyrene[a]

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

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

those derived from **3** and **4** are not completely stable after completion of the polymerization. It is found in addition to the electron-withdrawing effect of the substituents that the bulkiness of the *N*-arylimino groups of the monomers are very important to avoid the undesirable side reactions and to afford a stable living polymer. The high polymerizability stimulated with electron-withdrawing substituents can be predicted from the ^{13}C NMR chemical shift of the vinyl β-carbon of the monomer and is indeed clarified from the results of block copolymerization with comonomers. The anionic polymerizability of 4-[(*N*-arylimino)methyl]styrene is much higher than that of the *N*-alkylimino analog due to the stronger electron-withdrawing effect and the extended π-conjugation system of the *N*-aryl groups compared with *N*-alkyl groups. A poly(4-formylstyrene) having well-defined chain structures is quantitatively obtained by the complete deprotection of the CH═NAr moieties from the polymers.

Experimental Section

Materials. 4-Chlorostyrene, kindly supplied by Hokko Chemical Industry Co., Ltd., was used for the synthesis of 4-formylstyrene without further purification. 4-Formylstyrene was prepared by the Grignard reaction of 4-chlorostyrene and *N*,*N*-dimethylformamide (DMF), as previously reported.[11] Commercially available 4-cyanoaniline, 2,3,4,5,6-pentafluoroaniline, and triphenylmethane were used without purification. Aniline, 2-*tert*-butylaniline, 2,6-dimethylaniline, 2,6-diethylaniline, 2,6-diisopropylaniline, and diphenylmethane were dried over CaH_2 and distilled under vacuum. Styrene was distilled over CaH_2 in vacuo and further purified by distillation in the presence of benzylmagnesium chloride (THF solution) on a vacuum line. *tert*-Butyl methacrylate (tBMA) was distilled over CaH_2 and subsequently distilled from trioctylaluminum on the vacuum line.[21] 1,1-Diphenylethylene (DPE), supplied by Hokko Chemical Industry Co., Ltd., was purified by fractional distillation over CaH_2 and finally distilled from *n*-BuLi/heptane under vacuum. THF used as a polymerization solvent was refluxed over sodium wire for 6 h and distilled from $LiAlH_4$ and finally distilled through a vacuum line from the sodium naphthalenide solution.

Initiators. Lithium naphthalenide and potassium naphthalenide were prepared by the reactions of a small excess amount of naphthalene with the corresponding alkali metal in dry THF at room temperature. (Diphenylmethyl)potassium was prepared by the reaction of potassium naphthalenide and 1.5 molar excess of diphenylmethane in dry THF at room temperature for 3 days. (Triphenylmethyl)potassium was directly synthesized from potassium metal and a 1.2 molar excess of triphenylmethane in dry THF at room temperature for 2 days. These initiators were sealed off under high vacuum conditions in ampules equipped with breakseals and stored at −30 °C. The concentrations of initiators were determined by colorimetric titration with standardized 1-octanol in a sealed reactor under high vacuum conditions, as previously reported.[22]

***N*-(2,6-Diisopropylphenyl)-*N*-(4-vinylbenzylidene)amine (5).** A benzene (100 mL) solution of 4-formylstyrene (18.12 g, 137 mmol), 2,6-diisopropylaniline (24.15 g, 136 mmol), and *p*-toluenesulfonic acid (10 mg) was heated for 6 h under reflux with azeotropic separation of water by means of a Dean-Stark water trap. The reaction mixture was concentrated by rotary evaporator. After evaporation of the solvent, the residue was crystallized from methanol to afford a yellow solid. The resulting solid was further purified by the recrystallizations from methanol and hexane subsequently to afford a pale yellow crystal of **5** (23.96 g, 82.3 mmol, 60%, mp 79.1−80.1 °C). 90 MHz ^{1}H NMR ($CDCl_3$): δ 1.16 (d, 12H, $J = 6.7$ Hz, CH_3), 2.98 (m, 2H, $-CH(CH_3)_2$), 5.36 and 5.86 (2d, 2H, $J = 12$ and 18 Hz, $CH_2{=}$), 6.79 (dd, 1H, $=CH-$), 7.14 (m, 3H, aromatic), 7.48−7.92 (m, 4H, aromatic), 8.17 (s, 1H, $-CH{=}N-$). 23 MHz ^{13}C NMR ($CDCl_3$): δ 23.7 (CH_3), 28.1 ($CH(CH_3)_2$), 115.7 (vinyl, $CH_2{=}$), 123.1 (Ar, C7), 124.2 (Ar, C8), 126.7 (Ar, C2), 128.9 (Ar, C3), 135.6 (Ar, C4), 136.3 (vinyl, $-CH{=}$), 137.7 (Ar, C6), 140.7 (Ar, C1), 149.5 (Ar, C5), 161.5 ($-CH{=}N-$). IR (KBr, cm^{-1}): 3100−2800, 1640 ($-CH{=}N-$), 1603, 1464, 1300, 1165, 990, 920, 841, 769, 739. Anal. Calcd for $C_{21}H_{25}N$: C, 86.55; H, 8.65; N, 4.80. Found: C, 86.73; H, 8.64; N, 4.63.

Six other monomers, **1**−**4**, **6**, and **7**, were synthesized according to a similar procedure described above. The monomers thus obtained were characterized by elemental analysis and ^{1}H and ^{13}C NMR and IR spectroscopies. The following is the full list.

***N*-Phenyl-*N*-(4-vinylbenzylidene)amine (1).** Pale yellow crystals (mp 68.5−68.8 °C, 67%). 90 MHz ^{1}H NMR ($CDCl_3$): δ 5.34 and 5.84 (2d, 2H, $J = 11$ and 18 Hz, $CH_2{=}$), 6.77 (dd, 1H, $=CH-$), 7.17−7.38 (m, 5H, aromatic), 7.44−7.91 (m, 4H, aromatic), 8.43 (s, 1H, $-CH{=}N-$). 23 MHz ^{13}C NMR ($CDCl_3$): δ 115.6 (vinyl, $CH_2{=}$), 121.0 (Ar, C6), 126.0 (Ar, C8), 126.7 (Ar, C2), 129.2 (Ar, C3 and C7), 135.8 (Ar, C4), 136.4 (vinyl, $-CH{=}$), 140.6 (Ar, C1), 152.2 (Ar, C5), 159.9 ($-CH{=}N-$). IR (KBr, cm^{-1}): 3100−2900, 1624 ($-CH{=}N-$), 1587, 1484, 1451, 1405, 1363, 1074, 995, 915, 845, 769. Anal. Calcd for $C_{15}H_{13}N$: C, 86.92; H, 6.32; N, 6.76. Found: C, 86.98; H, 6.26; N, 6.73.

***N*-(2-*tert*-Butylphenyl)-*N*-(4-vinylbenzylidene)amine (2).** Pale yellow crystals (mp 43.3−43.6 °C, 51%). 90 MHz ^{1}H NMR ($CDCl_3$): δ 1.46 (s, 9H, CH_3), 5.35 and 5.84 (2d, 2H, $J = 11$ and 18 Hz, $CH_2{=}$), 6.78 (dd, 1H, $=CH-$), 6.7−7.43 (m, 4H, aromatic), 7.46−7.92 (m, 4H, aromatic), 8.29 (s, 1H, $-CH{=}N-$). 23 MHz ^{13}C NMR ($CDCl_3$): δ 30.6 (CH_3), 35.8 ($C(CH_3)$), 115.5 (vinyl, $CH_2{=}$), 119.2 (Ar, C10), 125.7 (Ar, C7), 126.1 (Ar, C8), 126.7 (Ar, C9), 127.1 (Ar, C2), 129.2 (Ar, C3), 130.1 (Ar, C4), 136.4 (vinyl, $-CH{=}$), 140.4 (Ar, C1), 143.2 (Ar, C6), 151.6 (Ar, C5), 157.5 ($-CH{=}N-$); IR (KBr, cm^{-1}): 3100−2800, 1622 ($-CH{=}N-$), 1604, 1481, 1437, 1358, 1192, 1170, 912, 841, 751. Anal. Calcd for $C_{19}H_{21}N$: C, 86.64; H, 8.04; N, 5.32. Found: C, 86.74; H, 7.97; N, 5.29.

***N*-(2,6-Dimethylphenyl)-*N*-(4-vinylbenzylidene)amine (3).** Yellow viscous liquid (49%). 90 MHz ^{1}H NMR (CDCl$_3$): δ 2.13 (s, 6H, CH$_3$), 5.35 and 5.84 (2d, 2H, J = 11 and 18 Hz, CH$_2$=), 6.76 (dd, 1H, =CH−), 6.94−7.03 (m, 3H, aromatic), 7.46−7.92 (m, 4H, aromatic), 8.18 (s, 1H, −CH=N−). 23 MHz ^{13}C NMR (CDCl$_3$): δ 18.3 (CH$_3$), 115.7 (vinyl, CH$_2$=), 123.8 (Ar, C8), 126.6 (Ar, C2), 127.2 (Ar, C6), 128.1 (Ar, C7), 128.8 (Ar, C3), 135.6 (Ar, C4), 136.3 (vinyl, −CH=), 140.8 (Ar, C1), 151.3 (Ar, C5), 162.2 (−CH=N−). IR (KBr, cm^{-1}): 3100−2800, 1640 (−CH=N−), 1593, 1562, 1469, 1300, 1187, 1170, 1089, 987, 915, 876, 842, 764. Anal. Calcd for C$_{17}$H$_{17}$N: C, 86.77; H, 7.28; N, 5.95. Found: C, 87.04; H, 7.16; N, 5.80.

***N*-(2,6-Diethylphenyl)-*N*-(4-vinylbenzylidene)amine (4).** Yellow viscous liquid (71%). 90 MHz ^{1}H NMR (CDCl$_3$): δ 1.13 (t, 6H, J = 7.4 Hz, CH$_3$), 2.50 (q, 4H, CH$_2$), 5.35 and 5.85 (2d, 2H, J = 11 and 18 Hz, CH$_2$=), 6.78 (dd, 1H, =CH−), 7.03−7.18 (m, 3H, aromatic), 7.47−7.92 (m, 4H, aromatic), 8.19 (s, 1H, −CH=N−). 23 MHz ^{13}C NMR (CDCl$_3$): δ 14.7 (CH$_3$), 24.8 (CH$_2$), 115.7 (vinyl, CH$_2$=), 124.0 (Ar, C8), 126.3 (Ar, C2), 126.6 (Ar, C7), 128.8 (Ar, C3), 133.2 (Ar, C6), 135.6 (Ar, C4), 136.3 (vinyl, −CH=), 140.7 (Ar, C1), 150.6 (Ar, C5), 162.2 (−CH=N−). IR (KBr, cm^{-1}): 3100−2800, 1641 (CH=N), 1606, 1562, 1453, 1300, 1184, 1168, 1102, 988, 912, 881, 841, 769. Anal. Calcd for C$_{19}$H$_{21}$N: C, 86.64; H, 8.04; N, 5.32. Found: C, 86.54; H, 7.99; N, 5.32.

***N*-(4-Cyanophenyl)-*N*-(4-vinylbenzylidene)amine (6).** Yellow crystal (mp 90.6−91.0 °C, 38%). 90 MHz ^{1}H NMR (DMSO-d_6): δ 5.40 and 5.97 (2d, 2H, J = 11 and 18 Hz, CH$_2$=), 6.82 (dd, 1H, =CH−), 7.33−7.98 (m, 8H, aromatic), 8.59 (s, 1H, −CH=N−). 23 MHz ^{13}C NMR (CDCl$_3$): δ 109.1 (Ar, C8), 116.3 (vinyl, CH$_2$=), 119.0 (C≡N), 121.6 (Ar, C6), 126.7 (Ar, C2), 129.5 (Ar, C3), 133.3 (Ar, C7), 134.9 (Ar, C4), 136.1 (vinyl, −CH=), 141.4 (Ar, C1), 156.0 (Ar, C5), 161.8 (−CH=N−). IR (KBr, cm^{-1}): 3100−2800, 2230 (C≡N), 1623 (−CH=N−), 1594, 1558, 1495, 1409, 1166, 995, 927, 889, 848, 841. Anal. Calcd for C$_{16}$H$_{12}$N$_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.91; H, 5.25; N, 11.84.

***N*-(2,3,4,5,6-Pentafluorophenyl)-*N*-(4-vinylbenzylidene)amine (7).** Yellow crystals (mp 118.6−119.0 °C, 58%). 90 MHz ^{1}H NMR (DMSO-d_6): δ 5.43 and 6.00 (2d, 2H, J = 11 and 18 Hz, CH$_2$=), 6.84 (dd, 1H, =CH−), 7.60−8.00 (m, 4H, aromatic), 8.77 (s, 1H, −CH=N−). 23 MHz ^{13}C NMR (DMSO-d_6): δ 116.8 (vinyl, CH$_2$=), 126.5 (Ar, C2), 129.3 (Ar, C3), 134.0 (Ar, C4), 135.7 (vinyl, −CH=), 141.5 (Ar, C1), 169.4 (−CH=N−). Four other carbon signals corresponding to the pentafluorophenyl ring were not observed probably due to the complicated coupling of the fluorine atoms and carbon atoms in the ^{13}C NMR spectrum of **7**. IR (KBr, cm^{-1}): 1627 (−CH=N−), 1601, 1506, 1376, 1303, 1230, 1177, 1114, 1006, 975, 922, 841. Anal. Calcd for C$_{15}$H$_8$NF$_5$: C, 60.60; H, 2.70; N, 4.70 F, 32.00. Found: C, 60.49; H, 2.51; N, 4.65.

Purification. After careful recrystallizations, the solid monomers of **1**, **2**, **5**, **6**, and **7** were sealed off in a glass apparatus equipped with a breakseal under high-vacuum conditions (10^{-6} mmHg) in the presence of CaH$_2$. The viscous liquid monomers of **3** and **4** were purified by column chromatography and sealed off under high-vacuum conditions in a glass apparatus equipped with a breakseal in the presence of CaH$_2$. The sealed mixture of monomers (ca. 3 g) and CaH$_2$ were diluted with dry THF (3 mL) in the apparatus and vigorously stirred for 24 h at room temperature. It was distilled from CaH$_2$ on a vacuum line into an ampule fitted with a breakseal and diluted subsequently 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 polymerization.

Polymerization Procedures. Polymerizations were carried out at −78 °C in a sealed all-glass apparatus equipped with breakseals with vigorous shaking under high-vacuum conditions as previously reported.[22] The polymerization was terminated with degassed methanol at −78 °C. The reaction solution was poured into a large excess of methanol to precipitate a polymer. The resulting polymer was purified by reprecipitations in THF/MeOH and by subsequent freeze-drying from the benzene solutions under vacuum conditions. The polymer thus obtained was characterized by ^{1}H and ^{13}C NMR and IR spectroscopies. The following is the full list.

Poly(3): 90 MHz ^{1}H NMR (CDCl$_3$) δ 1.0−2.5 (m, 3H, CH$_2$-CH), 2.1 (s, 6H, CH$_3$), 6.3−7.8 (m, 7H, aromatic), 8.1 (s, 1H, CH=N); 23 MHz ^{13}C NMR (CDCl$_3$) δ 18.4 (CH$_3$), 40−44 (CH$_2$-CH), 123.8 (Ar, C8), 127.8 (Ar, C7), 128.1 (Ar, C2, C3, and C6), 134.5 (Ar, C4), 148.4 (Ar, C1), 151.0 (Ar, C5), 162.1 (CH=N); IR (KBr, cm^{-1}) 3200−2900, 1640 (CH=N), 1607, 1473, 1303, 1187, 1174, 1089, 876, 828, 764.

Poly(4): 90 MHz ^{1}H NMR (CDCl$_3$) δ 0.8−1.2 (broad s, 6H, CH$_3$), 1.2−2.7 (m, 7H, CH$_2$CH and CH$_3$CH_2), 6.3−7.9 (m, 7H, aromatic), 8.15 (s, 1H, CH=N); 23 MHz ^{13}C NMR (CDCl$_3$) δ 14.7 (CH$_3$), 24.8 (CH$_2$), 40−44 (CH$_2$CH), 124.0 (Ar, C8), 126.3 (Ar, C7), 128.5 (Ar, C2 and C3), 133.0 (Ar, C6), 134.5 (Ar, C4), 148.5 (Ar, C1), 150.4 (Ar, C5), 162.0 (CH=N); IR (KBr, cm^{-1}) 3200−2900, 1640 (CH=N), 1608, 1453, 1303, 1171, 1100, 881, 828, 758.

Poly(5): 90 MHz ^{1}H NMR (CDCl$_3$) δ 0.6−2.4 (m, 15H, CH(CH_3)$_2$), CH$_2$CH), 2.6−3.1 (s, 2H, CH(CH$_3$)$_2$), 6.3−7.9 (m, 7H, aromatic), 8.15 (s, 1H, CH=N); 23 MHz ^{13}C NMR (CDCl$_3$) δ 23.6 (CH(CH_3)$_2$), 28.1 (CH(CH$_3$)$_2$), 40−44 (CH$_2$CH), 122.9 (Ar, C7), 124.0 (Ar, C8), 128.5 (Ar, C2 and C3), 134.5 (Ar, C4), 137.6 (Ar, C6), 148.5 (Ar, C1), 149.1 (Ar, C5), 161.5 (CH=N); IR (KBr, cm^{-1}) 3200−2900, 1641 (CH=N), 1608, 1458, 1437, 1363, 1302, 1170, 878, 826, 759.

Typical Procedure of Deprotection. A mixture of poly(**5**) (0.40 g, 1.4 mmol based on the monomer unit), THF (20 mL), and 12 N HCl (5 mL) was stirred at room temperature for 4 h. The reaction mixture was poured into an excess of 5% NaOH aqueous solution, and the layers were separated by using a separating funnel. To the resulting organic phase was added 5 mL of 12 N HCl dropwise, and the mixture was stirred at room temperature for 24 h. The THF solution was again poured into an excess of 5% NaOH aqueous solution, and the organic layer was collected by a separating funnel. After evaporation of the solvent, the residue was poured into methanol to precipitate a polymer. The resulting polymer was further purified by the reprecipitations and was dried in air to give a white powder of poly(4-formylstyrene) (0.16 g, 1.2 mmol based on the monomer unit, 88%). The analyses of IR and ^{1}H and ^{13}C NMR spectroscopies were identical to those of poly(4-formylstyrene) reported previously.[11,12,20] The deprotection reactions of poly(**3**) and poly(**4**) were carried out in a similar manner to give poly(4-formylstyrene).

Measurements. ^{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 ppm downfield relative to tetramethylsilane (δ 0) for ^{1}H NMR and to CDCl$_3$ (δ 77.1) for ^{13}C NMR as standards. Infrared spectra (KBr disk) were recorded on a JEOL JIR-AQS20M FT-IR spectrophotometer. Vapor pressure osmometry (VPO) measurements for number-average molecular weight determination were made with a Corona 117 instrument in benzene solution. Laser light scattering (LS) measurements for determination of M_w were performed with an Ootsuka Electronics DSL-600R instrument at 25 °C in benzene solution. Size exclusion chromatograms (SEC) for MWD determination were obtained at 40 °C with a TOSOH HLC-8020 instrument equipped with a series of 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 polymers were measured by differential scanning calorimetry using a Seiko Instrument DSC220 apparatus and analyzed by a SSC5200TA station. The sample was first heated to 200 °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*-Arylimino)methyl]styrenes.
(2) (a) Morton, M. *Anionic Polymerization: Principles and Practice;* Academic Press: New York, 1983. (b) Hsieh, H. L.;

Quirk, R. P. *Anionic Polymerization*; Marcel Dekker, Inc.: New York, 1996. (c) Konigsberg, I.; Jagur-Grodzinski, J. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2535, 2649. (d) Van Beylen, M.; Bywater, S.; Smets, G.; Szwarc, M. *Adv. Polym. Sci.* **1988**, *86*, 87. (e) Rempp, P.; Franta, E.; Herz, J-E. *Adv. Polym. Sci.* **1988**, *86*, 145.

(3) For a review, see: Nakahama, S.; Ishizone, T.; Hirao, A. *Makromol. Chem., Macromol. Symp.* **1993**, *67*, 223.

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

(5) (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* **1993**, *26*, 6985.

(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) Isaacs, N. S. *Physical Organic Chemistry*; Longman House: Essex, U.K., 1987; p 136.

(11) Hirao, A.; Nakahama, S. *Macromolecules* **1987**, *20*, 2968.

(12) Ishizone, T.; Sueyasu, N.; Sugiyama, K.; Hirao, A.; Nakahama, S. *Macromolecules* **1993**, *26*, 6976.

(13) (a) Burgi, H. B.; Dunitz, J. D. *Chem. Commun.* **1969**, 472. *Helv. Chim. Acta* **1970**, *53*, 1747. (b) Morgan, P. W.; Kwolek, S. L.; Pletcher, T. C. *Macromolecules* **1987**, *20*, 729. (c) Breitmaier, E.; Voetler, W. *Carbon-13 NMR Spectroscopy*, 3rd ed.; VCH: Weinheim, 1987; p 240.

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

(15) Ishizone, T.; Hirao, A.; Nakahama, S. *Macromolecules* **1993**, *26*, 6964.

(16) The β-carbon chemical shifts of the vinyl group of 4-[(*N*-alkylimino)methyl]styrenes were 115.1, 114.9, 114.9, 114.9, and 114.7 ppm, which corresponded to *N*-methyl, *N*-ethyl, *N*-isopropyl, *N*-cyclohexyl, and *N*-*tert*-butyl derivatives, respectively.

(17) (a) Campbell, K. N.; Helbing, C. H.; Florkowski, M. P.; Campbell, B. K. *J. Am. Chem. Soc.* **1948**, *70*, 3868. (b) Cliffe, I. A.; Crossley, R.; Shepherd, R. G. *Synthesis* **1985**, 1138.

(18) (Triphenylmethyl)potassium was not a useful initiator to control the molecular weight and the distribution of the polymer. Although the polymer yield was quantitative after 0.5 h, slow initiation was suggested by the SEC curve, which exhibited a significant tailing ($M_w/M_n = 1.26$). The estimated initiation efficiency was nearly 60%.

(19) For reviews, see: (a) Beak, P.; Snieckus, V. *Acc. Chem. Res.* **1982**, *15*, 306. (b) Gschwend, H. W.; Rodriguez, H. R. *Org. React. (N. Y.)* **1979**, *26*, 1. For examples, see: (c) Ziegler, F. E.; Fowler, K. W. *J. Org. Chem.* **1976**, *41*, 1564. (d) Flippin, L. A.; Muchowski, J. M.; Carter, D. S. *J. Org. Chem.* **1993**, *58*, 2463.

(20) Hirao, A.; Ishino, Y.; Nakahama, S. *Makromol. Chem.* **1986**, *187*, 141.

(21) Allen, R. D.; Long, T. E.; McGrath, J. E. *Polym. Bull.* **1986**, *152*, 127.

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

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