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Anionic Polymerization of Monomers Containing Functional Groups. 3.[1] Anionic Living Polymerization of *N,N*-Dialkyl-4-vinylbenzamides

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ABSTRACT: Anionic polymerizations of *N,N*-dimethyl- (**1a**), *N,N*-diethyl- (**1b**), *N,N*-dipropyl- (**1c**), *N,N*-diisopropyl- (**1d**), and *N,N*-diallyl-4-vinylbenzamide (**1e**), 1-(4-vinylbenzoyl)pyrrolidine (**1f**), and 1-(4-vinylbenzoyl)piperidine (**1g**) were carried out at −78 °C in tetrahydrofuran (THF). The initiators involved lithium, sodium, and potassium naphthalenide, oligo(α-methylstyryl)dilithium, -disodium, and -dipotassium, and cumylpotassium. Each of these polymerizations gave poly(**1**)s in quantitative yield. The polymerization reaction proceeded in a homogeneous system in the case of **1b–e** or **1g**, while poly(**1a**) and poly(**1f**) were precipitated during the polymerization. In each case, the obtained polymers had narrow molecular weight distributions and predictable molecular weights from the molar ratios of monomer to initiator, indicating that the anionic polymerizations of **1**s proceeded without chain transfer and termination reactions to give a stable living polymer. New block copolymers, poly(**1a**-*block*-styrene-*block*-**1a**), poly(**1b**-*block*-styrene-*block*-**1b**), poly(**1b**-*block*-isoprene-*block*-**1b**), poly(**1f**-*block*-styrene-*block*-**1f**), and poly[(*tert*-butyl methacrylate)-*block*-**1b**-*block*-(*tert*-butyl methacrylate)], were synthesized by using this living system. Poly(**1a**) was quantitatively converted into poly(4-vinylacetophenone) by reaction with methyllithium. Poly(**1b**) was metalated with *s*-BuLi/TMEDA (TMEDA = *N,N,N',N'*-tetramethylethylenediamine) in THF and the ortho-lithiated species were treated subsequently with trimethylsilyl chloride.

Introduction

The control of polymerization affording macromolecules with regulated chemical structures is an exciting target in current polymer synthesis,[2] where the living polymer plays an important role to give block copolymers of various architectures, macromonomers, and telechelomers as well as homopolymers with well-defined chain structures.

Our work has recently demonstrated that anionic living polymerizations of monomers having protected functions with suitable masking groups proceed under controlled conditions.[3] During the research, we have found that several styrene derivatives para-substituted with electron-withdrawing groups such as imine,[4] ester,[5], oxazoline,[6] and cyano[7] yielded stable anionic living polymers. These polar groups are susceptible to the nucleophilic addition of anionic initiators, such as organolithium compounds and Grignard reagents.[8] However, these anionic species attack the vinyl groups of the monomers not the polar substituents to initiate the polymerization. Moreover, during the course of polymerization, the anionic chain ends of the polymers coexist with the polar functional groups to produce the living polymers with functions and well-defined structures. The electron-withdrawing groups are thought to play an important role in the stabilization of propagating chain ends.[4–7]

As another electron-withdrawing group, carboxylic acid amide might possibly show the similar behavior. Unfortunately, in the anionic polymerization of the vinyl monomers containing primary amide groups, such as 4-vinylbenzamide, vinyl polymerization (1,2-addition) and hydrogen-transfer polymerization (1,8-addition) proceed simultaneously, resulting in a polymer of mixed repeating units,[9] as was observed in the cases of acrylamide and methacrylamide.[10] Such diversity of the propagation reaction may be avoided by employment of styrene derivatives with tertiary amide groups to obtain the polymer having uniform structure through anionic polymerization. Thus, we here concentrate the study on the anionic polymerization of *N,N*-dialkyl-4-vinylbenzamides.

In the preceding paper,[11] we have briefly reported the anionic polymerization of *N,N*-diisopropyl-4-vinylbenzamide (**1d**), bearing a sterically hindered tertiary amide group. The living nature of the anionic propagating chain end of poly(**1d**) in THF at −78 °C was suggested by formation of the homopolymer and block copolymer with controlled chain structures. As described previously in the anionic polymerization of alkyl 4-vinylbenzoate,[5] a bulky substituent like a *tert*-butyl group and a low polymerization temperature (−95 °C) were required to realize the anionic living polymerization of the monomer-containing polar ester moiety that might potentially be attacked by the nucleophilic propagating carbanion. Accordingly, in the anionic polymerizations of *N,N*-dialkyl-4-vinylbenzamides, use of bulky substituents or severe control of reaction conditions might also be required to avoid transfer and termination reactions.

The present paper describes the anionic polymerization of seven *N,N*-dialkyl-4-vinylbenzamides (**1**) and discusses the steric effects of alkyl substituents on the stability of the anionic propagating chain end (Scheme I). Furthermore, block copolymerization of **1**s and two polymer reactions of the resulting poly(**1**)s are also carried out.

Results and Discussion

Anionic Polymerization of *N,N*-Diethyl-4-vinylbenzamide (1b). Anionic polymerization of **1b** was carried out in THF at 14 to −78 °C with various initiators such as lithium, sodium, and potassium naphthalenides, 1,4-dilithio-1,1,4,4-tetraphenylbutane, oligo(α-methylstyryl)dilithium, -disodium, and -dipotassium, and cumylpotassium. Typically, when **1b** was added to the alkali-metal naphthalenide solutions, a rapid color change from dark green to orange red occurred, indicating that the initiation reaction took place. The red coloration remained unchanged at −78 °C even after 24 h and faded immediately

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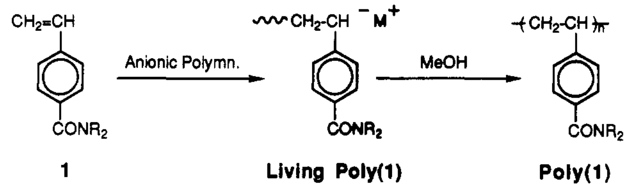
Scheme I



1a R = CH_3
1b R = CH_2CH_3
1c R = $CH_2CH_2CH_3$
1d R = $CH(CH_3)_2$
1e R = $CH_2CH{=}CH_2$
1f R_2 = $-(CH_2)_4-$
1g R_2 = $-(CH_2)_5-$

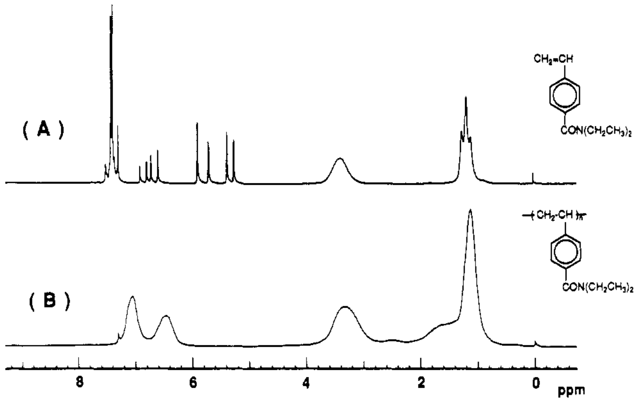


Figure 1. ^{1}H NMR spectra of **1b** (A) and poly(**1b**) (B) in $CDCl_3$.

on the addition of a small amount of methanol for quenching the polymerization. The polymer of white powder was quantitatively obtained after precipitation into a large excess of water and was purified by reprecipitation with a THF–hexane system and then freeze-dried from benzene. ^{1}H NMR spectrum of the resulting polymer shows the structure of the expected poly(*N*,*N*-diethyl-4-vinylbenzamide) as shown in Figure 1B. After the polymerization, signals due to vinyl protons (Figure 1A) of the monomer completely disappeared, and alternatively those of methylene and methine protons of the main chain were observed. In the ^{13}C NMR of the polymers, an amide carbonyl carbon at 170.9 ppm was detected in the same region of the monomer and the resonances due to vinyl carbons of the monomer completely disappeared. The infrared spectrum of the polymer showed a strong absorption of the amide carbonyl group at 1636 cm^{-1}, whereas that of **1b** was observed at 1619 cm^{-1}. These spectroscopic observations indicate that anionic polymerization of **1b** takes place in the vinyl polymerization mode exclusively.

In each case, the yield of poly(**1b**) was quantitative. The number-average molecular weights of poly(**1b**)s were measured by VPO. Table I summarizes the results of the anionic polymerization of **1b**. The good agreements between the molecular weights of poly(**1b**)s measured and those calculated from the molar ratios of monomer to initiator are observed regardless of the initiators and countercations employed. The molecular weight distributions (MWDs) of all resulting poly(**1b**)s are very narrow in the molecular weight range 7000–48 000. Even at higher polymerization temperatures, 0 and 14 °C, nearly monodisperse polymers are obtained. The representative GPC curves of poly(**1b**)s produced at −78 and 14 °C are shown in Figure 2. These results suggest that the anionic polymerization of **1b** proceeds without transfer and termination reactions even at room temperature. Moreover, to prove the living nature of the polymerization system at −78 °C, the postpolymerization was carried out. The second-stage polymerization proceeded with quantitative efficiency to produce the post-poly(**1b**) with a predictable molecular weight and narrow MWD when **1b** was added to the THF solution of pre-poly(**1b**) prepared from oligo(α-methylstyryl)dipotassium and **1b** at −78 °C for 30 min. This indicates that the propagating chain end of **1b** completely survives at least to −78 °C for 30 min. It is obvious from these results that the propagating carbanion of poly(**1b**) repeats 1,2-addition to the monomer vinyl group without carbonyl attack under the condition employed here.

Anionic Polymerization of *N*,*N*-Dimethyl- (1a), *N*,*N*-Dipropyl- (1c), *N*,*N*-Diisopropyl- (1d), and *N*,*N*-Diallyl-4-vinylbenzamide (1e), 1-(4-Vinylbenzoyl)pyrrolidine (1f), and 1-(4-Vinylbenzoyl)piperidine (1g). In the series of our studies, it was already confirmed that the stable living polymers formed at −78 °C from styrene derivatives containing electron-withdrawing groups, such as imino,[4] amide,[11] oxazolinyl,[6] and cyano.[7] Recently, additional results were obtained for the anionic polymerization of a styrene derivative with an ester moiety, *tert*-butyl 4-vinylbenzoate.[5] The living polymer is only stable below −95 °C and causes the carbonyl attack to broaden the MWD even at −78 °C. Moreover, the lithium salt initiators produce no polymer, although quantitative yields of polymers were achieved with sodium, potassium, and cesium salts as initiators. The polymerization of less-hindered methyl and allyl esters gave no polymeric products. Although isopropyl esters underwent anionic polymerization at least under a similar condition, polymers of broad MWD were produced in rather low yields, indicating that the propagating chain end of the polymer was quite unstable. In order to obtain a stable living polymer of the *tert*-butyl ester, polymerization requires both bulkiness of the alkyl substituent of the ester group and a very low reaction temperature. In contrast, the living polymer derived from a tertiary amide counterpart, **1b**, which has relatively less-hindered substituents, survives even at room temperature. This might be explained by resistivity of amide toward nucleophilic attack.[12]

Here, to investigate the limitation of living polymerization of **1**, the anionic polymerizations of the other five analogues having various alkyl substituents on the nitrogen atom were carried out under similar conditions. The results are discussed, including those of *N*,*N*-diisopropyl-4-vinylbenzamide (**1d**), obtained previously.[11]

Upon addition of **1c–e** and **1g** to the initiators, the anionic polymerizations proceeded homogeneously, as did that of **1b**, to yield poly(**1**)s quantitatively. The polymers produced were found to have the repeating unit of 2,1-addition by ^{1}H and ^{13}C NMR, IR spectroscopic measurements, and elemental analysis. Typically, Figure 3A,B shows the ^{13}C NMR spectra of **1e** and poly(**1e**) obtained by anionic polymerization, respectively. The vinyl polymerization of **1e** exclusively proceeds and the pendant allyl groups on poly(**1e**) remain intact without nucleophilic attack from anionic initiator or active chain end at −78 °C even for 24 h. As shown in Table II, the polymers of **1c–e** and **1g** possess the predicted molecular weights based on monomer to initiator ratios and narrow MWDs. These results indicate the living character of anionic polymerizations of **1c–e** and **1g**, similarly to the case of **1b**.

N,*N*-Dimethyl-4-vinylbenzamide and 1-(4-vinylbenzoyl)pyrrolidine (**1a** and **1f**) were similarly polymerized in THF at −78 °C. In these cases, the orange polymers were

Table I
Anionic Polymerization of 1b with Various Initiators in THF for 30–60 min[a]

run	**1b**, mmol	temp, °C	initiator, mmol	$10^{-4}\bar{M}_n$ calcd[b]	$10^{-4}\bar{M}_n$ obsd[c]	$\bar{M}_w/\bar{M}_n$
1	3.50	–78	Li-Naph,[d] 0.108	1.3	1.2	1.13
2	3.05	–78	Li-Naph, 0.133/DPE,[e] 0.251	0.97	0.72	1.09
3	3.92	–78	Li-Naph, 0.109/α-MeSt,[f] 0.883	1.7	1.4	1.06
4	3.59	–78	Na-Naph,[g] 0.125	1.2	1.1	1.13
5	2.82	–78	Na-Naph, 0.103/α-MeSt, 0.274	1.2	1.1	1.08
6	3.45	–78	K-Naph,[h] 0.135	1.0	1.1	1.09
7	3.45	14	K-Naph, 0.0840/α-MeSt, 0.360	1.8	1.2	1.13
8	4.95	0	K-Naph, 0.209/α-MeSt, 0.451	0.97	1.0	1.09
9	3.88	–78	K-Naph, 0.152/α-MeSt, 0.604	1.1	0.92	1.08
10	4.88	–78	K-Naph, 0.107/α-MeSt, 0.699	2.0	1.7	1.07
11	5.40	–78	K-Naph, 0.0666/α-MeSt, 0.461	3.5	3.3	1.13
12	6.40	–78	cumyl-K,[i] 0.0486/α-MeSt, 0.171	3.6	3.6	1.09
13	7.17	–78	cumyl-K, 0.0308/α-MeSt, 0.449	4.8	4.8	1.08

[a] Yields of polymers were almost quantitative in all polymerizations. [b] $\bar{M}_n$(calcd) = [monomer] × (MW of monomer) × f/[initiator] + MW of initiator; f = 1 or 2, corresponding to the functionality of the initiators. [c] $\bar{M}_n$(obsd) was obtained by VPO in benzene solution. [d] Lithium naphthalenide. [e] 1,1-Diphenylethylene. [f] α-Methylstyrene. [g] Sodium naphthalenide. [h] Potassium naphthalenide. [i] Cumylpotassium.

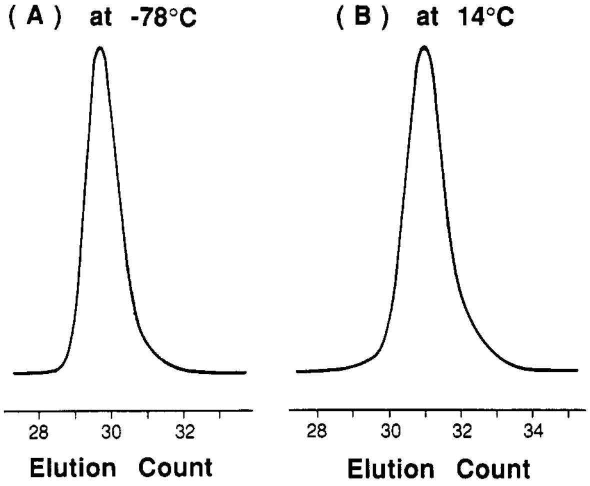


Figure 2. GPC curves of poly(**1b**) obtained with the potassium salts. Detailed data are shown in Table I: (A) run 13, at –78 °C, $\bar{M}_n$(obsd) = 4.8 × 10⁴, $\bar{M}_w/\bar{M}_n$ = 1.08; (B) run 7, at 14 °C, $\bar{M}_n$(obsd) = 1.2 × 10⁴, $\bar{M}_w/\bar{M}_n$ = 1.13.

immediately precipitated on addition of the monomers to anionic initiators with lithium and potassium countercations. The polymerization of **1a** proceeded slowly at –78 °C compared with those of the other monomers, probably due to heterogeneity of the reaction system. The precipitation seemed to be caused by association of ionic species at chain terminals since the poly(**1a**) isolated readily dissolved in THF at –78 °C. Poly(**1a**) of quantitative yield was achieved at –78 °C within 24 h. If the polymerization temperature is raised to 0 °C or room temperature, the reactions proceeded in homogeneous orange-red solutions to consume **1a** completely in 30 min.

The poly(**1a**)s produced with lithium initiators and poly(**1f**) with potassium have molecular weights[13] close to the calculated values and narrow MWDs regardless of reaction system, heterogeneous at –78 °C or homogeneous at 0 °C or room temperature (Table II). This suggests that the propagating active end survives in the course of the polymerization, while longer time is required to complete the reaction in the heterogeneous system (run 3). In contrast, the poly(**1a**)s obtained with potassium initiators possessed somewhat broad MWDs compared with the case of lithium initiator, although the exact reason could not be clearly discussed at this stage.

Thus, formation of the living polymers of all six styrene derivatives with tertiary amide groups is substantiated, in addition to the case of *N*,*N*-diisopropyl-4-vinylbenzamide (**1d**) previously reported.[11] In contrast to alkyl 4-vinylbenzoate, *N*,*N*-dialkyl-4-vinylbenzamides afford stable living polymers even at room temperature without steric protection of bulky alkyl group. This is consistent with the numerous reports that tertiary amides are resistant to nucleophilic attack compared with esters.[12]

Block Copolymerization of 1 with Styrene, Isoprene, and *tert*-Butyl Methacrylate. The most characteristic advantage of the living polymerization of 1 is that it is capable of the synthesis of various block copolymers having polar poly(1) segments with strictly controlled chain structure. In addition, the block copolymerizations may elucidate the relative reactivities of the monomer and the living end as well as the stability of the propagating end. At first, ABA-type triblock copolymers containing poly(1) segments (A) as both terminal blocks were synthesized by addition of **1a**, **1b**, and **1f** to the living polystyrene (B) prepared with either lithium or potassium naphthalide at –78 °C in THF. The reactions proceeded homogeneously and quantitatively to yield block copolymers having predictable molecular weights and narrow MWDs as shown in Table III. The content of poly(1) segment analyzed by ¹H NMR in each block copolymer agreed well with that calculated based on the molar ratio of the fed monomer. A well-defined block copolymer of **1b** and isoprene was also prepared in a similar manner.

Next, synthesis of the block copolymer with reversed sequence was attempted by addition of isoprene or styrene monomer to difunctional living poly(**1b**) at –78 °C in THF. However, the living poly(**1b**) did not initiate the polymerization of isoprene to recover homopoly(**1b**) quantitatively. On the other hand, styrene monomer was initiated with living poly(**1b**) to result in a mixture of virtual homopoly(**1b**) and block copolymer having a polystyrene segment of very high molecular weight.[14] The GPC and ¹H NMR analyses of the product reveal that only 2% of living poly(**1b**) reacts with styrene and the rest remains intact.

The polymerization of *tert*-butyl methacrylate (tBuMA) was initiated with difunctional living poly(**1b**) to produce poly(tBuMA-*b*-**1b**-*b*-tBuMA) with regulated block length and narrow MWD in quantitative yield as shown in Table III (run 4). GPC analyses of the resulting polymers showed that the peak of the starting poly(**1b**) block shifted toward the higher molecular weight side without a shoulder at the elution count of the homopolymer as shown in Figure 4. In addition to the postpolymerization, this result strongly demonstrates that a stable living polymer of *N*,*N*-diethyl-

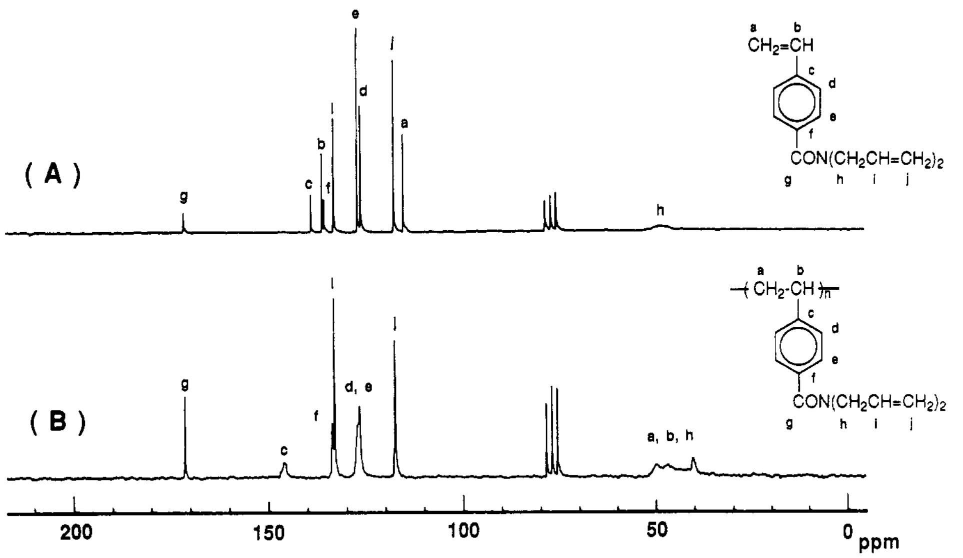


Figure 3. ^{13}C NMR spectra of **1e** (A) and poly(**1e**) (B) in $CDCl_3$.

Table II
Anionic Polymerization of 1a, 1c, 1d, 1e, 1f, and 1g in THF[a]

run	monomer, mmol	temp (°C), time	initiator, mmol	$10^{-4}\bar{M}_n$ calcd[b]	$10^{-4}\bar{M}_n$ obsd[c]	$\bar{M}_w/\bar{M}_n$
1	**1a**, 2.64	19, 30 min	Li-Naph,[d] 0.113/α-MeSt,[e] 0.358	0.90	0.81	1.11
2	**1a**, 2.37	0, 30 min	Li-Naph, 0.112/α-MeSt, 0.367	0.82	0.78	1.12
3	**1a**, 2.49	−78, 30 min	Li-Naph, 0.106/α-MeSt, 0.310	0.45	0.65	1.07
4	**1a**, 2.94	−78, 24 h	Li-Naph, 0.125/α-MeSt, 0.364	0.89	0.95	1.12
5	**1a**, 6.01	−78, 24 h	Li-Naph, 0.0782/α-MeSt, 0.711	2.9	3.4[f]	1.15
6	**1a**, 3.16	17, 30 min	K-Naph,[g] 0.129/α-MeSt, 0.430	0.94	0.99	1.19
7	**1a**, 4.09	0, 60 min	K-Naph, 0.117/α-MeSt, 0.525	1.3	1.5[f]	1.55
8	**1a**, 4.63	−78, 24 h	K-Naph, 0.0916/α-MeSt, 0.706	2.0	1.9[f]	1.94
9	**1c**, 2.74	−78, 2 h	cumyl-K,[h] 0.105	0.61	0.55	1.06
10	**1c**, 2.35	−78, 2 h	cumyl-K, 0.0476	1.2	1.1	1.07
11	**1d**, 2.36	−78, 30 min	Li-Naph, 0.111/α-MeSt, 0.305	1.1	1.0	1.08
12	**1d**, 4.42	−78, 30 min	K-Naph, 0.0981/α-MeSt, 0.202	2.1	2.2	1.06
13	**1e**, 5.12	−78, 22 h	Li-Naph, 0.207/α-MeSt, 0.506	1.2	1.2	1.12
14	**1e**, 3.93	−78, 30 min	K-Naph, 0.205/α-MeSt, 0.727	0.95	0.93	1.07
15	**1e**, 5.55	−78, 30 min	K-Naph, 0.0999/α-MeSt, 0.357	2.6	2.3	1.08
16	**1f**, 5.84	−78, 24 h	cumyl-K, 0.133	0.89	0.80[f]	1.09
17	**1g**, 3.89	−78, 30 min	K-Naph, 0.103/α-MeSt, 0.241	1.7	1.4	1.08
18	**1g**, 4.05	−78, 30 min	K-Naph, 0.0794/α-MeSt, 0.262	2.3	2.2	1.08

[a] Yields of polymers were almost quantitative except for run 3, where the poly(**1a**) was produced in 51% yield. [b] $\bar{M}_n$(calcd) = [monomer] × (MW of monomer) × f × (conversion of polymerization)/(100)[initiator] + MW of initiator; $f = 1$ or 2, corresponding to the functionality of the initiators. [c] $\bar{M}_n$(obsd) was obtained by VPO in benzene solution. [d] Lithium naphthalenide. [e] α-Methylstyrene. [f] $\bar{M}_n$(obsd) was obtained by GPC calibration using standard polystyrenes in DMF solution. [g] Potassium naphthalenide. [h] Cumylpotassium.

Table III
Block Copolymerization of 1s with Styrene, Isoprene, and *tert*-Butyl Methacrylate at −78 °C in THF[a]

run	block copolymer	A monomer	B monomer	block copolymer (homopolymer)[b] $10^{-4}\bar{M}_n$(calcd)	$10^{-4}\bar{M}_n$(obsd)	$\bar{M}_w/\bar{M}_n$
1	A–B–A	**1a**	styrene	2.8 (1.5)	3.2 (1.7)	1.11 (1.13)
2	A–B–A	**1b**	styrene	3.1 (1.5)	3.2 (1.6)	1.06 (1.09)
3	A–B–A	**1b**	isoprene	3.0 (1.2)	2.7 (1.1)	1.08 (1.08)
4	B–A–B	**1b**	tBuMA	1.9 (0.65)	2.3 (0.80)	1.13 (1.10)
5	A–B–A	**1f**	styrene	2.0 (0.95)	2.0 (1.0)	1.04 (1.08)

[a] Yields of polymers were nearly quantitative in each case. [b] Homopolymers were obtained at the first-stage polymerization.

4-vinylbenzamide forms at −78 °C.

Through our studies on the anionic polymerizations of *N*-(4-vinylbenzylidene)cyclohexylamine,[4] *tert*-butyl 4-vinylbenzoate,[5] 2-(4-vinylphenyl)-4,4-dimethyl-2-oxazoline,[6] and 4-cyanostyrene,[7] their active chain ends have been found to be stabilized by the electron-withdrawing effects of the substituents. The resulting living polymers are able to cause crossover reactions with these styrene derivatives and alkyl methacrylates to produce block copolymers but are ineffective to initiate styrene and isoprene. Similar results were obtained from the block copolymerizations of living poly(**1b**) with isoprene, styrene, and tBuMA. The lowered nucleophilicity of the carbanion derived from **1b** is roughly estimated to be at the same level as those of the living polymers generated from those monomers having electron-withdrawing groups. More precise ranking of the reactivities of these new type carbanions is under investigation.

Solubility of Poly(1)s. As shown in Table IV, poly(**1**)s are soluble in both polar and nonpolar solvents such

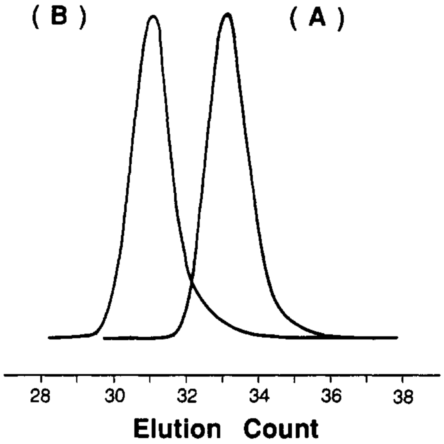


Figure 4. GPC curves of homopoly(**1b**) (A) at the first polymerization and of poly(tBuMA-*b*-**1b**-*b*-tBuMA) (B): peak A, $\bar{M}_n$(obsd) = 0.80×10^4, $\bar{M}_w/\bar{M}_n = 1.10$; peak B, $\bar{M}_n$(obsd) = 2.3×10^4, $\bar{M}_w/\bar{M}_n = 1.13$ (the second monomer was added 30 min after the first addition).

as methanol, ethanol, *N,N*-dimethylformamide, THF, 1,4-dioxane, chloroform, and benzene. The wide solubilities of poly(1)s may be caused by the amphiphilic characters of the polymers with polar tertiary amide groups and nonpolar polystyrene backbones. Some steric effects on the solubilities of poly(1)s are observed. Strong polarities of amide groups are reflected in the solubilities of poly(**1a**) and poly(**1f**), which are soluble even in 6 N HCl and insoluble in carbon tetrachloride and diethyl ether.

The Mark–Houwink parameters, *K* and *a*, for poly(**1b**) in THF at 40 °C were obtained by measuring intrinsic viscosities of five poly(**1b**) samples with $\bar{M}_n$s ranging from 9200 to 48 000 (Table V).[15,16] The plots of log [η] versus log $\bar{M}_n$ lead to a good linear relationship given by

$$[\eta]_{\mathrm{THF}}^{40\,^{\circ}\mathrm{C}} = (4.47 \times 10^{-4})\bar{M}^{0.554}$$

Although a molecular weight range for meaningful *K* and *a* is somewhat narrow, the preliminary value of *a* for poly(**1b**), 0.55, suggests a rather small hydrodynamic volume of the polymer in THF, where the polystyrene ($a = 0.72$) chain expands in THF at 40 °C. Accordingly, the molecular weight of poly(**1b**) tends to be underestimated in the GPC measurement by using the polystyrene standard calibration with THF as an eluting solvent as shown in Table V.

Reaction of Poly(1a) with Methyllithium. Since several reactions of tertiary benzamides are known in the field of organic synthesis, further chemical modifications on the poly(1)s are expected to derive new functional polymers. Gschwend and his colleagues demonstrated that *N,N*-dimethylbenzamide was directly converted to acetophenone with methyllithium in good yield.[17] Under the similar condition they employed, poly(**1a**) was allowed to react with methyllithium to convert into poly(4-vinylacetophenone) as shown in Scheme II. The IR spectrum of the polymer obtained shows the strong C=O stretching absorption of the ketone carbonyl group at 1680 cm^{-1}, whereas the amide carbonyl band at 1640 cm^{-1} disappears. In the ^{13}C NMR spectrum, after polymer reaction, a signal responsible for the amide carbonyl carbon of poly(**1a**) at 171.1 ppm completely disappeared and resonances due to acetyl group newly appeared at 197.4 (C=O) and 26.3 ppm (CH_3) as shown in Figure 5. Furthermore, no nitrogen was detected by elemental analysis of the resulting polymer. All evidence for these analyses indicates the quantitative conversion of poly(**1a**) into poly(4-vinylacetophenone). Since the GPC curve of the polymer after reaction was narrow and unimodal as well as that before reaction, the substitution reaction with methyllithium is considered not to accompany the cross-linking and degradation of the polymer backbone.

Aromatic Lithiation of Poly(1b). The aromatic direct metalation reaction followed by electrophilic reaction is a useful method for efficient and regiospecific preparation of polysubstituted aromatic compounds.[18] Beak and Brown reported that the bulkier tertiary benzamides showed the excellent directing ability of ortho-lithiation.[19] In a similar manner, as shown in Scheme III, lithiation of poly(**1b**) was carried out with *sec*-butyllithium/*N,N,N′,N′*-tetramethylethylenediamine (TMEDA) in THF at −78 °C for 1 h followed by quenching with trimethylsilyl chloride to estimate the conversion. From ^{1}H NMR analysis, 80% of the polymer phenylene ring was substituted by a trimethylsilyl group at ortho position to amide.[20] The GPC curve of the polymer still remained narrow and slightly shifted toward the higher molecular weight side, indicating the absence of cleavage of the main chain and cross-linking during the reaction. A variety of functional groups such as Br, CHO, and SR may be introduced into the polymers by the similar electrophilic reaction.[18]

In conclusion, we have demonstrated that the anionic polymerizations of seven para-substituted tertiary amide styrenes, **1a–g**, proceed without any chain-termination reactions to give living polymers under appropriate conditions. Polymers with regulated chain lengths were synthesized. Futhermore, the living nature of these polymerizations makes the preparation of a variety of block copolymers having poly(*N,N*-dialkyl-4-vinylbenzamide) segments possible. It has also been demonstrated that the reactions with either poly(**1a**) or poly(**1b**) can lead to new functional polymers that retain the desirable characteristic of these parent polymers, i.e., narrow MWD and controllable molecular weights.

Experimental Section

Materials. 4-Vinylbenzoic acid, kindly supplied from Hokko Chemical Industry Co., Ltd., was used without further purification. Diethylamine, dipropylamine, diisopropylamine, diallylamine, pyrrolidine, piperidine, and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) were dried and distilled over calcium hydride under nitrogen. Dimethylamine was distilled from a 40 wt % aqueous solution through a column packed with potassium hydroxide and trapped with a dry ice–acetone bath under nitrogen over calcium hydride. *tert*-Butyl methacrylate, α-methylstyrene, styrene, and isoprene were distilled over calcium hydride. 1,1-Diphenylethylene (DPE), prepared by a literature method,[21] was purified by fractional distillation and finally distilled from *n*-BuLi/pentane under vacuum. THF used as a polymerization solvent was refluxed over sodium wire for 5 h and distilled from lithium aluminum hydride and finally through vacuum line from sodium naphthalenide solution. Methyllithium (1.2 M solution) was prepared by the reaction of methyl iodide with lithium metal in ether. *sec*-BuLi as a 1.05 M solution in cyclohexane was purchased from Kanto Chemical Co., Ltd.

Initiators. Metal naphthalenides were prepared by the reactions of a small excess amount of naphthalene with the corresponding alkali metal in THF. The oligo(α-methylstyryl)dilithium, -disodium, and -dipotassium were freshly prepared just prior to 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. Cumylpotassium was prepared by the reaction of cumyl methyl ether with a potassium–sodium alloy in THF. These initiators were stored in ampules equipped with break-seals. The concentrations of initiators were determined by colorimetric titration with standardized 1-octanol in a sealed reactor under vacuum.

4-Vinylbenzoyl Chloride. To a mixture of thionyl chloride (28 mL) and 4-*tert*-butylpyrocatecol (10 mg) under nitrogen in

Table IV
Solubilities of Poly(1)s and Polystyrene[a]

solvent	poly(1a)	poly(1b)	poly(1c)	poly(1d)	poly(1e)	poly(1f)	poly(1g)	polystyrene
hexane	I	I	I	I	I	I	I	I
benzene	S[b]	S	S	S	S	S	S	S
carbon tetrachloride	I	S	S	S	S	I	S	S
chloroform	S	S	S	S	S	S	S	S
diethyl ether	I	Sw	S	S	Sw	I	I	S
ethyl acetate	Sw	S	S	S	S	Sw	Sw	S
1,4-dioxane	S	S	S	S	S	S	S	S
tetrahydrofuran	S	S	S	S	S	S	S	S
N,N-dimethylformamide	S	S	S	S	S	S	S	S
ethanol	S	S	S	S	S	S	S	I
methanol	S	S	S	S	S	S	S	I
water	I	I	I	I	I	I	I	I
6 N HCl	S	S	I	I	I	S	Sw	I

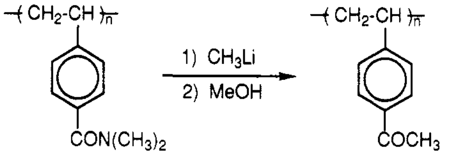
[a] I, insoluble; S, soluble; Sw, swelling. [b] Poly(1a) with molecular weight higher than 10 000 is not soluble in benzene.

Table V
Values of Intrinsic Viscosities and Molecular Weights for Poly(1b)s

[η] (THF 40 °C), dL/g	$10^{-4}\bar{M}_n$(VPO)	$10^{-4}\bar{M}_n$(GPC)[a]	$\bar{M}_w/\bar{M}_n$
0.0736	0.92	0.84	1.08
0.0844	1.4	1.2	1.06
0.0964	1.7	1.4	1.07
0.147	3.3	2.5	1.13
0.176	4.8	3.0	1.08

[a] Molecular weight of poly(1b) estimated by GPC in THF using polystyrene standard calibration.

Scheme II



Poly(1a)

an ice bath was added 4-vinylbenzoic acid (13.1 g, 88.5 mmol) in small portions with stirring below 10 °C for 4 h and at 40 °C for 1 h to afford a homogeneous solution. After removal of unreacted thionyl chloride, distillation gave 13.3 g (79.9 mmol, 90%) of 4-vinylbenzoyl chloride as a colorless liquid at 72–73 °C (0.3 mmHg) (lit.[22] 69.5–70.0 °C (0.1 mmHg)): 90-MHz ^{1}H NMR ($CDCl_3$) δ 5.44 and 5.88 (2d, 2 H, J = 11 and 17 Hz, CH_2=), 6.72 (dd, 1 H, CH=), 7.38–8.03 (m, 4 H, Ar); 23-MHz ^{13}C NMR ($CDCl_3$) δ 118.3 (vinyl, CH_2=), 126.5 (Ar, C3), 131.7 (Ar, C2), 132.1 (Ar, C1), 135.3 (vinyl, CH=), 144.4 (Ar, C4), 167.5 (C=O).

***N,N*-Dimethyl-4-vinylbenzamide (1a).** To a mechanically stirred solution of dimethylamine (10.2 g, 230 mmol) in dry ether (100 mL) under nitrogen, 4-vinylbenzoyl chloride (10.4 g, 62.5 mmol) in dry ether (50 mL) was added dropwise with cooling in an ice bath and then stirred overnight at room temperature. The precipitated ammonium salt was filtered off and the filtrate was washed two times with 1 N HCl (100 mL) and twice with saturated $NaHCO_3$ solution (100 mL) and then dried over anhydrous $MgSO_4$. After evaporation of ether, the residue was recrystallized from petroleum ether three times to yield pure white crystal of **1a** (10.1 g, 57.7 mmol, 92%; mp 55–56 °C): 90-MHz ^{1}H NMR ($CDCl_3$) δ 3.05 (s, 6 H, NCH_3), 5.31 and 5.79 (2d, 2 H, J = 11 and 18 Hz, CH_2=), 6.74 (dd, 1 H, CH=), 7.41 (m, 4 H, Ar); 23-MHz ^{13}C NMR ($CDCl_3$) δ 37.5 (br, NCH_3), 115.0 (vinyl, CH_2=), 126.0 (Ar, C3), 127.4 (Ar, C2), 135.6 (Ar, C1), 136.1 (vinyl, CH=), 138.7 (Ar, C4), 171.2 (C=O); IR (KBr, cm^{-1}) 1620 (C=O), 1520, 1500, 1410, 1390, 1270, 1080, 940, 860, 850. Anal. Calcd for $C_{11}H_{13}NO$: C, 75.40, H, 7.48, N, 8.00. Found: C, 75.16, H, 7.43, N, 7.89.

***N,N*-Diethyl-4-vinylbenzamide (1b).** The same procedure was followed as described above for **1a** using 4-vinylbenzoyl chloride (8.00 g, 52.9 mmol) and diethylamine (13.9 g, 190 mmol) in place of dimethylamine and recrystallization from petroleum ether gave 9.68 g (47.7 mmol, 90%, mp 57–58 °C) of **1b** as a white crystal: 90-MHz ^{1}H NMR ($CDCl_3$) δ 1.17 (t, 6 H, J = 7 Hz, CH_3), 3.41 (br, 4 H, NCH_2), 5.30 and 5.78 (2d, 2 H, J = 11 and 18 Hz, CH_2=), 6.73 (dd, 1 H, CH=), 7.38 (m, 4 H, Ar); 23-MHz ^{13}C NMR ($CDCl_3$) δ 13.5 (CH_3), 41.3 (NCH_2), 114.8 (vinyl, CH_2=), 126.1 (Ar, C3), 126.6 (Ar, C2), 136.1 (vinyl, CH=), 136.5 (Ar, C1), 138.3 (Ar, C4), 171.0 (C=O); IR (KBr, cm^{-1}) 1619 (C=O), 1480, 1460, 1430, 1380, 1320, 1290, 1100, 1010, 920, 860. Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81, H, 8.43, N, 6.89. Found: C, 76.51, H, 8.71, N, 7.10.

***N,N*-Dipropyl-4-vinylbenzamide (1c).** The same procedure was followed as described above for **1a** using 4-vinylbenzoyl chloride (5.12 g, 30.8 mmol) and dipropylamine (9.63 g, 95.3 mmol) in place of dimethylamine. Evaporation and suction drying gave 6.76 g (29.3 mmol, 95%) of **1c** as a colorless oil: 90-MHz ^{1}H NMR ($CDCl_3$) δ 0.88 (br, 6 H, CH_3), 1.60 (br, 4 H, CH_2), 3.31 (br, 4 H, NCH_2), 5.28 and 5.78 (2d, 2 H, J = 11 and 18 Hz, CH_2=), 6.73 (dd, 1 H, CH=), 7.37 (m, 4 H, Ar); 23-MHz ^{13}C NMR ($CDCl_3$) δ 10.9 (CH_3), 21.0 (CH_2), 48 (br, NCH_2), 114.5 (vinyl, CH_2=), 125.8 (Ar, C3), 126.5 (Ar, C2), 135.9 (vinyl, CH=), 136.4 (Ar, C1), 138.0 (Ar, C4), 171.2 (C=O); IR (KBr, cm^{-1}) 1630 (C=O), 1460, 1430, 1100, 910, 850. Anal. Calcd for $C_{15}H_{21}NO$: C, 77.88, H, 9.15, N, 6.06. Found: C, 77.64, H, 9.23, N, 5.97.

***N,N*-Diisopropyl-4-vinylbenzamide (1d).** **1d** was prepared according to the procedure previously described[11] and recrystallization from petroleum ether gave **1d** as a white crystal (75%, mp 82–83 °C): 90-MHz ^{1}H NMR ($CDCl_3$) δ 1.34 (br, 12 H, CH_3), 3.69 (br, 2 H, NCH), 5.28 and 5.76 (2d, 2 H, J = 11 and 18 Hz, CH_2=), 6.73 (dd, 1 H, CH=), 7.34 (m, 4 H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 20.8 (CH_3), 48.3 (NCH), 114.6 (vinyl, CH_2=), 126.0 (Ar, C3), 126.2 (Ar, C2), 136.1 (vinyl, CH=), 137.8 (Ar, C1), 138.2 (Ar, C4), 170.6 (C=O); IR (KBr, cm^{-1}) 1620 (C=O), 1450, 1370, 1340, 1040, 1010, 860, 840. Anal. Calcd for $C_{15}H_{21}NO$: C, 77.88, H, 9.15, N, 6.06. Found: C, 77.89, H, 9.14, N, 6.35.

***N,N*-Diallyl-4-vinylbenzamide (1e).** The same procedure was followed as described above for **1a** using 4-vinylbenzoyl chloride (9.03 g, 54.2 mmol) and diallylamine (15.8 g, 163 mmol) in place of dimethylamine and recrystallization from petroleum ether (−20 °C) gave 10.7 g (47.2 mmol, 87%, mp 16 °C) of **1e** as a colorless crystal: 90-MHz ^{1}H NMR ($CDCl_3$) δ 3.95 (br, 4 H, NCH_2), 5.0–6.1 (overlapping m, 8 H, allyl CH=CH_2 and vinyl CH_2=), 6.73 (dd, 1 H, CH=), 7.41 (m, 4 H, Ar); 23-MHz ^{13}C NMR ($CDCl_3$) δ 48 (br, NCH_2), 115.0 (vinyl, CH_2=), 117.4 (allyl, CH_2=), 126.0 (Ar, C3), 126.8 (Ar, C2), 132.9 (allyl, CH=), 135.3 (Ar, C1), 135.9 (vinyl, CH=), 138.7 (Ar, C4), 171.3 (C=O); IR (KBr, cm^{-1}) 1640 (C=O), 1460, 1410, 1290, 1260, 990, 920, 850. Anal. Calcd for $C_{15}H_{17}NO$: C, 79.26, H, 7.54, N, 6.16. Found: C, 79.24, H, 7.57, N, 6.27.

1-(4-Vinylbenzoyl)pyrrolidine (1f). The same procedure was followed as described above for **1a** using 4-vinylbenzoyl chloride (9.65 g, 58.0 mmol) and pyrrolidine (11.9 g, 168 mmol) in place of dimethylamine and recrystallization from petroleum ether gave 6.45 g (32.1 mmol, 55%, mp 87–88 °C) of **1f** as a white crystal: 90-MHz ^{1}H NMR ($CDCl_3$) δ 1.91 (br, 4 H, NCH_2CH_2), 3.54 (br, 4 H, NCH_2), 5.31 and 5.79 (2d, 2 H, J = 11 and 18 Hz, CH_2=), 6.73 (dd, 1 H, CH=), 7.46 (m, 4 H, Ar); 23-MHz ^{13}C NMR ($CDCl_3$) δ 25.4 (br, NCH_2CH_2), 47.8 (br, NCH_2), 115.0 (vinyl, CH_2=), 125.9 (Ar, C3), 127.4 (Ar, C2), 136.0 (vinyl, CH=), 136.3

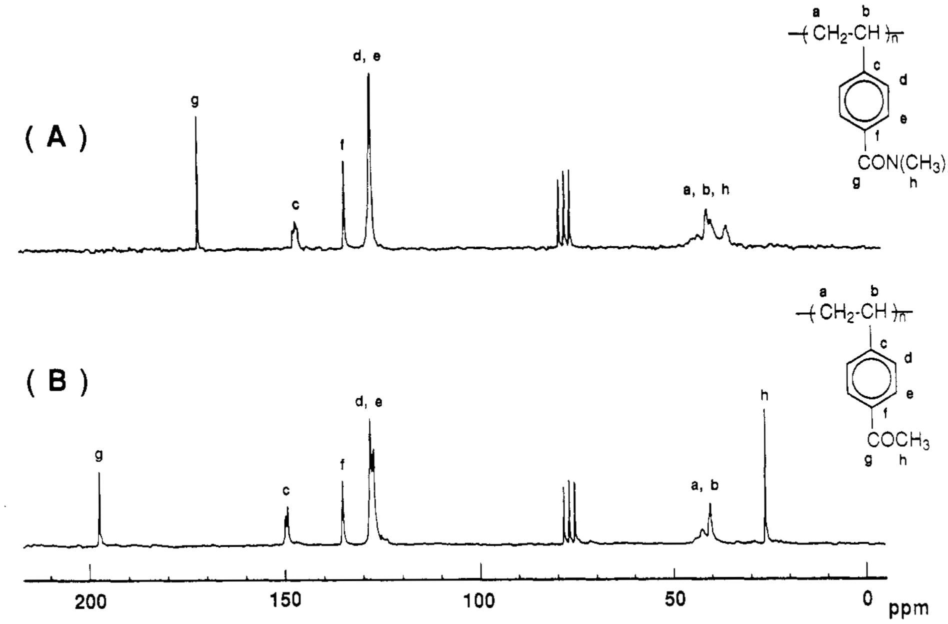
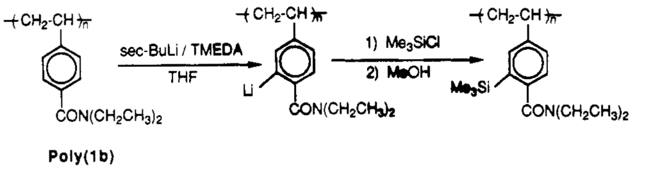


Figure 5. ^{13}C NMR spectra of the poly(**1a**) (A) and the poly(4-vinylacetophenone) obtained by the polymer reaction (B) in $CDCl_3$.

Scheme III



Poly(1b)

(Ar, C1), 138.9 (Ar, C4), 169.2 (C=O); IR (KBr, cm^{-1}) 1610 (C=O), 1440, 1000, 900, 860, 850, 770, 730. Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58, H, 7.51, N, 6.96. Found: C, 77.89, H, 7.44, N, 6.90.

1-(4-Vinylbenzoyl)piperidine (1g). The same procedure was followed as described above for **1a** using 4-vinylbenzoyl chloride (9.40 g, 56.5 mmol) and piperidine (13.8 g, 162 mmol) in place of dimethylamine and recrystallization from petroleum ether gave 10.2 g (47.3 mmol, 84%, mp 86–87 °C) of **1g** as a white crystal: 90-MHz ^1H NMR ($CDCl_3$) δ 1.64 (br, 6 H, $NCH_2CH_2CH_2$), 3.54 (br, 4 H, NCH_2), 5.30 and 5.78 (2d, 2 H, J = 11 and 18 Hz, CH_2=), 6.73 (dd, 1 H, CH=), 7.39 (m, 4 H, Ar); 23-MHz ^{13}C NMR ($CDCl_3$) δ 24.5 ($NCH_2CH_2CH_2$), 26.0 (NCH_2CH_2), 46.0 (br, NCH_2), 114.9 (vinyl, CH_2=), 126.1 (Ar, C3), 127.1 (Ar, C2), 135.7 (Ar, C1), 136.1 (vinyl, CH=), 138.6 (Ar, C4), 169.9 (C=O); IR (KBr, cm^{-1}) 1620 (C=O), 1470, 1430, 1290, 1270, 1000, 920, 860, 730. Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10, H, 7.96, N, 6.51. Found: C, 78.02, H, 8.04, N, 6.41.

Purification. After careful recrystallization, the purified monomer was dried over P_2O_5 for 48 h at ambient temperature in an apparatus equipped with a break-seal under vacuum (10^{-6} mmHg) and then diluted with 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. The viscous liquid monomers, **1c** and **1e**, were dried in a similar manner with ice-bath cooling for 48 h and the diluted with THF.

Polymerization Procedures. All polymerizations were carried out at low temperature with shaking under high-vacuum conditions in the all-glass apparatus equipped with break-seals as previously reported.[23] The polymerization was quenched with methanol. The reaction mixture was concentrated, redissolved in THF, and then poured into a large excess of water to precipitate the polymers. Polymers collected by filtration were purified by reprecipitation twice with a petroleum ether–THF system and by freeze-drying from benzene. Poly(1)s thus obtained were characterized by ^1H and ^{13}C NMR, IR, and elemental analysis. The following is the full list.

Poly(1a): 90-MHz ^1H NMR ($CDCl_3$) δ 1.0–2.5 (m, 3 H, CH_2CH), 3.0 (br, 6 H, NCH_3), 6.2–7.2 (m, 4 H, Ar); 23-MHz ^{13}C NMR ($CDCl_3$) δ 35–43 (overlapping, CH_2CH and NCH_3), 127 (Ar, C3 and C2), 133.7 (Ar, C1), 146.2 (Ar, C4), 171.1 (C=O); IR (KBr, cm^{-1}) 1640 (C=O), 1570, 1520, 1490, 1450, 1410, 1400, 1270, 1090, 850. Anal. Calcd for poly(**1a**), $(C_{11}H_{13}NO{\cdot}0.2H_2O)_n$: C, 73.88, H, 7.55, N, 7.83. Found: C, 73.70, H, 7.30, N, 7.05.

Poly(1b): 90-MHz ^1H NMR ($CDCl_3$) δ 0.8–2.0 (m, 9 H, CH_3, CH_2CH), 3.3 (br, 4 H, NCH_2), 6.2–7.2 (m, 4 H, Ar); 23-MHz ^{13}C NMR ($CDCl_3$) δ 13.4 (CH_3), 39–44 (overlapping, CH_2CH and NCH_2), 126–128 (Ar, C3 and C2), 134.7 (Ar, C1), 145.9 (Ar, C4), 170.9 (C=O); IR (KBr, cm^{-1}) 1636 (C=O), 1470, 1460, 1430, 1380, 1360, 1320, 1290, 1100, 840. Anal. Calcd for poly(**1b**), $(C_{13}H_{17}NO{\cdot}0.1H_2O)_n$: C, 76.14, H, 8.45, N, 6.83. Found: 76.07, H, 8.39, N, 6.80.

Poly(1c): 90-MHz ^1H NMR ($CDCl_3$) δ 0.5–1.1 (m, 6 H, CH_3), 1.1–2.0 (m, 7 H, CH_2CH and CH_2), 2.9–3.6 (m, 4 H, NCH_2), 6.2–7.3 (m, 4 H, Ar); 23-MH ^{13}C NMR ($CDCl_3$) δ 11.3 (CH_3), 21.2 (NCH_2CH_2), 40–50 (overlapping, CH_2CH and NCH_2), 126–128 (Ar, C3 and C3), 135.0 (Ar, C1), 145.5 (Ar, C4), 171.5 (C=O); IR (KB, cm^{-1}) 1640 (C=O), 1460, 1430, 1100. Anal. Calcd for poly(**1c**), $(C_{15}H_{21}NO)_n$: C, 77.88, H, 9.15, N, 6.06. Found: C 78.56, H, 9.41, N, 5.27.

Poly(1d): 90-MHz ^1H NMR ($CDCl_3$) δ 0.9–1.9 (m, 15 H, CH_2CH, CH_3), 3.6 (br, 2 H, NCH), 6.3–7.2 (m, 4 H, Ar); 23-MHz ^{13}C NMR ($CDCl_3$) δ 20.8 (CH_3), 40–48 (overlapping, CH_2CH and NCH), 125–128 (Ar, C3 and C2), 136.6 (Ar, C1), 146.4 (Ar, C4), 170.9 (C=O); IR (KBr, cm^{-1}) (1640 (C=O), 1440, 1370, 1340, 1040, 830. Anal. Calcd for poly(**1d**), $(C_{16}H_{21}NO{\cdot}0.1H_2O)_n$: C, 77.28, H, 9.17, N, 6.01. Found: C, 76.90, H, 8.83, N, 5.42.

Poly(1e): 90-MHz ^1H NMR ($CDCl_3$) δ 1.1–1.9 (m, 3 H, CH_2CH), 3.5–4.2 (m, 4 H, NCH_2), 5.0–5.3 (m, 4 H, allyl CH_2=), 5.5–6.0 (m, 2 H, allyl CH=), 6.3–7.2 (m, 4 H, Ar); 23-MHz ^{13}C NMR ($CDCl_3$) δ 40–50 (overlapping, CH_2CH and NCH_2), 117.5 (allyl, CH_2=), 126–128 (Ar, C3 and C2), 133.1 (allyl, CH=), 133.8 (Ar, C1), 146.3 (Ar, C4), 171.3 (C=O); IR (KBr, cm^{-1}) 1640 (C=O), 1460, 1410, 1260, 930. Anal. Calcd for poly(**1e**), $(C_{15}H_{17}NO)_n$: C, 79.26, H, 7.54, N, 6.16. Found: C, 79.20, H, 7.55, N, 5.96.

Poly(1f): 90-MHz ^1H NMR ($CDCl_3$) δ 1.2–2.1 (m, 7H, CH_2CH and NCH_2CH_2), 3.1–3.8 (m, 4 H, NCH_2), 6.3–7.3 (m, 4 H, Ar); 23-MHz ^{13}C NMR ($CDCl_3$) δ 24.1 and 26.1 (NCH_2CH_2), 40–46 (CH_2CH), 45.8 and 49.2 (NCH_2), 126.9 (Ar, C3 and C2), 134.4 (Ar, C1), 145.9 (Ar, C4), 169.0 (C=O); IR (KBr, cm^{-1}) 1610 (C=O), 1560, 1440, 850, 770, 720. Anal. Calcd for poly (**1f**), $(C_{13}H_{15}NO{\cdot}0.3H_2O)_n$: C, 75.55, H, 7.61, N, 6.78. Found: C, 75.27, H, 7.50, N, 6.47.

Poly(1g): 90-MHz NMR ($CDCl_3$) δ 0.9–2.1 (m, 9 H, CH_2CH and $CH_2CH_2CH_2$), 3.0–3.8 (m, 4 H, NCH_2), 6.2–7.2 (m, 4 H, Ar); 23-MHz ^{13}C NMR ($CDCl_3$) δ 24.3 ($NCH_2CH_2CH_2$), 25.8 (NCH_2CH_2), 40–49 (overlapping, CH_2CH and NCH_2), 126.8 (Ar, C3 and C2), 133.7 (Ar, C1), 145.7 (Ar, C4), 169.8 (C=O); IR (KBr, cm^{-1}) 1620 (C=O), 1440, 1280, 1110, 1000, 850. Anal. Calcd for poly-

(**1g**), $(C_{14}H_{17}NO\cdot 0.2H_2O)_n$: C, 76.82, H, 8.01, N, 6.40. Found: C, 76.94, H, 7.94, N, 6.33.

Reaction of Poly(1a) with Methyllithium. To a solution of poly(**1a**) (0.51 g, 2.9 mmol based on monomer unit) in dry THF (20 mL) methyllithium (20 mL of a 1.2 M ether solution, 24 mmol) was added dropwise at −78 °C under nitrogen. The reaction mixture was allowed to stir at −78 °C for 20 min and then at 0 °C for 2 h to afford a homogeneous system. When the reaction was quenched with methanol at −78 °C, a yield of dimethylamine was observed. To precipitate the polymer, the solution was poured into water. Subsequent reprecipitation and freeze-drying gave poly(4-vinylacetophenone) (0.33 g, 2.3 mmol based on monomer unit, 79%) characterized as follows. **Poly(4-vinylacetophenone)**: 90-MHz ^{1}H NMR ($CDCl_3$) δ 1.1–1.8 (m, 3 H, CH_2CH), 2.45 (br, 3 H, $COCH_3$), 6.2–7.7 (m, 4 H, Ar); 23-MHz ^{13}C NMR ($CDCl_3$) δ 26.3 (CH_3), 40–45 (CH_2CH), 126–129 (Ar, C3 and C2), 135.3 (Ar, C1), 149.4 (Ar, C4), 197.4 (C=O); IR (KBr, cm^{-1}) 1680 (C=O), 1610, 1420, 1360, 1270. Anal. Calcd for $(C_{10}H_{10}O)_n$: C, 82.16, H, 6.90, N, 0,00. Found: C, 81.57, H, 7.46, N, 0.00.

Aromatic Lithiation of Poly(1b) and Subsequent Reaction with Trimethylsilyl Chloride. To a solution of poly(**1b**) (0.20 g, 0.99 mmol based on monomer unit) and TMEDA (0.31 g, 2.7 mmol) in dry THF (20 mL), *sec*-BuLi (2.0 mL of a 1.05 M cyclohexane solution, 2.1 mmol) was added dropwise at −78°C under nitrogen. The reaction mixture was allowed to stir at −78 °C for 1 h. Then trimethylsilyl chloride (1.1 g, 10 mmol) was added at once at −78 °C. The color of solution changed from orange to yellow. After stirring for 1 h at −78 °C, the reaction was quenched with MeOH and the reaction mixture was poured into water for precipitation. The resulting polymer (0.25 g) was purified by reprecipitation from THF/hexane system and freeze-dried from benzene. Poly(**1b**) after polymer reaction: 90-MHz ^{1}H NMR ($CDCl_3$) δ 0.15 (br s, $SiCH_3$), 0.8–2.0 (m, CH_2CH and CH_3), 2.9–3.6 (m, NCH_2), 6.2–7.8 (m, Ar).

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) for ^{1}H NMR and to $CDCl_3$ (δ 77.1) for ^{13}C NMR as standard. Gel permeation chromatograms (GPC) for MWD determinations of poly(**1**)s were obtained at 40 °C with a Toyosoda HLC-802 instrument with ultraviolet (254 nm) or refractive index detection. THF was the carrier solvent at a flow rate of 1.4 mL min^{-1}. GPC analyses of poly(**1a**) and poly (**1f**) were performed at 40 °C in DMF solution at a flow rate of 0.8 mL min^{-1} with a Toyosoda HLC-8020 instrument. Vapor pressure osmometry (VPO) measurements for number-average molecular weight determination were made with a Corona 117 instrument in benzene solution with a highly sensitive thermoelectric couple and equipment of very exact temperature control. Intrinsic viscosities of poly(**1b**) and polystyrene were measured by using an Ubbelohde type capillary viscometer at 40 °C in THF.

References and Notes

(1) The main title of the series of studies was given to this one. Part 1: ref 11. Part 2: ref 7.

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(13) In the cases of samples with molecular weghts less than 10 000, the moleclar weight of poly(**1a**) was measured by VPO in benzene. Since for poly(**1a**) with a molecular weight higher than 10 000 it was difficult to determine the molecular weight dut to the insolubility in benzene, those molecular weights were estimated by using the polystyrene standard calibration with GPC measurement in DMF.

(14) The product of block copolymerization was roughly separable by precipitation into methanol or Soxhlet extraction. The filtrate was the virtual homopolymer of (**1b**), which did not concern the block copolymerization, while the precipitate was block copolymer containing a polystyrene segment of very high molecular weight.

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(20) In this polymer reaction, the regioselectivity is not clear at this stage. In ^{13}C NMR spectrum of the resulting polymer, four signals of aromatic carbons of poly(**1b**) were split into complicated signals, indicating the substitution of aromatic rings of poly(**1b**).

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Registry No. 1a, 2681-30-3; **1a** (homopolymer), 26836-88-4; (**1a**)(St) (block copolymer), 134879-82-6; **1b**, 2681-29-0; **1b** (homopolymer), 26836-89-5; (**1b**)(St) (block copolymer), 134879-83-7; (**1b**)(ISO) (block copolymer), 134879-84-8; (**1b**)($H_2C{=}CHCO_2$-Bu-*t*) (block copolymer), 134879-86-0; **1c**, 134879-76-8; **1c** (homopolymer), 134879-79-1; **1d**, 101614-59-9; **1d** (homopolymer), 101614-60-2; **1e**, 134879-77-9; **1e** (homopolymer), 134879-80-4; **1f**, 134879-78-0; **1f** (homopolymer), 134879-81-5; (**1f**)(St) (block copolymer), 134879-85-9; **1g**, 2681-28-9; **1g**, 26936-69-6; TMEDA, 110-18-9; lithium naphthalenide, 7308-67-0; sodium naphthalenide, 3481-12-7; potassium naphthalenide, 4216-48-2; oligo(α-methylstyryl)dilithium, 57486-16-5; oligo(α-methylstyryl)disodium, 37244-89-6; oligo(α-methylstyryl)dipotassium, 88384-52-5; cumylpotassium, 3003-91-6; vinylacetophenone, 26836-91-9; trimethylsilyl chloride, 75-77-4; 4-vinylbenzoic acid, 1075-49-6; 4-vinylbenzoyl chloride, 1565-41-9.