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Anionic Polymerization of Monomers Containing Functional Groups. 13. Anionic Polymerizations of 2-, 3-, and 4-(3,3-Dimethyl-1-butynyl)styrenes,[1] 2-, 3-, and 4-(1-Hexynyl)styrenes,[2] and 4-(Phenylethynyl)styrene

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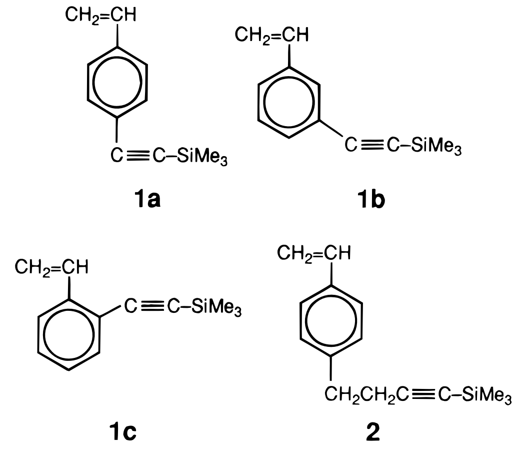
ABSTRACT: The anionic polymerizations of 4-, 3-, and 2-(3,3-dimethyl-1-butynyl)styrenes (**3a**, **3b**, and **3c**), 4-, 3-, and 2-(1-hexynyl)styrenes (**4a**, **4b**, and **4c**), and 4-(phenylethynyl)styrene (**5**) were carried out in THF at −78 °C with oligo(α-methylstyryl)dipotassium and *sec*-butyllithium. The polymerizations of these monomers proceeded quantitatively at −78 °C for 0.5 h. The resulting polymers all possessed the predicted molecular weights based on the molar ratios of monomer to initiator and the narrow molecular weight distributions ($M_w/M_n = 1.03-1.15$). The living character of the propagating carbanion derived from these monomers was further confirmed by the quantitative initiation efficiency in the second-stage polymerization. A variety of novel block copolymers with well-defined chain structures were synthesized by the sequential block copolymerization of **3a**, **4a**, **5**, and 4-((trimethylsilyl)ethynyl)styrene (**1a**) with isoprene, styrene, 2-vinylpyridine, and *tert*-butyl methacrylate. Furthermore, the relative reactivities of the monomers and the resultant living polymers were evaluated from the results of the anionic block copolymerizations. Higher reactivity of **3a**, **4a**, **5**, and **1a** and lower nucleophilicity of their living polymers were clearly demonstrated, compared with those of styrene and living polystyrene, respectively. Both of these features can be explained by the electron-withdrawing character of the ethynyl substituents and the extended π-conjugation system including the carbon−carbon triple bond. The anionic polymerizabilities of **3a**, **4a**, **5**, and **1a** are estimated to be the same level of 2-vinylpyridine.

Introduction

Ethynylstyrenes are a typical class of attractive dual-functional monomers that contain two polymerizable functions of vinyl group and acetylene moiety in the skeleton. Both functions are expected to be readily polymerizable under the various reaction conditions. If the chemoselective polymerization of each function proceeds well, the ideal linear polymer bearing another polymerizable function in each monomer unit can be obtained. However, it has been reported that the free-radical polymerization of 4-ethynylstyrene gives the insoluble polymeric product only in low yield, probably due to the serious cross-linking of the polymer.[3] The polymerization proceeds in a nonselective way and the radical addition toward the acetylene moiety might also take place along with the expected vinyl polymerization. Similar to the radical pathway, the anionic process will also meet the same problem in the selectivity of the polymerizable functions.[4] More seriously, the presence of the acidic acetylene protons on ethynylstyrenes are particularly problematic when one attempts to anionically polymerize ethynylstyrenes. It is easy to imagine that the proton abstraction from the C≡CH group ($pK_a = 25$)[5] readily occurs with the strongly basic anionic initiators and/or the propagating benzylic carbanions at the initiation step or during the propagation.

These difficulties have been successfully circumvented by introducing the trimethylsilyl protecting group[6] on the C≡C moiety to mask the acidic acetylene proton during the course of the anionic polymerization. The polymerizations of the newly designed protected ethynylstyrenes, ((trimethylsilyl)ethynyl)styrenes (**1**s), proceeded quantitatively to afford the anionic living polymers having predicted molecular weights and narrow molecular weight distributions (MWD)s (Chart 1).[7] Furthermore, the living character of the polymerization systems also allows one to prepare the tailored block copolymers containing poly(**1**) segments. The trimethylsilyl protecting group of the resulting polymers can be easily and quantitatively removed by treating with F^- [8] or OH^- [9] to give the expected poly(ethynylstyrene)s

Chart 1



1a **1b**

1c **2**

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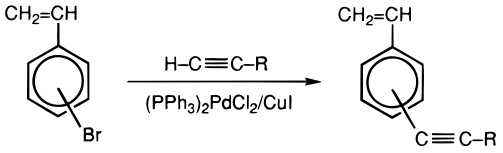
Scheme 1



3a : R = Bu^t, *para*
3b : R = Bu^t, *meta*
3c : R = Bu^t, *ortho*
4a : R = Bu, *para*
4b : R = Bu, *meta*
4c : R = Bu, *ortho*
5 : R = Ph, *para*

having well-defined chain structures. Thus, the undesirable side reactions such as the acetylene proton abstraction and the nucleophilic addition toward the C≡C bond are completely eliminated by the protection of the terminal acetylene proton with a trimethylsilyl group.

We similarly succeeded in the controlled anionic polymerization of 4-(4′-(trimethylsilyl)-3′-butynyl)styrene (**2**), the protected form of 4-(3′-butynyl)styrene.[10] However, the propagating chain end derived from **2** is gradually deactivated with time at −78 °C, although the fine controls of M_n values and MWDs of the polymer are attained. At −95 °C, the deactivation becomes negligible to form the well-defined block copolymer with styrene efficiently. The most likely cause for this side reaction is the deprotonation from the methylene group adjacent to the C≡C bond, since those protons are known to be considerably acidic.[11] Thus, the C≡CCH_2 moiety in the styrene monomer also contains a serious problem to realize the anionic living polymerization even at −78 °C besides the C≡CH function.

In this report, we have newly synthesized three ethynylstyrene derivatives to extend the range of functional monomers capable of the living anionic polymerizations and to design the novel macromolecules that have well-defined chain structures as well as the C≡C bond in each monomer unit. The employed monomers are 4-(3,3-dimethyl-1-butynyl)styrene (**3a**),[1] 4-(1-hexynyl)styrene (**4a**),[2] and 4-(phenylethynyl)styrene (**5**) (Scheme 1). In these monomers, the acidic acetylene proton of 4-ethynylstyrene is purposefully substituted with the *tert*-butyl, *n*-butyl, or phenyl group, instead of the trimethylsilyl group for **1a**. Our primary interest is the additional substituent effect on the β-position of the ethynyl group on the anionic polymerizability of a series of β-substituted ethynylstyrenes, which will be clarified by the comparison of polymerization behaviors. We also attempted to polymerize *meta* (**3b** and **4b**) and *ortho* isomers (**3c** and **4c**) to evaluate the effect of substituent position. All the monomers possess the β-substituted ethynyl groups, which conjugate with the styrene framework similarly to the case of **1a**. On the polymerization of **4**s, the presence of the acidic methylene protons adjacent to the C≡C linkage can be particularly problematic, as is observed in the case of **2**.[10] In the case of **5**, the phenylethynyl substituent will provide the widely extended π-conjugation system and induce the enhanced anionic polymerizability of the monomer and the stabilization of the propagating species.[12] However, it is reported that diphenylacetylene suffers from the nucleophilic addition of the carbanionic species easily due to the high electrophilicity of the extended conjugation system.[13] Therefore, the polymerization behavior of **5** is a considerable interest in terms of the stability of the ArC≡CPh moiety toward the carbanionic species compared with the normal disubstituted C≡C linkage. Thus, we here report the results of homopolymerization and sequential block copolymerization of **3a**−**3c**, **4a**−**4c**, and **5** to elucidate the general polymerization behaviors and the anionic polymerizabilities of these dual-functional styrenes with C≡C groups.

Results and Discussion

Anionic Polymerization of 3a−3c, 4a−4c, and 5 in THF. The new monomers used here were readily synthesized by the transition metal-mediated coupling reaction[9] between 2-, 3-, and 4-bromostyrenes and the corresponding monosubstituted acetylenes, as shown in Scheme 1. The yields of monomers were good to moderate, which showed the versatility of this reaction to synthesize ethynylstyrene derivatives, as was reported previously for the syntheses of ((trimethylsilyl)ethynyl)styrenes.[7]

The anionic polymerizations of *para*-substituted monomers, **3a**, **4a**, and **5**, were carried out in THF at −78 °C for 0.5 h. The initiators included cumylpotassium, potassium naphthalenide, (diphenylmethyl)potassium (Ph_2CHK), oligo(α-methylstyryl)dipotassium and -lithium, *n*-BuLi, and *s*-BuLi. On the addition of monomers, the reaction mixtures always showed a typical red color that resembled that of anionic living polystyrene over the course of polymerization. The red coloration instantaneously disappeared by quenching with degassed methanol. After termination, a polymer was obtained in 100% yield in each case. It is elucidated from the analyses of the resulting polymers by the ^1H and ^{13}C NMR and IR spectroscopies that the vinyl polymerization exclusively proceeds to afford the polymer having the expected repeating units.

Table 1 shows the results of polymerization. All the polymerizations of **3a**, **4a**, and **5** were completed in THF at −78 °C within 0.5 h, and the polymers were produced in quantitative yields. The size exclusion chromatograms (SEC) of the polymers showed unimodal and symmetrical peaks, suggesting the absence of the intermolecular side reaction of the resulting polymers. The polydispersity index, M_w/M_n values estimated from the SEC calibration using polystyrene standards, were around 1.1, indicating the narrow MWDs of the resulting polymers. The number-average molecular weights of the polymer samples were determined by the vapor pressure osmometry (VPO) in benzene solution. The M_n values thus obtained agreed well with the calculated values based on the molar ratios of monomers and the employed initiators. The agreement in the M_n values supports the quantitative initiation efficiency of the polymerization and the rapid initiation reaction. Hence, the fine controls of M_n's and the MWDs of the resulting polymers are attained. However, there were some exceptions as follows. The poly(**3a**) produced with Ph_2CHK (Table 1, run 4) possessed the M_n value higher than the calculated one, and the SEC curve showed a significant tailing toward a low molecular weight region. This can be accounted for by the low initiation efficiency of Ph_2CHK for **3a** because of the steric hindrance and the low nucleophilicity of this anion. The SEC curve of the poly(**4a**) formed at 0 °C (Table 1, run 12) apparently

Table 1. Anionic Polymerization of 3a−3c, 4a−4c, and 5 in THF at − 78 °C for 0.5 h[a]

run	amt of monomer, mmol	amt of initiator, mmol	amt of α-MeSt,[b] mmol	$10^{-3}M_n$		M_w/M_n[e]
				calcd[c]	obsd[d]	
1	**3a**, 2.66	Cumyl-K,[f] 0.102		4.9	4.9	1.06
2	**3a**, 2.11	K-Naph,[g] 0.0557		13	14	1.08
3	**3a**, 3.92	K-Naph, 0.0604	0.233	25	24	1.05
4	**3a**, 2.69	Ph$_2$CHK,[h] 0.0385		13	18	1.15
5	**3a**, 2.48	*s*-BuLi, 0.0414		11	11	1.15
6	**3a**, 3.16	*s*-BuLi, 0.0504	0.211	12	16	1.11
7	**3b**, 1.72	K-Naph, 0.0456	0.267	15	14	1.14
8	**3c**, 1.68	K-Naph, 0.0529	0.232	13	9.7	1.14
9	**4a**, 2.26	Cumyl-K, 0.0622		6.8	7.2	1.07
10	**4a**, 2.11	K-Naph, 0.0616	0.207	13	10	1.07
11	**4a**, 4.44	K-Naph, 0.0783	0.342	22	20	1.10
12[i]	**4a**, 2.90	K-Naph, 0.0956	0.342	13	13	1.21
13	**4a**, 2.71	*s*-BuLi, 0.0504		10	11	1.15
14	**4a**, 3.42	*s*-BuLi, 0.0493	0.236	13	16	1.06
15	**4b**, 3.32	Cumyl-K, 0.0853		7.3	6.0	1.10
16	**4b**, 3.19	K-Naph, 0.126	0.436	10	9.5	1.11
17	**4b**, 4.55	K-Naph, 0.0806	0.343	22	21	1.14
18	**4b**, 2.75	*s*-BuLi, 0.0460		11	12	1.09
19	**4b**, 3.19	*s*-BuLi, 0.0604	0.244	11	13	1.15
20	**4c**, 3.01	Cumyl-K, 0.0969		5.4	5.2	1.09
21	**4c**, 4.46	Cumyl-K, 0.0424		19	17	1.13
22	**4c**, 3.29	K-Naph, 0.112	0.382	12	12	1.12
23	**4c**, 2.97	*s*-BuLi, 0.0486		11	11	1.10
24	**5**, 2.25	Cumyl-K, 0.0566		8.2	7.7	1.07
25	**5**, 2.06	K-Naph, 0.0837	0.346	11	10	1.08
26	**5**, 2.31	*n*-BuLi, 0.0678		7.0	7.6	1.11
27	**5**, 1.48	*s*-BuLi, 0.0636		4.8	6.0	1.08
28[j]	**5**, 1.53	*s*-BuLi, 0.0440	0.327	8.0	9.0	1.09
29	**5**, 4.54	*s*-BuLi, 0.0345	0.264	28	27	1.09

[a] Yields of polymers were quantitative in all cases. [b] α-Methylstyrene. [c] M_n(calcd) = [monomer] × (MW of monomer) × *f*/[initiator] + MW of initiator residue; *f* = 1 or 2, corresponding to the functionality of the initiators. [d] M_n(obsd) was obtained by VPO measurement in benzene. [e] M_w/M_n was obtained by SEC calibration using polystyrene standards in THF solution. [f] Cumylpotassium. [g] Potassium naphthalenide. [h] (Diphenylmethyl)potassium. [i] At 0 °C. [j] For 4 h.

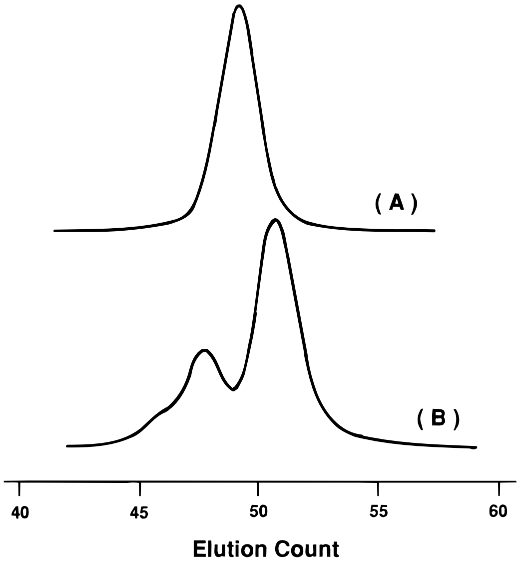


Figure 1. SEC curves of poly(**5**) produced at −78 °C for 4 h in THF (A) (Table 1, run 28) and poly(**4a**) (B) (Table 2, run 30) at 40 °C for 1 h in benzene.

possessed a higher molecular weight shoulder with a relatively broad MWD (M_w/M_n = 1.21). The intermolecular side reaction between the active chain end of poly(**4a**) and the pendant C≡CBu moiety might occur to some extent at the elevated temperature of 0 °C in THF, as was seriously observed in the polymerization in benzene. This will be discussed later. It is also noteworthy that the poly(**5**) maintained a unimodal and narrow MWD at −78 °C at least for 4 h, as can be seen in Figure 1A. This means the satisfactory stability of the conjugated ArC≡CPh moiety in the presence of the polystyryl anion derived from **5** over the course of polymerization.

The *meta* and *ortho* isomers, **3b**, **3c**, **4b**, and **4c**, also underwent the anionic polymerization quantitatively in THF at −78 °C for 0.5 h. The resultant polymers had the predicted molecular weights and fairly narrow MWDs. In particular, polydispersities of the *meta* isomers, poly(**3b**) and poly(**4b**), were always within 1.15 and were narrower than the reported values of poly(**1b**)s, which always possessed relatively broad MWDs (M_w/M_n = 1.22−1.39).[7]

The results obtained above clearly indicate the living character of the polymerizations of all novel monomers, **3a**−**3c**, **4a**−**4c**, and **5**, in THF solution at −78 °C. This is further confirmed by the postpolymerization of the monomers under identical conditions. For example, after the completion of a first-stage polymerization of **4a** with cumylpotassium in THF at −78 °C for 0.5 h, a second feed of **4a** was added to the polymerization system. The second-stage polymerization was continued for an additional 0.5 h. After the termination with methanol, both prepolymer and postpolymer were obtained in quantitative yields. The SEC curve of the postpolymer shifted toward a higher molecular weight side with keeping the sharp shape of the chromatogram. The pre- and postpoly(**4a**) possessed M_n values of 7200 (M_w/M_n = 1.07) and 17 000 (M_w/M_n = 1.08), which were very close to the calculated ones, 6800 and 16 000. These indicate that the propagating carbanion of living poly(**4a**) is stable at −78 °C at least for 0.5 h to initiate the further polymerization with a quantitative efficiency after the complete consumption of the monomer. Similar to the case of **4a**, the persistencies of the active chain ends derived from **3a**, **4c**, and **5** in THF at −78 °C were

Scheme 2

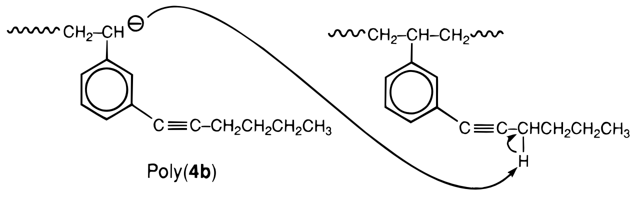


Table 2. Anionic Polymerization of 4a with *s*-BuLi in Benzene for 1 h

run	amt of **4a**, mmol	amt of *s*-BuLi, mmol	temp, °C	yield, %	$10^{-3}M_n$ calcd	$10^{-3}M_n$ obsd[a]	M_w/M_n
30	3.15	0.0554	40	100	11	14	*b*
31	3.55	0.0593	20	100	11	14	*b*
32	3.33	0.0463	0	61	8.1	10	1.09

[a] M_n(obsd) was obtained by VPO in benzene. [b] The MWD was multimodal, probably due to the intermolecular side reaction of the resulting polymers.

also substantiated by the same procedures using 2-vinylpyridine (2VP) as a second feed monomer.

It should be, however, mentioned that the terminal carbanion of poly(**4b**) was not sufficiently stable even at −78 °C. About 12% of chain ends of poly(**4b**) were found to be deactivated at −78 °C after 0.5 h. After 12 h, the percentage of the deactivated terminals increased to up to 30%, although a prepolymer maintained a unimodal and a very narrow MWD ($M_w/M_n = 1.10$). This suggests that a detectable deactivation indeed occurs particularly after the complete consumption of the monomer. The deactivation reaction of the living poly(**4b**) might not be an intermolecular nucleophilic addition toward the C≡C bond but a proton abstraction from the methylene group adjacent to the C≡C group (Scheme 2), as was observed in the case of **2**. Such deactivations were not observed in the cases of the corresponding *para* and *ortho* isomers of **4a** and **4c**. In addition, the propagating carbanion derived from *tert*-butylethynyl counterpart **3b** was also found to be stable, since it contained no acidic $C{\equiv}CCH_2$ type proton. It is considered that resonance stabilization[12] by the *meta*-substituted C≡CBu group might not be enough for the terminal benzylic carbanion of poly(**4b**) to suppress the acidic proton abstraction in contrast to the sufficient stabilization effects of *para* and *ortho* isomers, **4a** and **4c**. Thus, the position of the substituent is also important to realize the anionic living polymerization of styrenes containing the C≡CBu groups.

Anionic Polymerization of 4a in Benzene. In the preceding section, we have succeeded in anionically polymerizing the ethynylstyrene derivatives in a living manner in THF at −78 °C. Since it is established that the anionic living polymerization of styrene can also be realized in a nonpolar solvent at an elevated temperature,[14] the polymerization of **4a** is herein attempted with *s*-BuLi in benzene solution at 0, 20, and 40 °C for 1 h. The results are shown in Table 2. The reaction mixture of *s*-BuLi and **4a** always showed an orange color and the polymers were quantitatively obtained after the termination with methanol. However, the SEC curve of the resulting polymer produced at 40 °C showed multimodal peaks having relatively broad MWD, as shown in Figure 1B. The distribution of the main peak was fairly narrow but there were some additional peaks or shoulders at the higher M_n region. The estimated M_n value of the main peak was in accordance with the calculated molecular weight, and the peaks at the higher M_n region corresponded to the double and triple M_n's of the main peak. These suggest that the polymerization of **4a** at first proceeded well to afford a polymer having a controlled M_n and a narrow MWD but then the side reaction of the propagating carbanion and the pendant C≡CBu moiety occurred intermolecularly (and intramolecularly) to result in the multimodal MWD after the completion of the polymerization (Scheme 3). This side reaction could not be completely suppressed at 20 °C, although the SEC shoulders at the higher M_n region became much smaller than those observed at 40 °C. At 0 °C, the polymerization of **4a** was not complete within 1 h and the yield of polymer was 61%. The SEC curve of poly(**4a**) obtained at 0 °C was almost unimodal and very narrow ($M_w/M_n = 1.09$) and possessed the predicted M_n value, strongly indicating the absence of the intermolecular side reactions leading to the multimodal MWDs. This also supports that the side reaction might mainly take place not during the propagation but after the completion of the polymerization. The results obtained here demonstrated the possibility of controlled anionic polymerization of **4a** at 0 °C in a nonpolar solvent such as benzene as well as in a polar solvent of THF, while great care is needed with the polymerization temperature.

Block Copolymerization between 1a, 3a, 4a, and 5 and Isoprene (Isp), Styrene (St), 2-Vinylpyridine (2VP), and *tert*-Butyl Methacrylate (tBMA). One of the most important advantages of living polymerization is a synthesis of well-defined block copolymers possessing the predicted M_n's and the narrow MWDs through the sequential addition of comonomers. The success in the anionic living polymerization of new functional styrenes **3**−**5** allows one to prepare those tailored block copolymers having polystyrene segments bearing alkyl- or arylethynyl side chains. In addition to the synthetic advantage, the results of sequential block copolymerization of **3**−**5** may offer important information concerning relative reactivities of these novel monomers and the resulting living polymers. We herein employed four conventional comonomers, isoprene (Isp), styrene (St), 2-vinylpyridine (2VP), and *tert*-butyl methacrylate (tBMA), as a reference to evaluate the anionic polymerizabilities of **1a**, **3a**, **4a**, and **5**, as reported previously.[15] The conditions of the block copolymerization were standardized as much as possible according to our previous study.[15] The sequential copolymerizations were performed similarly to the procedure of postpolymerization in THF at −78 °C with organopotassium initiators such as cumylpotassium and potassium naphthalenide except for some cases.

At first, we carried out the sequential copolymerizations of **1a**, **3a**, **4a**, and **5** with the anionic living polymers of Isp, St, 2VP, and tBMA to prepare block copolymers. Furthermore, the reactivities of **1a**, **3a**, **4a**, and **5** can be evaluated from the polymerization results. The results are summarized in Table 3. Yield refers to the polymer yield at the second-stage polymerization, and initiation efficiency presents the efficiency of the crossover reaction between the living polymer at the first-stage and the second monomer. As expected, living polyisoprene and polystyrene could initiate the polymerization of **1a**, **3a**, **4a**, and **5** quantitatively to afford the block copolymers having narrow MWDs and the predicted M_n's. The compositions of the block copolymers, which were determined from the ^{1}H NMR, were

Scheme 3

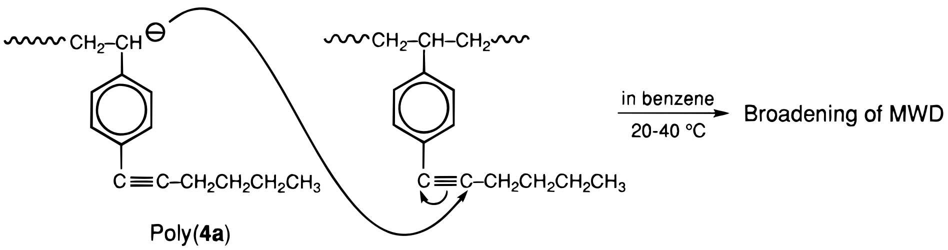


Table 3. Block Copolymerization of 1a, 3a, 4a, and 5 with Living Polymers Derived from Isp, St, 2VP, and TBMA in THF at −78 °C

run	countercation	1st monomer	2nd monomer	yield,[b] %	block copolymer (homopolymer[a]) $10^{-3}M_n$ calcd	obsd[c]	M_w/M_n	initiation efficiency, %[d]
33	K^+	Isp	**3a**	100	22 (9.4)	26 (11)	1.11 (1.11)	100
34	K^+	Isp	**4a**	100	22 (6.4)	24 (8.0)	1.13 (1.13)	100
35	K^+	Isp	**1a**	100	23 (14)	26 (15)	1.05 (1.05)	100
36	K^+	Isp	**5**	100	18 (6.0)	21 (7.3)	1.16 (1.14)	100
37	K^+	St	**3a**	100	16 (7.6)	16 (8.0)	1.03 (1.06)	100
38	K^+	St	**4a**	100	18 (6.1)	19 (6.7)	1.07 (1.06)	100
39	K^+	St	**1a**	100	21 (12)	22 (10)	1.06 (1.03)	100
40	Li^+	St	**5**	100	18 (5.1)	18 (5.3)	1.10 (1.05)	100
41	K^+	2VP	**3a**	100	16 (6.8)	*e* (7.1)	*e* (1.13)	~60
42	K^+	2VP	**4a**	100	15 (6.8)	*e* (6.9)	*e* (1.10)	~60
43	Li^+	2VP	**1a**	100	22 (8.4)	*e* (11)	*e* (1.04)	~80
44	K^+	2VP	**5**	100	16 (6.5)	17 (6.4)	1.08 (1.09)	100
45	K^+	tBMA	**3a**	100	15 (5.3)	*e* (4.9)	*e* (1.05)	~5
46	K^+	tBMA	**4a**	100	14 (5.4)	*e* (4.7)	*e* (1.06)	~5
47	K^+	tBMA	**1a**	100	16 (5.4)	*e* (4.9)	*e* (1.05)	~20
48	K^+	tBMA	**5**	100	16 (6.3)	*e* (7.3)	*e* (1.06)	~40

[a] Homopolymers were quantitatively obtained at the first-stage polymerization in all cases. [b] Yield of the second-stage polymerization. [c] M_n(obsd) values of the block copolymers were determined by using the molecular weight of the homopolymer and the molar ratios of the monomer units in the block copolymer analyzed by ^{1}H NMR. [d] Initiation efficiency in the second-stage polymerization. [e] The initiation efficiency was not quantitative, forming a mixture of homopolymer and block copolymer.

well regulated by the feed molar ratio of both monomers. All SEC curves of the block copolymers showed narrow unimodal peaks and shifted completely toward the higher molecular weight side. These indicate the efficiency of the crossover reaction between the living polymers of Isp and St and **1a**, **3a**, **4a**, and **5** is quantitative to give the well-defined block copolymers in any combination.

With the use of living polymer derived from 2VP or tBMA at the first stage, the further polymerizations of **1a**, **3a**, **4a**, and **5** also proceeded to consume all the monomers and gave polymeric products. However, the initiation efficiency of the second-stage polymerization was not quantitative and varied widely in each of these cases. The only exception was the polymerization of living poly(2VP) with **5**, which gave a well-defined block copolymer in quantitative efficiency. In other cases, all the SEC curves of the polymeric products showed the bimodal peaks consisted of the homopolymers of 2VP or tBMA and the block copolymers having the M_n's much higher than the expected values due to the partial initiation followed by rapid consumption of the second monomers. The efficiency can be estimated to be 5−80% from the SEC analyses, as can be seen in Table 3 (runs 41−48). It is very surprising and noteworthy that even the low nucleophilic enolate anion of poly(tBMA) can initiate the polymerization of styrene derivatives **1a**, **3a**, **4a**, and **5** although the efficiency is only 5−40% in each case. The higher anionic polymerizability (electrophilicity) of these monomers than of styrene is thus evident from the above fact, since it is already known that the living poly(alkyl methacrylate)s have no ability to initiate the anionic polymerization of styrene at all.[11,15]

Next, by changing the addition order of the comonomers, the sequential copolymerization of Isp, St, 2VP, and tBMA was investigated by using the living polymers derived from **1a**, **3a**, **4a**, and **5**. In this case, reactivities (nucleophilicities) of these living polymers can be clarified. As can be seen in Table 4, a series of the well-defined block copolymers of 2VP and tBMA could be quantitatively obtained by the initiation of the anionic living polymers formed from **1a**, **3a**, **4a**, and **5**. For example, the SEC curve of the block copolymer shifted from that of homopoly(**4a**) toward the higher molecular weight side with keeping the narrow MWD after the addition of 2VP, as shown in Figure 2. Similar to this example, all the block copolymers possessed narrow MWDs (M_w/M_n < 1.1) and controlled M_n's as well as the tailored compositions. Accordingly, the crossover polymerizations of 2VP or tBMA readily proceed with the living polymers of ethynylstyrene derivatives in the quantitative efficiencies. These results confidently reconfirm the living character of the propagating carbanions derived from **1a**, **3a**, **4a**, and **5**.

On the other hand, the results using St and Isp as second monomers were complicated. With the use of St, the initiation efficiencies were largely varied from 100 to 5% (Table 4, runs 49−56), although St was completely polymerized with the living polymer of **1a**, **3a**, **4a**, or **5**. Interestingly, only the living poly(**3a**) could initiate the second-stage polymerization of St quantitatively and a well-defined block copolymer was obtained. The low initiation efficiencies (5−10%) of living poly(**1a**) and poly(**5**) clearly suggest the lower nucleophilicities of the propagating carbanions than those of poly(**3a**) (100%) and poly(**4a**) (70%). Figure 3B shows

Table 4. Block Copolymerization of Isp, St, 2VP, and TBMA with Living Polymers Derived from 1a, 3a, 4a, and 5 in THF at −78 °C

run	countercation	1st monomer	2nd monomer	yield,[b] %	block copolymer (homopolymer[a])			initiation efficiency, %[d]
					$10^{-3}M_n$			
					calcd	obsd[c]	M_w/M_n	
49	K^+	**3a**	Isp	100	19 (4.6)	*e* (4.5)	*e* (1.08)	~50
50	K^+	**4a**	Isp	~0	20 (5.9)	*f* (6.1)	*f* (1.06)	0[f]
51	K^+	**1a**	Isp	0	25 (8.9)	*g* (7.6)	*g* (1.07)	0
52	K^+	**5**	Isp	0	35 (7.0)	*g* (5.5)	*g* (1.07)	0
53	K^+	**3a**	St	100	50 (13)	51 (14)	1.15 (1.08)	100
54	K^+	**4a**	St	100	16 (6.5)	*e* (5.7)	*e* (1.06)	~70
55	K^+	**1a**	St	100	25 (11)	*e* (11)	*e* (1.12)	~5
56	K^+	**5**	St	100	16 (5.9)	*e* (4.8)	*e* (1.06)	~10
57	K^+	**3a**	2VP	100	14 (5.1)	13 (4.3)	1.08 (1.07)	100
58	K^+	**4a**	2VP	100	17 (6.4)	15 (5.8)	1.07 (1.06)	100
59	Li^+	**1a**	2VP	100	21 (9.6)	19 (7.1)	1.09 (1.10)	100
60	K^+	**5**	2VP	100	26 (8.2)	24 (7.7)	1.04 (1.05)	100
61	K^+	**3a**	tBMA	100	14 (4.9)	14 (4.9)	1.07 (1.06)	100
62	K^+	**4a**	tBMA	100	15 (5.8)	15 (6.0)	1.08 (1.06)	100
63	K^+	**1a**	tBMA	100	18 (6.2)	16 (5.2)	1.09 (1.06)	100
64	K^+	**5**	tBMA	100	16 (7.3)	16 (7.3)	1.07 (1.08)	100

[a] Homopolymers were quantitatively obtained at the first-stage polymerization in all cases. [b] Yield of the second-stage polymerization. [c] M_n(obsd) values of the block copolymers were determined by using the molecular weight of the homopolymer and the molar ratios of the monomer units in the block copolymer analyzed by ^1H NMR. [d] Initiation efficiency in the second-stage polymerization. [e] The initiation efficiency was not quantitative, forming a mixture of homopolymer and block copolymer. [f] A side reaction occurs during the course of the second-stage polymerization, and the initiation efficiency was quite low. [g] No polymerization proceeded at the second-stage, resulting in a quantitative recovery of the homopolymer of the first monomer.

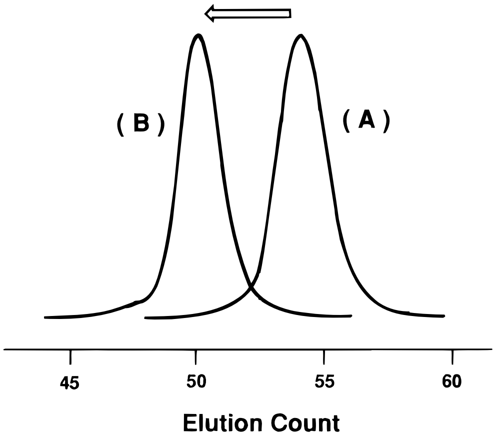


Figure 2. SEC curves of poly(**4a**) at the first-stage polymerization (A) and of poly(2VP-*b*-**4a**-*b*-2VP) obtained at −78 °C (B) (Table 4, run 58): peak A, M_n(obsd) = 5800, M_w/M_n = 1.06; peak B, M_n(obsd) = 15 000, M_w/M_n = 1.07 (the second monomer was added 0.5 h after the first-stage polymerization).

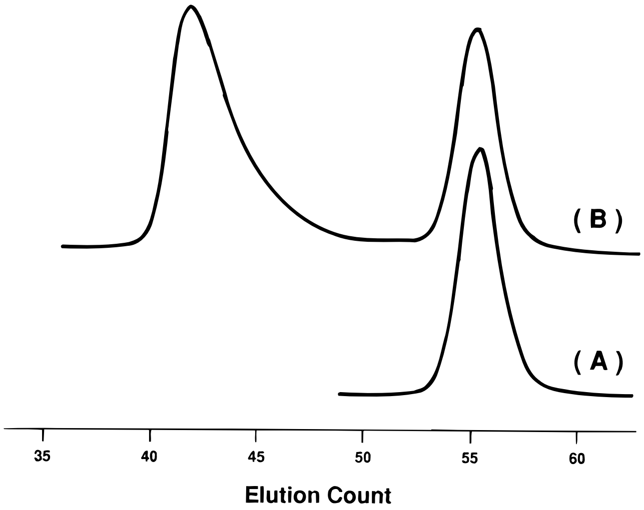


Figure 3. SEC curves of poly(**5**) at the first-stage polymerization (A) and of the copolymerization product after the second-stage polymerization of St in THF at −78 °C for 0.5 h (B) (Table 4, run 56): peak A, M_n(obsd) = 4800, M_w/M_n = 1.06.

an SEC curve in the polymerization of St with living poly(**5**), typical for the slow initiation with rapid consumption of the second monomer by the newly formed polystyryl anion. Less electrophilic Isp monomer was more difficult to polymerize with each of these living polymers. No crossover reactions of Isp occurred with the living poly(**1a**) and poly(**5**) at all and homopolymers of **1a** and **5** were virtually recovered from the reaction mixtures. With the initiation of living poly(**3a**), Isp was completely consumed, resulting in a mixture of the homopoly(**3a**) and block copolymer of the unexpected chain length. The efficiency of the crossover reaction was estimated to be 50% in this case. In the case of living poly(**4a**), initiation of Isp was also achieved, as evident by the color change of the reaction system from yellow to red, but the red color slowly faded with time. Only a few units of isoprene were detected in the products from ^1H NMR analysis. The SEC trace did not shift from the starting homopoly(**4a**) and only showed the broadening of the MWD toward the higher molecular weight region. We speculate that methylene proton abstraction from the $C{\equiv}CCH_2$ moiety of the poly(**4a**) segment rapidly takes place with the newly forming terminal carbanion of polyisoprene before the completion of the second-stage propagation of Isp, since the allylic carbanion ($pK_a = 43$) of the resulting polyisoprene is more basic than the benzylic anion ($pK_a = 41$) of poly(**4a**). The presence of the $C{\equiv}CCH_2$ type pendant group is also a serious problem if one wishes to prepare the block copolymer of **4a** and diene monomers in this sequence. Thus, the lowered nucleophilicity of a series of polystyryl anions derived from **1a**, **3a**, **4a**, and **5** is clearly demonstrated from the initiation efficiencies of the crossover reaction, comparing the fact that anionic living polystyrene itself can quantitatively initiate the further polymerization of Isp.

The results of the sequential block copolymerization are then classified into four categories for easy comparison. They are summarized in Table 5. Our previous results for Isp, St, 2VP, and tBMA[15] are added to

Table 5. Summary of the Results of Block Copolymerization (Crossover Reaction) between Various Monomers and Their Living Polymers[a]

living polymer	monomer (initiation efficiency)							
	Isp	St	**3a**	**4a**	**1a**	**5**	2VP	tBMA
poly(Isp)$^-$	++	++	++	++	++	++	++	++
poly(St)$^-$	++	++	++	++	++	++	++	++
poly(**3a**)$^-$	+(~50)	++	++	na	na	na	++	++
poly(**4a**)$^-$	SR	+(~70)	na	++	na	na	++	++
poly(**1a**)$^-$	−	+(~5)	na	na	++	na	++	++
poly(**5**)$^-$	−	+(~10)	na	na	na	++	++	++
poly(2VP)$^-$	−	SR	+ (~60)	+ (~60)	+ (~80)	++	++	++
poly(tBMA)$^-$	−	−	+ (~5)	+ (~5)	+ (~20)	+ (~40)	−	++

[a] Key: (++) quantitative initiation efficiency resulting in the block copolymers with narrow MWDs ($M_w/M_n < 1.2$); (+) initiation efficiency was not quantitative (5−80%), resulting in a mixture of homopolymer and block copolymer showing a bimodal and broad MWD; (SR) these polymeric products had multimodal and broad MWDs, probably due to the serious side reaction: (−) no reaction between the living polymer and the second monomer occurred, resulting in a quantitative recovery of the homopolymer of the first monomer; (na) not attempted.

these data, although the crossover reactions between **1a**, **3a**, **4a**, and **5** and their living polymers have not been attempted. The symbol (++) shows that a tailored block copolymer having a narrow MWD ($M_w/M_n = 1.03-1.15$), a predicted M_n, and a controlled composition is formed in quantitative yield. The second one (+) indicates that a second-stage polymerization proceeds with a low initiation efficiency (5−80%), generally resulting in a mixture of virtual homopolymer and block copolymer with ill-controlled structure. (SR) indicates that some side reaction occurs after the addition of a second monomer, resulting in formation of complicated products with multimodal and broad MWDs. The last one (−) shows no crossover reaction at the second-stage. From Table 5, one can easily choose the suitable additional order of the comonomers to synthesize a well-defined block copolymer. Living polymers of St and Isp are useful macroinitiators for the polymerization of **1a**, **3a**, **4a**, and **5** but neither living polymer of 2VP nor tBMA is effective. On the other hand, either tBMA or 2VP can be added to the living polymer of **1a**, **3a**, **4a**, and **5** as a second monomer to prepare the block copolymers of well-regulated chain structures. Only two combinations of **3a**/St and **5**/2VP enable one to give tailored block copolymers regardless of a sequential additional order of two comonomers, indicating that the reactivities of **3a** and **5** are comparable to those of St and 2VP, respectively.

More interestingly, the relative reactivities of monomers and the living polymers are clearly evaluated from Table 5. The monomer reactivity order of **1a**, **3a**, **4a**, and **5** increases as follows: Isp = St < **3a** ~ **4a** < **1a** < **5** = 2VP < tBMA. On the other hand, the relative nucleophilicity of the propagating carbanions of living polymers can be expressed in the following order: living poly(Isp) ~ living polystyrene > living poly(**3a**) > living poly(**4a**) > living poly(**1a**) ~ living poly(**5**) ~ living poly(2VP) > living poly(tBMA). As expected, the less reactive monomers produce the more reactive living polymers and vice versa.

We have recently reported the results of block copolymerization of *para*-substituted styrenes containing a series of electron-withdrawing groups[16] such as *N,N*-dialkylamide,[17] *N*-alkylimine,[18] *N*-arylimine,[19] oxazoline,[20] *tert*-butyl ester,[21] *N,N*-dialkylsulfomamide,[22] and cyano groups.[23] From the results of the sequential block copolymerization,[15] the enhanced anionic polymerizability of these monomers and the lowered nucleophilicity of the propagating carbanions are clearly demonstrated due to the strong electron-withdrawing effects of the substituents. The resonance stabilization of the terminal benzylic carbanion is also attained by the contribution of the extended π-conjugation system, including the C=O, C=N, S=O, and C≡N linkages.[12] The observed reactivity of **3a**, **4a**, **1**, and **5** also suggests the effect of the electron-withdrawing C≡C substituents, resulting in the enhanced anionic polymerizability of monomers and in the reduced nucleophilicity of the living polymers. The electron-withdrawing natures of the carbon−carbon triple bond such as C≡CH, C≡CMe, and C≡CPh moieties are supported from the reported Hammett σ_p values as 0.23, 0.03, and 0.16, respectively.[24] In addition to this, the C≡C bond attached to the styrene frameworks in **3a**, **4a**, **1**, and **5** also provides an above-mentioned π-resonance stabilization for the resultant active chain ends.[12]

As another useful parameter, we previously clarified the correlation between the reactivities of the *para*-substituted styrenes containing the electron-withdrawing groups and their living polymers with the ^{13}C NMR chemical shifts of the β-carbon of the vinyl groups.[15,25] The monomers showing the downfield chemical shifts of the β-carbons had a higher anionic polymerizability, and the resulting living polymer showed a lower nucleophilicity, both of which were induced by the electron-withdrawing character of the substituents. In other words, the anionic polymerizability of the styrene monomers can be estimated and ranked in the order of reactivity from the ^{13}C NMR chemical shifts.[15] Actually, the β-carbon chemical shifts for **3a**, **4a**, **1a**, and **5** appeared at downfield resonances of 114.2, 114.3, 114.8, and 114.8 ppm, respectively, while that of styrene itself is at 113.8 ppm. The order of these ^{13}C NMR chemical shifts is consistent with the observed relative reactivity of a series of β-substituted ethynylstyrenes and the observed nucleophilicity of the living polymers, as shown above. The downshifted chemical shifts also indicate the electron-withdrawing characters of the β-substituted ethynyl substituents such as C≡CBu^t, C≡CBu, C≡C-SiMe$_3$, and C≡CPh and clearly show the ranking of the substituent effects. By changing the β-substituents on the ethynyl group, we can vary to a certain extent the anionic polymerizability of ethynylstyrene derivatives from the level of St (=**3a**) to a much higher one comparable to 2VP (=**5**). It should be noted here that the very small difference in the β-carbon chemical shifts ($\Delta\delta = 0.4-1.0$) reflected the apparent relative reactivity of the employed monomers, supporting the effectiveness of this method. Thus, we have successfully reconfirmed the availability of ^{13}C NMR chemical shifts of styrene derivatives to evaluate the reactivities of the monomers and the resulting living polymers.

Table 6. Solubility of Poly(3−5) and Related Polymers[a]

solvent	polymer									polystyrene
	poly(**3a**)	poly(**3b**)	poly(**3c**)	poly(**4a**)	poly(**4b**)	poly(**4c**)	poly(**5**)	poly(**1a**)	poly(**2**)	
hexane	S	S	S	S	S	S	I	S	S	I
benzene	S	S	S	S	S	S	S	S	S	S
diethyl ether	S	S	S	S	S	S	I	S	S	S
ethyl acetate	S	S	S	S	S	S	S	S	S	S
chloroform	S	S	S	S	S	S	S	S	S	S
acetone	S	S	S	S	S	S	S	S	S	S
1,4-dioxane	S	S	S	S	S	S	S	S	S	S
THF	S	S	S	S	S	S	S	S	S	S
DMF	S	S	I	S	S	I	S	S	S	S
dimethyl sulfoxide	I	I	I	I	I	I	I	I	I	I
ethanol	I	I	I	I	I	I	I	I	I	I
methanol	I	I	I	I	I	I	I	I	I	I
water	I	I	I	I	I	I	I	I	I	I

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

Table 7. Glass Transition Temperatures (T_g) of Poly(3−5)s[a]

polymer	$10^{-3}M_n$(obsd)	M_w/M_n	T_g, °C
poly(**3a**)	9.7	1.07	169
poly(**3a**)	24	1.05	174
poly(**3b**)	14	1.14	113
poly(**3c**)	9.7	1.14	109
poly(**4a**)	10	1.07	75
poly(**4a**)	20	1.10	75
poly(**4b**)	12	1.09	35
poly(**4b**)	21	1.14	40
poly(**4c**)	11	1.10	33
poly(**4c**)	17	1.13	37
poly(**5**)	17	1.09	163
poly(**1a**)	21	1.13	165
poly(**2**)	11	1.09	48

[a] T_g was measured in the second heating scan at a rate of 20 °C/min.

Solubility and Glass Transition Temperatures of the Polymers. All the resulting polymers obtained in this study were off-white powders and were stable in air at least for several months regardless of the substituents and the substituent positions. Table 6 summarizes the solubility of the poly(**3**−**5**)s and the related polymers. In particular, the poly(**3**)s and poly(**4**)s were readily soluble in a wide range of organic solvents and both showed similar solubilities in most solvents. A small difference in the solubility was observed in terms of the substituent position. DMF was a useful polar solvent for *para*- and *meta*-substituted polymers, but it was ineffective for the polymers having *ortho* substituents. The solubility of poly(**5**) having the phenylethynyl substituent was slightly different from the solubilities of poly(**3**)s and poly(**4**)s.

Table 7 shows the glass transition temperatures (T_g's) of the resulting polymers measured by differential scanning calorimetry (DSC). In general, the *para*-substituted polymers presented much higher T_g values compared with those of the *meta* and *ortho* isomers. Apparently, the T_g's of poly(**4**)s were lower than the corresponding poly(**3**) analogues, probably due to the high flexibility of the *n*-butylethynyl side chain on the repeating units, compared with the *tert*-butylethynyl moiety. As expected, poly(**5**) showed a high T_g value that was comparable to those of poly(**1a**) and poly(**3a**). Thus, one can easily vary the T_g's of polystyrenes bearing the C≡CR functionalities from 30 to 170 °C by only changing the C≡CR substituents and/or the substituent position.

In conclusion, we succeed in the living anionic polymerizations of novel functional monomers, (*tert*-butylethynyl)styrenes (**3**s), (butylethynyl)styrenes (**4**s), and 4-(phenylethynyl)styrene (**5**), to give well-defined polymers with narrow MWDs and tailored M_n's. The polymerization conditions such as temperature and solvent are important for realizing the controlled anionic polymerization of these monomers. The enhanced anionic polymerizability of **3**−**5** as styrene derivatives, stimulated with the electron-withdrawing C≡CR groups, is clarified from the results of the sequential block copolymerization and is actually ranked between those of St and 2VP. The difference in the polymerizability of **3**−**5** can be well accounted for by the ^{13}C NMR chemical shifts of the vinyl β-carbons of the monomers.

Experimental Section

Materials. Bromostyrenes were synthesized according to the reported procedure.[23] Monomer **1a** was synthesized from 4-bromostyrene and (trimethylsilyl)acetylene according to our previous report.[7] Commercially available *tert*-butylacetylene, 1-hexyne, phenylacetylene, triphenylphosphine, bis(triphenylphosphine)palladium(II) chloride, and copper(I) iodide were used without purification. Diethylamine, triethylamine, and piperidine were dried over CaH_2 and distilled under nitrogen. St, α-methylstyrene, and Isp were distilled over CaH_2 and further purified by distillation in the presence of benzylmagnesium chloride (THF solution) on a vacuum line. 2VP and tBMA were distilled over CaH_2 and subsequently distilled from CaH_2 or trioctylaluminum,[26] respectively, on the vacuum line. THF used for polymerization was refluxed over sodium wire for 5 h and distilled from $LiAlH_4$ and finally distilled through the vacuum line from the sodium naphthalenide solution.

Initiators. Commercially available *s*-BuLi (1.0 M cyclohexane solution) and *n*-BuLi (1.6 M hexane solution) were diluted with *n*-heptane and used for the anionic polymerization. Potassium naphthalenide was prepared from naphthalene and potassium metal in dry THF at room temperature. Cumylpotassium was prepared by the reaction of cumyl methyl ether and sodium−potassium alloy in THF at room temperature. (Diphenylmethyl)potassium was prepared by the reaction of potassium naphthalenide and a 1.5 molar excess of diphenylmethane in THF at room temperature for 3 days. Oligo(α-methylstyryl)lithium and -dipotassium were freshly prepared just prior to the polymerization from *s*-BuLi or potassium naphthalenide and a 2−4 M quantity of α-methylstyrene at 20 °C for 1 min and then at −78 °C for 10 min. These initiators were stored at −30 °C in ampules equipped with breakseals. The concentration of initiators was determined by colorimetric titration with standardized 1-octanol in a sealed reactor under vacuum.[27]

4-(3,3-Dimethyl-1-butynyl)styrene (3a).[1] Nitrogen was bubbled into a mixture of 4-bromostyrene (9.29 g, 50.8 mmol), *tert*-butylacetylene (5.65 g, 68.8 mmol), copper(I) iodide (0.10 g, 0.53 mmol), triphenylphosphine (0.21 g, 0.80 mmol), and dry diethylamine (80 mL) at room temperature for 1 h. Bis-

(triphenylphosphine)palladium(II) chloride (0.22 g, 0.31 mmol) was added, and the mixture was stirred at 38 °C for 100 h under nitrogen. The reaction mixture was filtered and concentrated under vacuum. The residue was diluted with hexane (150 mL) and washed with 2 N HCl and with water. The organic layer was dried over anhydrous Na_2SO_4 and concentrated by a rotary evaporator. The residue was purified by column chromatography (silica gel, hexane), and vacuum distillation gave a colorless liquid of **3a** (4.75 g, 25.8 mmol, 51%, bp 80−82 °C/2 mmHg): ^{1}H NMR ($CDCl_3$, 300 MHz) $\delta = 1.31$ (s, 9H, CH_3), 5.25 and 5.73 (2d, 2H, $J = 11$ and 18 Hz, $CH_2{=}$), 6.67 (dd, 1H, $-CH{=}$), 7.27−7.37 (m, 4H, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz) $\delta = 28.1$ ($\mathit{C}CH_3$), 31.1 (CH_3), 79.1 ($Ar{-}C{\equiv}\mathit{C}$), 99.3 ($Ar{-}\mathit{C}{\equiv}C$), 114.2 ($CH_2{=}$), 123.5 (Ar, C4), 126.0 (Ar, C2), 131.8 (Ar, C3), 136.5 ($-CH{=}$), 136.7 (Ar, C1); IR (KBr, cm^{-1}) 908, 987, 1111, 1205, 1290, 1362, 1404, 1458, 1475, 1508, 1628, 2235 ($C{\equiv}C$), 2968. Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.06; H, 8.89.

3-(3,3-Dimethyl-1-butynyl)styrene (3b).[1] The same procedure was followed as described above for **3a** using 3-bromostyrene (25.2 g, 138 mmol), *tert*-butylacetylene (15.14 g, 184 mmol), copper(I) iodide (0.26 g, 1.8 mmol), triphenylphosphine (0.59 g, 2.2 mmol), dry diethylamine (220 mL), and bis(triphenylphosphine)palladium(II) chloride (0.58 g, 0.83 mmol). The coupling reaction was continued at 55 °C for 44 h. Distillation in vacuo gave a colorless liquid of **3b** (18.31 g, 99.5 mmol, 72%, bp 79−82 °C/0.7 mmHg): ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 1.32$ (s, 9H, CH_3), 5.24 and 5.74 (2d, 2H, $J = 11$ and 18 Hz, $CH_2{=}$), 6.65 (dd, 1H, $-CH{=}$), 7.26−7.43 (m, 4H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 28.0$ ($\mathit{C}CH_3$), 31.1 (CH_3), 79.0 ($Ar{-}C{\equiv}\mathit{C}$), 98.6 ($Ar{-}\mathit{C}{\equiv}C$), 114.4 ($CH_2{=}$), 124.4 (Ar, C3), 125.4 (Ar, C6), 128.4 (Ar, C5), 129.5 (Ar, C4), 131.0 (Ar, C2), 136.4 ($-CH{=}$), 137.6 (Ar, C1); IR (KBr, cm^{-1}) 798, 849, 894, 910, 1201, 1294, 1362, 1458, 1473, 1576, 1595, 1631, 2216 ($C{\equiv}C$), 2966. Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.25; H, 8.61.

2-(3,3-Dimethyl-1-butynyl)styrene (3c).[1] The same procedure was followed as described above for **3a** using 2-bromostyrene (25.38 g, 139 mmol), *tert*-butylacetylene (15.28 g, 186 mmol), copper(I) iodide (0.28 g, 1.5 mmol), triphenylphosphine (0.60 g, 2.3 mmol), dry diethylamine (220 mL), and bis(triphenylphosphine)palladium(II) chloride (0.58 g, 0.83 mmol). The coupling reaction was continued at 55 °C for 122 h. Distillation in vacuo gave a colorless liquid of **3c** (7.71 g, 41.9 mmol, 30%, bp 71−73 °C/0.6 mmHg): ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 1.34$ (s, 9H, CH_3), 5.32 and 5.79 (2d, 2H, $J = 11$ and 18 Hz, $CH_2{=}$), 7.14−7.54 (m, 5H, $-CH{=}$ and Ar); ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 28.2$ ($\mathit{C}CH_3$), 31.1 (CH_3), 81.2 ($Ar{-}C{\equiv}\mathit{C}$), 103.5 ($Ar{-}\mathit{C}{\equiv}C$), 115.0 ($CH_2{=}$), 122.8 (Ar, C2), 124.5 (Ar, C6), 127.4 (Ar, C4), 127.6 (Ar, C5), 132.5 (Ar, C3), 135.2 ($-CH{=}$), 138.7 (Ar, C1); IR (KBr, cm^{-1}) 912, 991, 1205, 1273, 1291, 1362, 1448, 1458, 1473, 1628, 2237 ($C{\equiv}C$), 2966. Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 88.47; H, 8.82.

4-(1-Hexynyl)styrene (4a).[2] The same procedure was followed as described above for **3a** using 4-bromostyrene (9.29 g, 50.8 mmol), 1-hexyne (5.00 g, 60.9 mmol), copper(I) iodide (0.10 g, 0.53 mmol), triphenylphosphine (0.21 g, 0.80 mmol), dry triethylamine (75 mL), and bis(triphenylphosphine)palladium(II) chloride (0.22 g, 0.31 mmol). The coupling reaction was continued at 70 °C for 8.5 h. Distillation in vacuo gave a colorless liquid of **4a** (6.89 g, 37.4 mmol, 74%, bp 115−120 °C/2 mmHg): ^{1}H NMR ($CDCl_3$, 300 MHz) $\delta = 0.94$ (t, 3H, $J = 7$ Hz, CH_3), 1.41−1.64 (m, 4H, $C\mathit{H}_2C\mathit{H}_2CH_3$), 2.41 (t, 2H, $J = 7$ Hz, $\equiv CCH_2$), 5.24 and 5.72 (2d, 2H, $J = 11$ and 17 Hz, $CH_2{=}$), 6.67 (dd, 1H, $-CH{=}$), 7.27−7.38 (m, 4H, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz) $\delta = 13.7$ (CH_3), 19.3 ($\equiv C\mathit{C}H_2$), 22.1 ($\mathit{C}H_2CH_3$), 30.9 ($\equiv CCH_2\mathit{C}H_2$), 80.6 ($Ar{-}C{\equiv}\mathit{C}$), 91.2 ($Ar{-}\mathit{C}{\equiv}C$), 114.3 ($CH_2{=}$), 123.6 (Ar, C4), 126.1 (Ar, C2), 131.8 (Ar, C3), 136.4 ($-CH{=}$), 136.7 (Ar, C1); IR (KBr, cm^{-1}) 908, 989, 1111, 1329 1402, 1458, 1506, 1628, 2229 ($C{\equiv}C$), 2956. Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.27; H, 8.77.

3-(1-Hexynyl)styrene (4b).[2] The same procedure was followed as described above for **3a** using 3-bromostyrene (15.0 g, 82.0 mmol), 1-hexyne (10.00 g, 122 mmol), copper(I) iodide (0.16 g, 0.84 mmol), triphenylphosphine (0.34 g, 1.30 mmol), dry triethylamine (121 mL), and bis(triphenylphosphine)palladium(II) chloride (0.53 g, 0.75 mmol). The coupling reaction was continued at 70 °C for 46 h. Distillation in vacuo gave a colorless liquid of **4b** (6.89 g, 37.4 mmol, 77%, bp 86−89 °C/3 mmHg): ^{1}H NMR ($CDCl_3$, 90 MHz) $\delta = 0.94$ (t, 3H, $J = 7$ Hz, CH_3), 1.27−1.73 (m, 4H, $C\mathit{H}_2C\mathit{H}_2CH_3$), 2.41 (t, 2H, $J = 7$ Hz, $\equiv CCH_2$), 5.24 and 5.72 (2d, 2H, $J = 11$ and 18 Hz, $CH_2{=}$), 6.66 (dd, 1H, $-CH{=}$), 7.23−7.44 (m, 4H, Ar); ^{13}C NMR ($CDCl_3$, 22.5 MHz) $\delta = 13.7$ (CH_3), 19.2 ($\equiv C\mathit{C}H_2$), 22.1 ($\mathit{C}H_2$-CH_3), 30.9 ($\equiv CCH_2\mathit{C}H_2$), 80.5 ($Ar{-}C{\equiv}\mathit{C}$), 90.5 ($Ar{-}\mathit{C}{\equiv}C$), 114.4 ($CH_2{=}$), 124.4 (Ar, C3), 125.4 (Ar, C6), 128.4 (Ar, C5), 129.4 (Ar, C2), 130.9 (Ar, C4), 136.3 ($-CH{=}$), 137.7 (Ar, C1); IR (KBr, cm^{-1}) 894, 911, 988, 1328, 1429, 1466, 1478, 1572, 1596, 2228 ($C{\equiv}C$), 2872, 2958. Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 90.95; H, 8.86.

2-(1-Hexynyl)styrene (4c).[2] The same procedure was followed as described above for **3a** using 2-bromostyrene (15.0 g, 82.0 mmol), 1-hexyne (10.00 g, 122 mmol), copper(I) iodide (0.16 g, 0.84 mmol), triphenylphosphine (0.34 g, 1.30 mmol), dry triethylamine (121 mL), and bis(triphenylphosphine)palladium(II) chloride (0.53 g, 0.75 mmol). The coupling reaction was continued at 70 °C for 46 h. Distillation in vacuo gave a colorless liquid of **4c** (7.40 g, 40.2 mmol, 49%, bp 86−89 °C/3 mmHg): ^{1}H NMR ($CDCl_3$, 90 MHz) $\delta = 0.95$ (t, 3H, $J = 7$ Hz, CH_3), 1.47−1.62 (m, 4H, $C\mathit{H}_2C\mathit{H}_2CH_3$), 2.46 (t, 2H, $J = 7$ Hz, $\equiv CCH_2$), 5.31 and 5.77 (2d, 2H, $J = 11$ and 18 Hz, $CH_2{=}$), 7.13−7.60 (m, 5H, $-CH{=}$ and Ar); ^{13}C NMR ($CDCl_3$, 22.5 MHz) $\delta = 13.7$ (CH_3), 19.4 ($\equiv C\mathit{C}H_2$), 22.1 ($\mathit{C}H_2CH_3$), 31.0 ($\equiv CCH_2\mathit{C}H_2$), 79.0 ($Ar{-}C{\equiv}\mathit{C}$), 95.3 ($Ar{-}\mathit{C}{\equiv}C$), 115.0 ($CH_2{=}$), 123.0 (Ar, C2), 124.5 (Ar, C6), 127.4 and 127.7 (Ar, C4 and C5), 132.6 (Ar, C3), 135.3 ($-CH{=}$), 138.9 (Ar, C1); IR (KBr, cm^{-1}) 912, 993, 1100, 1328, 1429, 1448, 1478, 1626, 2226 ($C{\equiv}C$), 2931. Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.29; H, 8.87.

4-(Phenylethynyl)styrene (5). The same procedure was followed as described above for **3a** using 4-bromostyrene (8.15 g, 44.5 mmol), phenylacetylene (5.00 g, 49.0 mmol), copper(I) iodide (0.085 g, 0.45 mmol), triphenylphosphine (0.19 g, 0.71 mmol), dry piperidine (54 mL), and bis(triphenylphosphine)palladium(II) chloride (0.19 g, 0.27 mmol). The coupling reaction was continued at 90 °C for 3 h and at 50 °C for 7 h. Recrystallizations from methanol and hexane gave a white solid of **5** (7.28 g, 35.7 mmol, 80%, mp 81.3−82.0 °C): ^{1}H NMR ($CDCl_3$, 90 MHz) $\delta = 5.29$ and 5.77 (2d, 2H, $J = 11$ and 18 Hz, $CH_2{=}$), 6.72 (dd, 1H, $-CH{=}$), 7.30−7.60 (m, 4H, Ar); ^{13}C NMR ($CDCl_3$, 22.5 MHz) $\delta = 89.5$ ($Ph{-}\mathit{C}{\equiv}C$), 90.2 ($Ph{-}C{\equiv}\mathit{C}$), 114.8 ($CH_2{=}$), 122.7 (Ar, C4), 123.4 (Ar′, C1), 126.2 (Ar, C2), 128.3 (Ar′, C4), 128.4 (Ar′, C3), 131.7 (Ar, C3), 131.9 (Ar′, C2), 136.3 ($-CH{=}$), 137.8 (Ar, C1); IR (KBr, cm^{-1}) 845, 904, 995, 1443, 1509, 1624, 2218 ($C{\equiv}C$), 3054. Anal. Calcd for $C_{16}H_{12}$: C, 94.08; H, 5.92. Found: C, 93.85; H, 5.89.

Monomer Purification. The liquid monomers, **3a**−**3c** and **4a**−**4c**, were purified by fractional distillations over CaH_2 in vacuo and sealed off under a degassed condition in an apparatus equipped with a breakseal. Phenylmagnesium chloride (5.0 mL, 0.20 M in THF) was added to the monomer (40 mmol) to remove impurities in the monomer, and the mixture was stirred for 0.5 h at room temperature. It was distilled under vacuum conditions into an ampule fitted with breakseals and diluted with dry THF. For the polymerization in benzene, **4a** was distilled from Bu_2Mg solution in heptane and diluted with dry benzene. The solid monomer, **5**, was purified by the recrystallizations from methanol and hexane and finally distilled from CaH_2 under high vacuum conditions. The resulting monomer solutions (ca. 0.5 M) were stored at −30 °C until ready to use for the polymerization.

Polymerization Procedures. All polymerizations of **3**−**5** were carried out under high vacuum conditions in the all-glass apparatus equipped with breakseals as previously reported.[27] The polymerization was quenched with degassed methanol, and the reaction mixture was poured into a large excess of methanol to precipitate a polymer. Polymers collected by filtration were purified by reprecipitations twice with a THF−methanol system and by freeze-drying from the benzene solution. The resultant poly(**3**−**5**)s were then characterized by ^{1}H and ^{13}C NMR and IR spectroscopy. The following is the full list.

Poly(3a): ^{1}H NMR ($\mathrm{CDCl_3}$, 300 MHz) $\delta = 1.33$ (s, 9H, $\mathrm{CH_3}$), 0.9−1.9 (m, 3H, $\mathrm{CH_2CH}$), 6.2−7.3 (m, 4H, Ar); ^{13}C NMR ($\mathrm{CDCl_3}$, 75 MHz) $\delta = 28.4$ ($\mathit{C}\mathrm{CH_3}$), 31.6 ($\mathrm{CH_3}$), 40−43 ($\mathrm{CH_2CH}$), 79.6 ($\mathrm{Ar{-}C{\equiv}}\mathit{C}$), 98.1 ($\mathrm{Ar{-}}\mathit{C}\mathrm{{\equiv}C}$), 121.8 (Ar, C4), 127.8 (Ar, C2), 131.9 (Ar, C3), 144.6 (Ar, C1); IR (KBr, cm^{-1}) 833, 1203, 1292, 1362, 1451, 1475, 1501, 2237 ($\mathrm{C{\equiv}C}$), 2968.

Poly(3b): ^{1}H NMR ($\mathrm{CDCl_3}$, 400 MHz) $\delta = 1.32$ (s, 9H, $\mathrm{CH_3}$), 0.6−2.2 (m, 3H, $\mathrm{CH_2CH}$), 5.9−7.5 (m, 4H, Ar); ^{13}C NMR ($\mathrm{CDCl_3}$, 100 MHz) $\delta = 28.0$ ($\mathit{C}\mathrm{CH_3}$), 31.3 ($\mathrm{CH_3}$), 39−45 ($\mathrm{CH_2CH}$), 79.6 ($\mathrm{Ar{-}C{\equiv}}\mathit{C}$), 97.8 ($\mathrm{Ar{-}}\mathit{C}\mathrm{{\equiv}C}$), 123.9 (Ar, C3), 128.0 (Ar, C6), 129.5 (Ar, C4 and C5), 130.6 (Ar, C2), 145.1 (Ar, C1); IR (KBr, cm^{-1}) 793, 893, 1219, 1294, 1362, 1456, 1473, 1597, 2220 ($\mathrm{C{\equiv}C}$), 2970.

Poly(3c): ^{1}H NMR ($\mathrm{CDCl_3}$, 400 MHz) $\delta = 1.34$ (s, 9H, $\mathrm{CH_3}$), 0.6−3.2 (m, 3H, $\mathrm{CH_2CH}$), 6.2−7.4 (m, 4H, Ar); ^{13}C NMR ($\mathrm{CDCl_3}$, 100 MHz) $\delta = 27.9$ ($\mathit{C}\mathrm{CH_3}$), 31.1 ($\mathrm{CH_3}$), 35−37 ($\mathrm{CH_2CH}$), 78.0 ($\mathrm{Ar{-}C{\equiv}}\mathit{C}$), 100.8 ($\mathrm{Ar{-}}\mathit{C}\mathrm{{\equiv}C}$), 123.4 (Ar, C2), 124.6 (Ar, C6), 126.8 (Ar, C4 and C5), 132.8 (Ar, C3), 147.6 (Ar, C1); IR (KBr, cm^{-1}) 1203, 1297, 1362, 1444, 1475, 2235 ($\mathrm{C{\equiv}C}$), 2968.

Poly(4a): ^{1}H NMR ($\mathrm{CDCl_3}$, 300 MHz) $\delta = 0.95$ (s, 3H, $\mathrm{CH_3}$), 1.1−1.9 (m, 7H, $\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}$ and $\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 2.40 (s, 2H, $\mathrm{{\equiv}CCH_2}$), 6.2−7.3 (m, 4H, Ar); ^{13}C NMR ($\mathrm{CDCl_3}$, 75 MHz) $\delta =$ 13.7 ($\mathrm{CH_3}$), 19.3 ($\mathrm{{\equiv}C}\mathit{C}\mathrm{H_2}$), 22.2 ($\mathit{C}\mathrm{H_2CH_3}$), 31.2 ($\mathrm{{\equiv}CCH_2}\mathit{C}\mathrm{H_2}$), 81.0 ($\mathrm{Ar{-}C{\equiv}}\mathit{C}$), 89.5 ($\mathrm{Ar{-}}\mathit{C}\mathrm{{\equiv}C}$), 121.7 (Ar, C4), 127.6 (Ar, C2), 131.5 (Ar, C3), 144.4 (Ar, C1); IR (KBr, cm^{-1}) 758, 833, 1107, 1217, 1329, 1454, 1504, 2229 ($\mathrm{C{\equiv}C}$), 2956.

Poly(4b): ^{1}H NMR ($\mathrm{CDCl_3}$, 300 MHz) $\delta = 0.93$ (s, 3H, $\mathrm{CH_3}$), 1.1−2.2 (m, 7H, $\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}$ and $\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 2.37 (s, 2H, $\mathrm{{\equiv}CCH_2}$), 6.2−7.3 (m, 4H, Ar); ^{13}C NMR ($\mathrm{CDCl_3}$, 75 MHz) $\delta =$ 13.8 ($\mathrm{CH_3}$), 19.2 ($\mathrm{{\equiv}C}\mathit{C}\mathrm{H_2}$), 22.2 ($\mathit{C}\mathrm{H_2CH_3}$), 31.0 ($\mathrm{{\equiv}CCH_2}\mathit{C}\mathrm{H_2}$), 81.0 ($\mathrm{Ar{-}C{\equiv}}\mathit{C}$), 89.7 ($\mathrm{Ar{-}}\mathit{C}\mathrm{{\equiv}C}$), 123.8 (Ar, C3), 126−131 (Ar, C6, C5, C2, and C4), 145.0 (Ar, C1); IR (KBr, cm^{-1}) 792, 893, 1429, 1481, 1599, 2228 ($\mathrm{C{\equiv}C}$), 2931.

Poly(4c): ^{1}H NMR ($\mathrm{CDCl_3}$, 90 MHz) $\delta = 0.82$ (s, 3H, $\mathrm{CH_3}$), 0.9 (m, 7H, $\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}$ and $\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 2.66 (s, 2H, $\mathrm{{\equiv}CCH_2}$), 6.5−7.3 (m, 4H, Ar); ^{13}C NMR ($\mathrm{CDCl_3}$, 22.5 MHz) $\delta = 13.7$ ($\mathrm{CH_3}$), 19.2 ($\mathrm{{\equiv}C}\mathit{C}\mathrm{H_2}$), 22.1 ($\mathit{C}\mathrm{H_2CH_3}$), 30.9 ($\mathrm{{\equiv}CCH_2}\mathit{C}\mathrm{H_2}$), 79.1 ($\mathrm{Ar{-}C{\equiv}}\mathit{C}$), 92.8 ($\mathrm{Ar{-}}\mathit{C}\mathrm{{\equiv}C}$), 123.4 (Ar, C2), 124.5 (Ar, C6), 126.7 (Ar, C4 and C5), 131.7 (Ar, C3), 148.4 (Ar, C1); IR (KBr, cm^{-1}) 751, 942, 1029, 1104, 1192, 1378, 1445, 1484, 2228 ($\mathrm{C{\equiv}C}$), 2933.

Poly(5): ^{1}H NMR ($\mathrm{CDCl_3}$, 90 MHz) $\delta = 1.0{-}2.2$ ($\mathrm{CH_2CH}$), 6.3−7.6 (m, 9H, Ar); ^{13}C NMR ($\mathrm{CDCl_3}$, 22.5 MHz) $\delta = 40{-}44$ ($\mathrm{CH_2CH}$), 89.7 ($\mathrm{Ph{-}}\mathit{C}\mathrm{{\equiv}C}$), 91.6 ($\mathrm{Ph{-}C{\equiv}}\mathit{C}$), 120.9 (Ar, C4), 123.6 (Ar′, C1), 128.3 (Ar, C2, Ar′, C3 and C4), 131.7 (Ar, C3 and Ar′, C2), 145.8 (Ar, C1); IR (KBr, cm^{-1}) 753, 831, 1443, 1509, 1596, 2214 ($\mathrm{C{\equiv}C}$), 2921.

Block Copolymerization. The first-stage polymerizations of **1a**, **3a**, **4a**, and **5** were carried out to prepare their living polymers with cumylpotassium or potassium naphthalenide in THF at −78 °C for 0.5 h. The second-stage polymerizations of **1a**, **3a**, **4a**, and **5** were similarly performed with the living polymers of Isp, St, 2VP, and tBMA at −78 °C for 0.5 h. Isp, St, 2VP, and tBMA were polymerized to complete the propagation in THF at −78 °C for 3, 0.5, 3, and 2 h, respectively. Potassium naphthalenide was used for the homopolymerizations of Isp and St. In the case of 2VP, cumylpotassium was the initiator. The first-stage polymerization of tBMA was initiated with (diphenylmethyl)potassium.

Measurements. Infrared spectra (KBr disk) were measured on a JEOL JIR-AQS20M FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (90 MHz ^{1}H and 22.5 MHz ^{13}C) or a JNM-EX400 (400 MHz ^{1}H and 100 MHz ^{13}C) or a Bruker DPX300S (300 MHz ^{1}H and 75 MHz ^{13}C) in $\mathrm{CDCl_3}$. Chemical shifts were reported in ppm downfield relative to tetramethylsilane (δ 0) for ^{1}H NMR and to $\mathrm{CDCl_3}$ (δ 77.1) for ^{13}C NMR as standards. Vapor pressure osmometry (VPO) measurements for M_n determination were made with a Corona 117 instrument in benzene. Size exclusion chromatograms (SEC) for MWD determination were obtained in THF (1.0 mL min^{-1}) at 40 °C with a TOSOH HLC-8020 instrument equipped with three polystyrene gel columns (TOSOH G5000H$_\mathrm{XL}$, G4000H$_\mathrm{XL}$, and G3000H$_\mathrm{XL}$) with ultraviolet (254 nm) and refractive index detectors. The glass transition temperature (T_g) was measured by differential scanning calorimetry using a Seiko Instruments SSC/5200. The samples were first heated to 200 °C, cooled rapidly to room temperature, and then scanned again at a rate of 20 °C min^{-1}.

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