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Anionic Polymerization of Monomers Containing Functional Groups. 6. Anionic Block Copolymerization of Styrene Derivatives Para-Substituted with Electron-Withdrawing Groups

Takashi Ishizone, Akira Hirao,* and Seiichi Nakahama*

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

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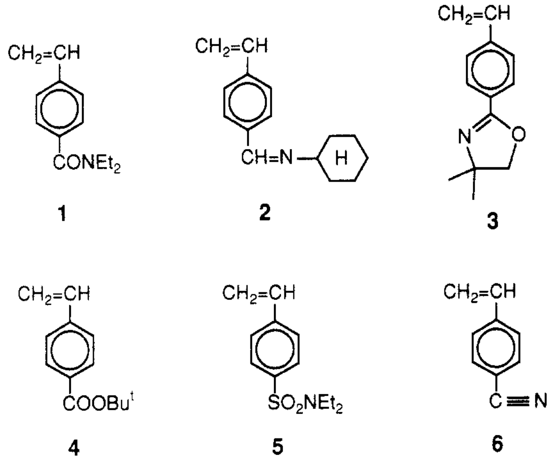
ABSTRACT: The anionic block copolymerizations between six styrene derivatives para-substituted with electron-withdrawing groups and four conventional comonomers (isoprene, styrene, 2-vinylpyridine (2VP), and *tert*-butyl methacrylate (tBMA)) were mainly carried out with oligo(α-methylstyryl)dipotassium in tetrahydrofuran (THF) at -78 °C by sequential addition of two monomers. The six styrene monomers employed were *N,N*-diethyl-4-vinylbenzamide (**1**), *N*-(4-vinylbenzylidene)cyclohexylamine (**2**), 2-(vinylphenyl)-4,4-dimethyl-2-oxazoline (**3**), *tert*-butyl 4-vinylbenzoate (**4**), *N,N*-diethyl-4-vinylbenzenesulfonamide (**5**), and 4-cyanostyrene (**6**). From the analyses of the copolymerization products, the results of crossover reactions were classified into four categories as follows: (a) successful synthesis of a block copolymer with a narrow molecular weight distribution and a controlled segment composition, (b) synthesis of a block copolymer having a relatively broad molecular weight distribution, (c) examples proceeding with a low initiation efficiency and/or including some side reactions at the second-stage polymerization, and (d) no polymerization at the second stage. From the results, higher reactivities of **1**-**6** and lower nucleophilicities of their living polymers have been demonstrated, compared with those of styrene and living polystyrene. Both of these characteristic features may be accounted for by the strong electron-withdrawing effects of the substituents of **1**-**6**. For example, the polymerizations of **1**-**6** were initiated with the low nucleophilic living polymers derived from 2VP and tBMA. By contrast, the living polymers derived from **1**-**6** were ineffective in initiating further polymerizations of isoprene and styrene. Thus, the anionic polymerizability of **1**-**6** can be evaluated as being between those of 2VP and alkyl methacrylates. The reactivity ranking of **1**-**6** can also be estimated from the chemical shifts of the vinyl β-carbons for these para-substituted styrenes in the ^{13}C NMR spectra, which is consistent with the present copolymerization results.

Introduction

Although a variety of living polymerization systems have been developed, particularly over the past few years,[1] the conventional anionic living polymerization method of conjugated hydrocarbon monomers such as styrene, 1,3-butadiene, and isoprene is believed to be still the most established method from the viewpoint of synthesizing polymers with precisely controlled molecular weights and extremely narrow molecular weight distributions.[2] The highly reactive but stable carbanionic character of the living polymers from these monomers also provides the best method for synthesizing well-defined block copolymers. In fact, many previous reports demonstrate that block copolymers obtained by this method could have been of very good uniformity.[3] On the other hand, a major drawback of these living polymers is their intolerance to most polar functional groups. This means that limitations are encountered when one attempts the anionic living polymerization of styrene and 1,3-dienoic monomers with functional groups.

Chart I



As one solution to overcome this longstanding problem,[4] we have deliberately introduced an electron-withdrawing group into the phenyl ring of a styrene monomer to change the reactivities of the monomer and the resulting living polymer.[5] We particularly anticipated that the nucleophilicity of the carbanion at the growing chain end of the living polymer would be lowered by reducing the electron density on the carbanion through the electron-withdrawing effect, thereby allowing the electron-withdrawing group to coexist with the carbanion of lowered reactivity. Actually, the following styrene derivatives have been found to undergo anionic living polymerization without problem. They are the styrenes *para*-substituted with *N,N*-diethylamido (**1**),[6] *N*-cyclohexylimino (**2**),[7] oxazolinyl (**3**),[8] *tert*-butyl ester (**4**),[9] *N,N*-diethylsulfonamido (**5**),[10] and cyano (**6**)[11] groups, which are normally susceptible to react with living polystyrene (Chart I). This may be attributed to the decrease of electron densities on the propagating carbanions of the living polymers. In these cases, resonance stabilization of the carbanions through extended π-conjugated systems[12] involving the multiple bonds of C=O, C=N, S=O, and C≡N and the benzene rings also plays an important role for the success of the living polymerization. The reduced reactivity of these living polymers is evident from crossover reactions with styrene. Thus, our developed methodology opens a route for providing new anionic living polymers substituted with

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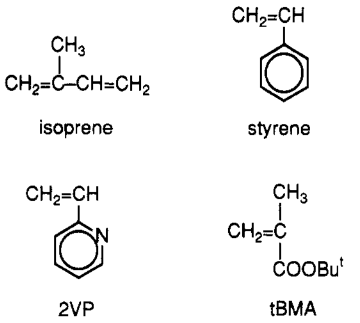
Chart II


isoprene

styrene

2VP

tBMA

polar functional groups having an electron-withdrawing character.[5-11]

We can imagine from the reduced reactivity of the carbanions that these styrenes become more anionically reactive than styrene in principle by a similar electron-withdrawing effect. This is strongly supported by the fact that nucleophilic initiators that do not initiate styrene polymerization[13] can initiate **1**–**6** to afford polymers. Furthermore, all of the ^{13}C NMR chemical shifts of the vinyl β-carbons of these monomers shifted to lower field than that of styrene, indicating the decreased electron densities of the vinyl groups in **1**–**6**. This observation also suggests the higher reactivities of **1**–**6** toward nucleophilic attack under anionic polymerization conditions. Accordingly, introduction of an electron-withdrawing group may influence both the reactivities of the carbanions produced and the monomers themselves.

In our preliminary experiment on the crossover block copolymerizations of styrene and **1**, **3**, **4**, **5**, and **6**,[6,8-11] we have found that these monomers and their living polymers do not behave as styrene and living polystyrene as expected. Their different behaviors led us to investigate the crossover block copolymerizations using these monomers in a more general sense. The resulting information seems to be every important not only to clarify the anionic polymerizabilities of **1**–**6** but also to synthesize block copolymers especially by the sequential addition of different monomers.

In the present paper, we report the results of our thorough investigations into the block copolymer syntheses of **1**–**6** with four conventional monomers capable of producing anionic living polymers, namely isoprene, styrene, 2-vinylpyridine (2VP), and *tert*-butyl methacrylate (tBMA) (Chart II). The overall objectives of this work are the following: (1) to evaluate the reactivities of **1**–**6** and their living polymers by crossover block copolymerization and (2) to explore the possibility of synthesizing block copolymers with the polar functional groups shown here.

Experimental Section

Monomers and Solvents. The six para-substituted styrene derivatives, **1**,[6] **2**,[7], **3**,[8] **4**,[9] **5**,[10] and **6**,[11] were synthesized according to our preceding papers, respectively. Isoprene, styrene, and α-methylstyrene were distilled over calcium hydride and finally distilled from benzylmagnesium chloride under vacuum. 1,1-Diphenylethylene was purified by fractional distillation over calcium hydride and finally distilled from *n*-BuLi under vacuum. 2-Vinylpyridine (2VP) was first dried with potassium hydroxide and then distilled over calcium hydride under vacuum. *tert*-Butyl methacrylate (tBMA) was distilled over calcium hydride and finally distilled from trioctylaluminum on the vacuum line.[14] The monomers were diluted by dry THF as 0.3–0.8 M solutions and were stored at -30 °C in glass ampules equipped with breakseals until ready to use for the anionic polymerizations. THF used as a polymerization solvent was refluxed over sodium wire for 5 h and distilled over lithium aluminum hydride and finally through a vacuum line from its sodium naphthalenide solution. Heptane was refluxed and distilled over *n*-BuLi and finally distilled through the vacuum line in the presence of (1,1-diphenylhexyl)lithium.

Initiators. Potassium naphthalenide and lithium naphthalenide were prepared by the reaction of a small excess molar quantity of naphthalene with the corresponding alkali metal in THF. Cumylpotassium was prepared by the reaction of cumyl methyl ether with sodium–potassium alloy in THF at room temperature. Commercially available *n*-BuLi (1.6 M hexane solution) was diluted by heptane and used for the anionic polymerization. These initiators were stored at -30 °C in ampules equipped with breakseals. The oligo(α-methylstyryl)dilithium 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. The (1,1,4,4-tetraphenylbutanediyl)dipotassium was similarly prepared by the reaction of potassium naphthalenide and 1,1-diphenylethylene. The concentration of initiators was determined by a colorimetric titration with standardized 1-octanol in a sealed reactor under vacuum as previously reported.[15]

Polymerization Procedures. All of the block copolymerizations were carried out at -78 to -95 °C with shaking under high-vacuum conditions in the all-glass apparatus equipped with breakseals. The first monomer was polymerized to complete the first-stage polymerization under the appropriate conditions (Table I). In the presented conditions, a stable living polymer was obtained from each monomer. The conversions of the first monomers were always quantitative under the conditions. After an aliquot of the reaction mixture was withdrawn for the analysis of the homopolymer at the first-stage polymerization, the second monomer was then added to the residue of the reaction system. After the polymerization system was allowed to stand under the appropriate conditions according to the second monomer as listed also in Table I, the second-stage polymerization was terminated with methanol. The reaction mixture was poured into a large excess of a suitable solvent to precipitate the polymer. The conversion of the second monomer and the yield of the resulting polymeric product were first checked to estimate the character of the second-stage polymerization. The copolymerization products collected by filtration were then analyzed by size exclusion chromatography (SEC) either in THF or in DMF solution. The molecular weights and the distributions of the first-stage polymers were determined by the SEC calibration curves for each homopolymer. The molecular weight distribution of the block copolymer was directly estimated from the SEC calibration using standard polystyrenes. In most cases, the molecular weights of the block copolymers were determined by using the molecular weight of the homopolymer and the molar ratios of the monomer units in the copolymer analyzed by ^{1}H NMR spectaroscopy.

Typical Procedure of Block Copolymerization (Table III, Run 22). Polymerization of styrene (7.51 mmol) was carried out with potassium naphthalenide (0.133 mol) as an initiator in THF (16.0 mL) at -78 °C in vacuo for 10 min in the all-glass apparatus equipped with breakseals. To determine the characteristics of the first-stage polymer, an aliquot of the reaction mixture (3.7 mL) was withdrawn. Precooled 4-cyanostyrene at -78 °C (**6**, 3.98 mmol, 0.743 M solution in THF) was quickly added to the residual THF solution (12.3 mL) of the difunctional living polystyrene (central block) and reacted for 30 min at -78 °C to complete the second-stage polymerization. After quenching with methanol, both homopolystyrene (0.19 g) and the copolymerization product (1.13 g) were quantitatively obtained by pouring them into a large excess of methanol. The composition of the copolymerization product was analyzed by ^{1}H NMR spectroscopy. The segment ratio between the polystyrene block and the poly(**6**) block in the copolymer agreed well with the calculated value from the molar ratio of the feed monomers. As shown in Figure 1 and in Table III (run 22), the homopolymer and the copolymer possessed molecular weights of 12 000 ($\bar{M}_w/\bar{M}_n$ = 1.04) and 21 000 ($\bar{M}_w/\bar{M}_n$ = 1.07), close to the theoretical values, 12 000 and 22 000, respectively. These results strongly indicate that the polymer obtained after the second stage is an expected A–B–A type triblock copolymer, poly(**6**-*b*-styrene-*b*-**6**), with a narrow molecular weight

Table I. Reaction Conditions of Various Monomers for the Block Copolymerization in THF[a]

	first-stage polymerization[b]		second-stage polymerization[c]	
monomer	initiator system	conditions	countercation	conditions
isoprene	K-Naph[d]	-78 °C, 4 h	K^+	-78 °C, 4 h
styrene	K-Naph or Cumyl-K[e]	-78 °C, 10 min	K^+	-78 °C, 2 h
			Li^+	-78 °C, 2 h
2VP[f]	Li-Naph[g]/DPE[h]	-78 °C, 1 h	Li^+	-78 °C, 2 h
	K-Naph/DPE	-78 °C, 1 h	K^+	-78 °C, 2 h
1	K-Naph/α-MeSt[i]	-78 °C, 30 min	K^+	-78 °C, 1 h
	Li-Naph/α-MeSt	-78 °C, 30 min	Li^+	-78 °C, 1 h
2	K-Naph/α-MeSt	-78 °C, 30 min	K^+	-78 °C, 1 h
	Li-Naph/α-MeSt	-78 °C, 4 h	Li^+	-78 °C, 4 h
3	K-Naph/α-MeSt	-78 °C, 10 min	K^+	-78 °C, 1 h
	Li-Naph/α-MeSt	-78 °C, 10 min	Li^+	-78 °C, 2 h
4[j]	K-Naph/α-MeSt	-95 °C, 4 h	K^+	-95 °C, 4 h
5	K-Naph/α-MeSt	-78 °C, 30 min	K^+	-78 °C, 2 h
	Li-Naph/α-MeSt	-78 °C, 30 min	Li^+	-78 °C, 2 h
6	K-Naph/DPE	-78 °C, 30 min	K^+	-78 °C, 2 h
	Li-Naph/DPE	-78 °C, 30 min	Li^+	-78 °C, 2 h
tBMA	K-Naph/α-MeSt	-78 °C, 2 h	K^+	-78 °C, 2 h
	n-BuLi/DPE	-78 °C, 2 h	Li^+	-78 °C, 2 h

[a] Under these conditions, the polydispersity index ($\bar{M}_w/\bar{M}_n$) of the resulting polymers at the first stage was within 1.2. [b] Reaction conditions of monomers to produce their living homopolymer quantitatively. [c] Reaction conditions of monomers for the second-stage polymerization corresponding to the countercation used. [d] Potassium naphthalenide. [e] Cumylpotassium. [f] By using the initiator containing potassium countercation, the polydispersity index of the resulting poly(2VP) was around 1.3. [g] Lithium naphthalenide. [h] 1,1-Diphenylethylene. [i] α-Methylstyrene. [j] By using the initiators containing lithium countercation, no poly(4) was produced under various conditions; see ref 9.

distribution and a predictable molecular weight. This block copolymer showed glass transition temperatures at 152 and 106 °C,[11] corresponding to those of the poly(4-cyanostyrene) segment and the central polystyrene block, indicating microphase separation in the bulk.

Measurements. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (89.6 MHz, ^1H; 22.53 MHz, ^{13}C) in $CDCl_3$ or DMF-d_7. Chemical shifts are reported in ppm downfield relative to tetramethylsilane (δ 0.00) for ^1H NMR and relative to $CDCl_3$ (δ 77.1) for ^{13}C NMR. Chemical shifts in DMF-d_7 are reported in ppm downfield relative to DMF-d_7 (δ 8.05 for ^1H NMR and δ 162.5 and ^{13}C NMR). Infrared spectra (KBr disk) were measured on a JEOL JIR-AQS20M FT-IR spectrophotometer. Size exclusion chromatograms (SEC) for the determination of the molecular weight distributions of the polymers were mainly obtained at 40 °C with a TOSOH HLC-8020 instrument equipped with three polystyrene gel columns (TOSOH G5000H$_{XL}$, G4000H$_{XL}$, and G3000H$_{XL}$) with an ultraviolet (270 nm in DMF or 254 nm in THF) or a refractive index detector. THF or DMF was the carrier solvent at a flow rate of 1.0 mL min^{-1}. The glass transition temperature of the polymer was measured by differential scanning calorimetry using a Seiko Instruments DSC220 apparatus. The polymer sample was first heated to 240 °C, cooled rapidly to -20 °C, and then scanned at a rate of 20 °C min^{-1}.

Results and Discussion

As mentioned in the Introduction, the method of anionic living polymerization allows one to synthesize well-defined block copolymers in which each block has a predictable molecular weight and a narrow molecular weight distribution. However, this method, in some cases, may yield different results, depending on the order in which the monomers are added. For example, the sequential addition of styrene at first and then tBMA provides a well-defined block copolymer, but not vice versa. Thus, considerable care is needed for sequential addition of different monomers to synthesize block copolymers.

Such a restriction observed in the block copolymerization, however, may offer an advantage to estimate the reactivities of the monomers and the resulting living polymers. Therefore, the sequential block copolymerization with different monomers is a good probe to clarify the reactivities of new monomers as well as the resulting new living polymers. We have used here the new monomers **1**–**6** in addition to four conventional monomers for understanding the reactivities as well as for synthesizing a variety of novel block copolymers.

Before discussing our work, we should recall the addition order of four conventional monomers from the previous works[2,3,16–19] and our results on block copolymerizations among these monomers. Table II shows our polymerization results under the specified conditions according to our standard as mentioned later. As can be seen, well-defined block copolymers were synthesized by the sequential polymerization of isoprene at first and then styrene and vice versa. Accordingly, they are mutually replaceable in the sequential addition. These results from our data are consistent with the previous works reported so far.[2,3] Furthermore, several researchers have actually demonstrated that their living polymers can initiate the polymerizations of both 2VP[16,17] and tBMA[18] to produce the desired block copolymers.[20] These results again agree with our data shown here.

On the other hand, no polymerization of isoprene occurred with the living poly(2VP). The crossover reaction of styrene with living poly(2VP) is somewhat complicated (run 6). Styrene could be initiated from the living poly(2VP) only with a low efficiency, and the conversion of styrene was low and far from quantitative under our polymerization conditions. Size exclusion chromatography (SEC) analysis of the copolymerization product showed a multimodal peak with a broad distribution. Since it was previously reported that the pyridine ring was susceptible to react with the carbanionic species,[21] we could speculate on the nature of the polymerization result as follows: living poly(2VP) reacted very slowly with styrene to transform the styryl anion at the growing chain end to a small extent, and the newly formed polystyryl anion might possibly attack the pyridine ring to terminate the propagation reaction before complete consumption of styrene. Thus, our attempt to synthesize the well-defined block copolymer by this addition order was not successful. Compared with the reactivities of living poly(2VP) toward isoprene and styrene as described above, it is certain that styrene is more anionically reactive than isoprene. The block copolymerizations of these combinations impose the additional restrictions that (a) isoprene or styrene must be polymerized first and (b) 2VP should be added to the

Table II. Anionic Block Copolymerization of Isoprene, Styrene, 2-Vinylpyridine (2VP), and *tert*-Butyl Methacrylate (tBMA) at −78 °C in THF

						block copolymer (homopolymer[a])		
						$10^{-3}\bar{M}_n$		
run	countercation	block sequence	1st monomer (A)	2nd monomer (B)	yield,[b] %	calcd[c]	obsd[d]	$\bar{M}_w/\bar{M}_n$
1[e]	K^+	B–A–B	isoprene	styrene	100	17 (6.9)	21[f]	1.14
2[g]	K^+	B–A–B	isoprene	tBMA	100	24 (13)	28 (14)	1.08 (1.09)
3[e]	K^+	B–A–B	styrene	isoprene	100	24 (12)	26[f]	1.06
4	K^+	A–B	styrene	tBMA	100	12 (6.9)	14 (7.1)	1.07 (1.12)
5[h]	K^+	B–A–B	2VP	isoprene	0	26 (12)	*h* (9.6)	*h* (1.18)
6[i]	Li^+	B–A–B	2VP	styrene	11	23 (11)	11 (8.2)	1.44 (1.06)
7	Li^+	B–A–B	2VP	tBMA	100	24 (11)	20 (10)	1.23 (1.05)
8[h]	K^+	B–A–B	tBMA	isoprene	0	23 (11)	*h* (9.8)	*h* (1.10)
9[h]	K^+	B–A–B	tBMA	styrene	0	31 (16)	*h* (16)	*h* (1.18)
10[h]	Li^+	B–A–B	tBMA	2VP	0	27 (10)	*h* (9.2)	*h* (1.06)

[a] Homopolymers were quantitatively obtained at the first-stage polymerization in all cases. [b] Yield of the second-stage polymerization. [c] $\bar{M}_n$(calcd) = [monomer] × (MW of monomer) × f/[initiator] + MW of initiator unit. $f = 1$ or 2, corresponding to the functionality of the initiators. [d] The molecular weights 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. [e] Homopolymer of the first monomer was not isolated in these cases. [f] The molecular weight of block copolymer was directly estimated from the GPC calibration using polystyrene standards. [g] The second-stage polymerization was carried out after end-capping of the living polymer with 1,1-diphenylethylene. [h] No polymerization proceeded at the second stage, resulting in a quantitative recovery of the homopolymer of the first monomer. [i] Side reaction may occur during the second-stage polymerization.

resulting living polymers, since the anion of poly(2VP) is not sufficiently nucleophilic to initiate quantitatively the polymerizations of isoprene and styrene.

The living polymer of 2VP could initiate the polymerization of tBMA quantitatively to afford the block copolymer with a well-defined structure as reported recently by Hogen-Esch and co-workers,[19] while the sequential addition of tBMA at first and then 2VP resulted in a quantitative recovery of homopoly(tBMA) as shown in run 10. No polymerization of 2VP took place with living poly(tBMA). These results indicate that the living polymer of 2VP is more reactive than that of tBMA and the synthesis of block copolymer must proceed in the order of 2VP as a first monomer and then tBMA addition. As can be expected, the living poly(tBMA) has no ability to initiate the polymerizations of both isoprene and styrene.

It is obvious from the results of block copolymerizations that the nucleophilicity of living polymer appears to increase in the following order: living polyisoprene = living polystyrene > living poly(2VP) > living poly(tBMA). In contrast, the reactivity (or electrophilicity) of monomer is reversed as expected, i.e., tBMA > 2VP > styrene > isoprene. In this regard, it is interesting to examine the reactivities of **1**–**6** and their anionic living polymers in the sequential block copolymerization, since the electron-withdrawing groups introduced can be expected to affect considerably their reactivities.

Sequential Polymerizations of 1–6 with Living Polymers from Conventional Monomers. In this section, we discuss the reactivities of **1**–**6** toward the anionic living polymers from isoprene, styrene, 2VP, and tBMA. In other words, **1**–**6** are employed as second monomers in the sequential polymerization to synthesize block copolymers.

For an easy comparison, the conditions of living polymerization of **1**–**6** were standardized as much as possible. All of the polymerizations were carried out in THF at −78 °C except for the polymerizations of *tert*-butyl 4-vinylbenzoate (**4**), which were performed at −95 °C to avoid the significant side reactions at −78 °C previously reported.[9] The anionic initiator used mainly was oligo(α-methylstyryl)dipotassium which was prepared from potassium naphthalenide and α-methylstyrene just prior to the polymerization. The anionic polymerization of 4-cyanostyrene (**6**) was initiated with (1,1,4,4-tetraphenylbutanediyl)dipotassium to prevent the cyano group from the nucleophilic attack by using a bulky diphenylethylene-capped carbanion. The corresponding lithium salt was employed in the polymerizations using 2VP,[19,21] since the polymers with relatively broad molecular weight distributions were obtained with the initiator bearing K^+. The first monomer was polymerized for the appropriate reaction time (Table I), and an aliquot of the mixture was withdrawn to analyze the first polymer. Then the second monomer was added to the residue of the mixture and allowed to stand under the appropriate conditions (Table I). In some cases, the living polymers of isoprene and styrene were capped with 1,1-diphenylethylene to avoid attack of the polar functional groups of **1**–**6** before the second monomers were polymerized.[22] The resulting carbanion thus formed is a sterically hindered poorer nucleophile than the uncapped anions. It is, however, believed to be more reactive than the carbanions derived from 2VP and tBMA. Therefore, comparison is possible taking this into consideration. The results are summarized in Table III, where $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values of the polymers at the first and second polymerizations are listed. Yields refer to the polymer yields at the second stage of polymerization.

As can be seen, living polymers of isoprene and styrene are capable of initiating **1**–**6** to quantitatively afford the polymers in all runs, although the 1,1-diphenylethylene-capped anion is often employed. The polymerization mixtures always became dark red upon addition of **1**–**6**, which remained unchanged until quenching with methanol. In the ^{1}H NMR spectra of the resulting polymers, signals corresponding to either polyisoprene or polystyrene and poly(**1**–**6**) were observed. The compositions determined from the integral ratios of the NMR signals are nearly equal to those calculated from both monomers fed. In every case, the $\bar{M}_n$ value of the resulting polymer is in good agreement with that predicted from the monomer to initiator ratio. All of the SEC traces of the resulting polymers revealed sharp single peaks and the absence of the any peaks at the elution counts for homopolymers. The $\bar{M}_w/\bar{M}_n$ values were around 1.1 for all polymer samples, indicating that the copolymers possessed narrow molecular weight distributions. As a typical example, Figure 1 shows chromatograms of the starting polystyrene and the resulting block copolymer of styrene and **6**. These analytical results clearly indicate the quantitative formation of B–A–B type triblock copolymers with the desired and well-

Table III. Anionic Block Copolymerization of 1–6 with Living Polymers Derived from Isoprene, Styrene, 2VP, and tBMA at −78 °C in THF[a]

						block copolymer (homopolymer[b])		
						$10^{-3}\bar{M}_n$		
run	countercation	block sequence	1st monomer (A)	2nd monomer (B)	yield,[c] %	calcd[d]	obsd[e]	$\bar{M}_w/\bar{M}_n$
11	K^+	B-A-B	isoprene	1	100	30 (12)	27 (11)	1.08 (1.08)
12	K^+	B-A-B	isoprene	2	100	22 (11)	19 (14)	1.08 (1.08)
13	K^+	B-A-B	isoprene	3	100	29 (16)	28 (15)	1.11 (1.08)
14[f]	K^+	B-A-B	isoprene	4	100	27 (15)	25 (12)	1.13 (1.07)
15[f]	K^+	B-A-B	isoprene	5	100	21 (11)	23 (13)	1.16 (1.09)
16[f]	K^+	B-A-B	isoprene	6	100	25 (14)	23 (12)	1.15 (1.08)
17	K^+	B-A-B	styrene	1	100	31 (15)	32 (16)	1.06 (1.09)
18	K^+	B-A-B	styrene	2	100	23 (12)	25 (13)	1.11 (1.06)
19	K^+	B-A-B	styrene	3	100	25 (11)	27 (11)	1.12 (1.09)
20[f]	K^+	B-A-B	styrene	4	100	25 (14)	25 (14)	1.13 (1.06)
21	K^+	B-A-B	styrene	5	100	22 (13)	19 (12)	1.12 (1.08)
22	K^+	B-A-B	styrene	6	100	22 (12)	21 (12)	1.07 (1.04)
23[f]	K^+	B-A-B	styrene	6	100	23 (13)	25 (14)	1.09 (1.07)
24	Li^+	B-A-B	2VP	1	100	25 (12)	21 (13)	1.14 (1.11)
25	Li^+	B-A-B	2VP	2	100	18 (9.1)	18 (8.7)	1.15 (1.13)
26	Li^+	B-A-B	2VP	3	100	23 (13)	22 (12)	1.06 (1.05)
27	K^+	B-A-B	2VP	4	100	22 (12)	20 (15)	1.36 (1.27)
28	Li^+	B-A-B	2VP	5	100	21 (9.5)	20 (9.5)	1.16 (1.09)
29	Li^+	B-A-B	2VP	6	100	23 (8.6)	19 (7.9)	1.11 (1.07)
30[g]	K^+	B-A-B	tBMA	1	100	27 (16)	*g* (15)	*g* (1.23)
31[g]	K^+	B-A-B	tBMA	2	100	22 (10)	*g* (10)	*g* (1.13)
32[g]	K^+	B-A-B	tBMA	3	100	22 (11)	*g* (8.5)	*g* (1.12)
33	K^+	B-A-B	tBMA	4	100	23 (11)	28 (9.1)	1.17 (1.12)
34	K^+	B-A-B	tBMA	5	100	23 (13)	20 (12)	1.14 (1.12)
35	K^+	B-A-B	tBMA	6	100	22 (10)	18 (6.8)	1.06 (1.08)

[a] Polymerization reaction concerning monomer 4 was carried out at −95 °C to avoid the serious side reaction; see ref 9. [b] Homopolymers were quantitatively obtained at the first-stage polymerization in all cases. [c] Yield of the second-stage polymerization. [d] $\bar{M}_n$(calcd) = [monomer] × (MW of monomer) × 2/[initiator] + MW of initiator unit. [e] The molecular weights 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. [f] The second-stage polymerization was carried out after end-capping of the living polymer with 1,1-diphenylethylene. [g] Initiation efficiency of the crossover reaction was moderate (50–60%), resulting in a copolymerization product showing a bimodal and broad molecular weight distribution, which consisted of a virtual homopolymer and a block copolymer having a high molecular weight.

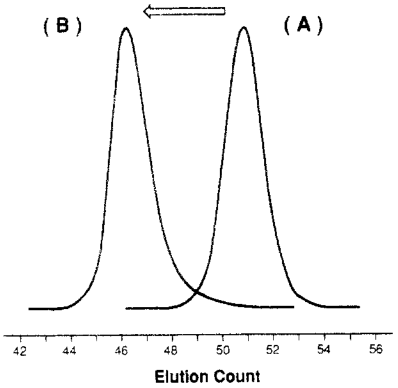


Figure 1. SEC curves (DMF) of polystyrene at the first-stage polymerization (A) and of poly(**6**-*b*-styrene-*b*-**6**) (B) (Table III, run 22): peak A, $\bar{M}_n$(obsd) = 12 000, $\bar{M}_w/\bar{M}_n$ = 1.04; peak B, $\bar{M}_n$(obsd) = 21 000, $\bar{M}_w/\bar{M}_n$ = 1.07.

defined structures. Accordingly, the polymerization by sequential addition of isoprene or styrene with 1–6 quantitatively proceeds to synthesize successfully tailor-made block copolymer in every combination.

Next we attempted to polymerize 1–6 with living poly(2VP). Unfortunately, homopolymers of 2VP having relatively broad molecular weight distributions were always obtained by the polymerization of 2VP with organopotassium initiators in THF at −78 °C. Therefore, we synthesized instead the living poly(2VP) bearing Li^+ by initiation with (1,1,4,4-tetraphenylbutanediyl)dilithium. The resulting polymers of 2VP thus obtained at the first-stage were always found to possess narrow molecular weight distributions and predictable molecular weights. Contrary to our expectation, each of these styrene derivatives containing electron-withdrawing groups can undergo anionic polymerization quantitatively with living poly(2VP). This is also inferred from the color changes of the reaction systems observed during polymerizations. The dark red color, typical of the polystyryl anions from 1–6, appeared immediately upon addition of 1–6 to living poly(2VP). Successful syntheses of well-defined block copolymers by this sequential order were clearly evidenced from the sharpness of the single peaks and the absence of homopolymers in their SEC charts as well as the fact that the $\bar{M}_n$ values and the compositions agreed with those predicted within experimental accuracy. It should be noted that the living poly(2VP) bearing K^+ was used in the polymerization of 4 (Table III, run 27), since no appreciable homopolymerization of 4 was previously observed to occur with the anionic initiators with Li^+ as a countercation under various conditions.[9] As expected, the resulting polymers at the first and second stage possessed somewhat broad molecular weight distributions, the $\bar{M}_w/\bar{M}_n$ values being 1.27 and 1.36, respectively. We believe from the analytical results that a block copolymer with the desired structure is also formed in this polymerization.

This is in sharp contrast to the polymerization of either isoprene or styrene with living poly(2VP) where either no polymerization or slow reaction occurs as mentioned before. The results of block copolymerizations obtained here indicate that the reactivities of 1–6 seems to be at least comparable to that of 2VP and more anionically reactive than those of isoprene and styrene, although they are the styrene derivatives. Clearly, introduction of the

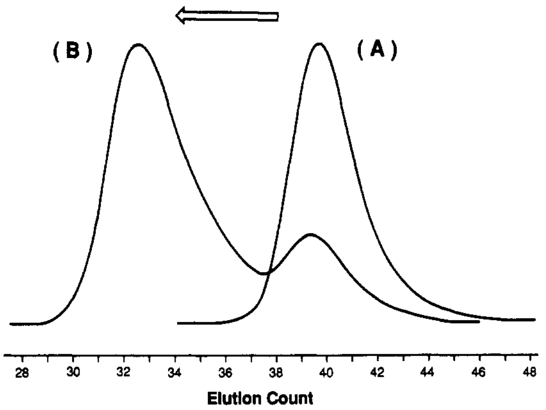


Figure 2. SEC curves (THF) of poly(tBMA) at the first-stage polymerization (A) and of the copolymerization product after the second-stage polymerization of 2 in THF at −78 °C for 1 h (B) (Table III, run 31): peak A, $\bar{M}_n$(obsd) = 10 000, $\bar{M}_w/\bar{M}_n$ = 1.13; peak B, $\bar{M}_w/\bar{M}_n$ = 1.57.

electron-withdrawing groups into the styrene framework reduces the charge densities of the vinyl groups of 1–6, allowing these monomers to become more reactive than styrene itself in the anionic polymerization.

We finally attempted the sequential polymerizations by addition of tBMA as a first monomer and then 1–6. The most interesting aspect of the polymerization is whether the further polymerizations of 1–6 can proceed with the low nucleophilic carbanion produced from tBMA. The difunctional living polymer of tBMA was successfully synthesized by the polymerization of tBMA with oligo(α-methylstyryl)dipotassium in THF at −78 °C for 2 h. The control of molecular weight and the narrow molecular weight distribution were actually attained under the polymerization conditions.

Upon addition of 1–3 to the living poly(tBMA), the color of the reaction mixture slowly changed from pale violet to orange-red, and a quantitative conversion was realized for each case. The copolymerization products were obtained in quantitative yield. However, the SEC charts always showed bimodal peaks of broad molecular weight distributions. A typical example is shown in Figure 2. The peaks on the low molecular weight side correspond to homopolymers of tBMA, which are not involved in the initiation of 1–3. The nonquantitative initiation of the second monomer may result in the formation of the block copolymer which was observed in the higher molecular weight region of Figure 2. The copolymerization products are therefore estimated to consist of virtual homopolymers of tBMA and the block copolymers with poly(1) to poly(3) segments of higher molecular weights than expected.

From these results, it can be concluded that the initiation reactions of 1–3 occur slowly with living poly(tBMA) and the residual monomers are consumed rapidly by the newly formed living polymers from 1–3. Some of unreacted living poly(tBMA) still remains even after the conclusion of polymerizations of 1–3. Accordingly, the synthesis of well-defined block copolymer is not successful by the sequential addition of tBMA and 1–3 in this order. However, it is surprising that the styrene derivatives of 1–3 can be initiated with the propagating carbanion of living poly(tBMA), even though their initiation efficiencies are not quantitative. For example, the estimated efficiency of the initiation reaction of 2 with living poly(tBMA) was ca. 60%. The contrasting result of no polymerization of 2VP with living poly(tBMA) indicates that 1–3 may be more reactive than 2VP. It is of course certain that they are anionically less reactive than tBMA.

More surprising are the results of the polymerizations of the sequential addition of 4–6 to the living poly(tBMA). Upon addition of 4–6 to living poly(tBMA), the colors of the polymerization systems changed immediately from pale violet to bright red, characteristic to the polystyryl anions produced from 4–6. The red coloration remained unchanged at −78 °C after 2 h, indicating no side reactions of the polar substituents with the active growing ends. All of the conversions of 4–6 were quantitative.

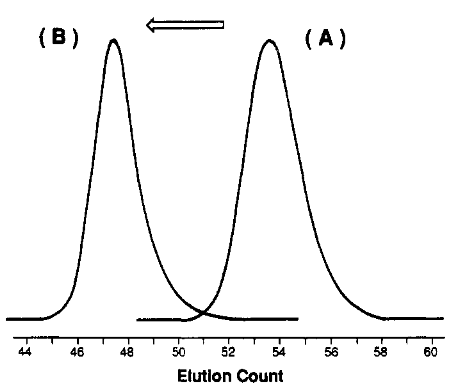


Figure 3. SEC curves (DMF) of poly(tBMA) at the first-stage polymerization (A) and of poly(6-*b*-tBMA-*b*-6) (B) (Table III, run 35): peak A, $\bar{M}_n$(obsd) = 6800, $\bar{M}_w/\bar{M}_n$ = 1.08; peak B, $\bar{M}_n$(obsd) = 18 000, $\bar{M}_w/\bar{M}_n$ = 1.06.

The compositions of the resulting polymers were analyzed by ^{1}H NMR and agreed well with the calculated values of both monomers fed. The observed molecular weights were in close accord with the theoretical ones assuming the living polymerizations of 4–6 at the second stage. The SEC analyses exhibited that the resulting polymers all possessed narrow molecular weight distributions eluted at the higher molecular weight sides without the corresponding homopolymers of tBMA. A representative chromatogram is shown in Figure 3, which offers convincing evidence of the formation of the B–A–B triblock copolymer of tBMA and 6, poly(6-*b*-tBMA-*b*-6), with a well-defined chain structure. It is obvious from these results that the second-stage polymerizations of 4–6 proceed in a living manner with the carbanion of living poly(tBMA) to afford tailor-made pure block copolymers. Thus, the anionic polymerization behaviors of 4–6 are apparently different from those of 1–3 as mentioned before.

Considering the results of block copolymerizations using 1–6, the monomers of 4–6 can be classified as anionically more reactive monomers than 1–3. The reactivities of 4–6 might be comparable to that of tBMA and are undoubtedly more than that of 2VP, although they are styrene derivatives. It is also interesting that the monomer reactivity can be changed by the electron-withdrawing groups introduced, varying the anionic reactivity from styrene to tBMA. From all the results in this section, we can evaluate the order of monomer reactivity (or in other words, the electrophilicity of the monomer). Thus, the order of reactivity by the effect of the monomer skeleton and the electron-withdrawing group introduced is increased as follows: isoprene < styrene < 2VP < 1–3 < tBMA = 4–6

Sequential Polymerizations of Conventional Monomers with Living Polymers from 1–6. In the preceding section, we have discussed the anionic block copolymerizations by sequential addition of 1–6 to the living polymers from conventional monomers such as isoprene, styrene, 2VP, and tBMA. Successful synthesis of block copolymers and evaluation of the monomer reactivity have been demonstrated. In particular, the reactivities of 1–6 are found to be remarkably enhanced by introducing electron-withdrawing groups into the phenyl ring of styrene. In this section, we evaluate the nucleophilicities of the living

Table IV. Anionic Block Copolymerization of Isoprene, Styrene, 2VP, and tBMA with Living Polymers Derived from 1–6 at −78 °C in THF[a]

						block copolymer (homopolymer[b])		
						$10^{-3}\bar{M}_n$		
run	countercation	block sequence	1st monomer (A)	2nd monomer (B)	yield,[c] %	calcd[d]	obsd[e]	$\bar{M}_w/\bar{M}_n$
36[f]	K+	B–A–B	1	isoprene	0	27 (11)	*f* (8.5)	*f* (1.08)
37[f]	K+	B–A–B	2	isoprene	0	22 (8.1)	*f* (8.4)	*f* (1.13)
38[f]	K+	B–A–B	3	isoprene	0	36 (10)	*f* (10)	*f* (1.03)
39[f]	K+	B–A–B	4	isoprene	0	43 (13)	*f* (12)	*f* (1.19)
40[f]	K+	B–A–B	5	isoprene	0	19 (7.7)	*f* (7.6)	*f* (1.12)
41[f]	K+	B–A–B	6	isoprene	0	42 (11)	*f* (9.3)	*f* (1.08)
42[g]	K+	B–A–B	1	styrene	100	28 (15)	*g* (12)	*g* (1.09)
43[g]	K+	B–A–B	2	styrene	100	21 (8.3)	*g* (7.0)	*g* (1.04)
44[g]	K+	B–A–B	3	styrene	100	19 (7.0)	*g* (7.0)	*g* (1.02)
45[f]	K+	B–A–B	4	styrene	0	23 (9.8)	*f* (9.8)	*f* (1.11)
46[f]	K+	B–A–B	5	styrene	0	18 (8.9)	*f* (9.5)	*f* (1.15)
47[f]	K+	B–A–B	6	styrene	0	24 (9.4)	*f* (8.8)	*f* (1.06)
48	Li+	B–A–B	1	2VP	100	26 (9.0)	24 (9.5)	1.16 (1.10)
49	Li+	B–A–B	2	2VP	100	20 (7.7)	19 (9.6)	1.26 (1.14)
50	Li+	B–A–B	3	2VP	100	24 (9.6)	21 (9.0)	1.08 (1.05)
51[h]	K+	B–A–B	4	2VP	100	17 (7.5)	41[i] (8.5)	1.90 (1.20)
52	Li+	B–A–B	5	2VP	100	21 (12)	21 (13)	1.17 (1.15)
53[j]	Li+	B–A–B	6	2VP	100	21 (12)	*j* (10)	*j* (1.09)
54	K+	B–A–B	1	tBMA	100	19 (6.5)	15 (7.5)	1.13 (1.10)
55	K+	B–A–B	2	tBMA	100	25 (12)	23 (12)	1.07 (1.10)
56	K+	B–A–B	3	tBMA	100	18 (8.9)	17 (8.4)	1.08 (1.03)
57	K+	B–A–B	4	tBMA	100	27 (7.8)	27 (9.0)	1.24 (1.15)
58	K+	B–A–B	5	tBMA	100	26 (12)	23 (9.9)	1.10 (1.08)
59	K+	B–A–B	6	tBMA	100	16 (8.8)	16 (8.5)	1.17 (1.11)

[a] Polymerization reaction concerning monomer 4 was carried out at −95 °C to avoid the serious side reaction; see ref 9. [b] Homopolymers were quantitatively obtained at the first-stage polymerization in all cases. [c] Yield of the second-stage polymerization. [d] $\bar{M}_n$(calcd) = [monomer] × (MW of monomer) × 2/[initiator] + MW of initiator unit. [e] The molecular weights 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. [f] No polymerization proceeded at the second stage, resulting in a quantitative recovery of the homopolymer of the first monomer. [g] Initiation efficiency of the crossover reaction was low (2–10%), resulting in a copolymerization product showing a bimodal and broad molecular weight distribution, which consisted of a virtual homopolymer and a block copolymer having a very high molecular weight. [h] A side reaction may occur during the second-stage polymerization. [i] The molecular weight of the block copolymer was directly estimated from the GPC calibration using polystyrene standards. [j] An insoluble product was quantitatively obtained from the reaction mixture, probably due to the crosslinking reaction of the polymer.

polymers from 1–6 by the sequential addition of isoprene, styrene, 2VP, or tBMA to the living poly(1–6)s. The difunctional living polymers bearing K+ were prepared from 1–6 and used to synthesize block copolymers with isoprene, styrene, and tBMA. The living polymers with Li+ were employed for the synthesis of block copolymers using 2VP to avoid broadening of the molecular weight distribution of the resulting poly(2VP) block. The results are summarized in Table IV.

As was seen at first, all of the living polymers from 1–6 were found not to initiate the polymerization of isoprene at all even for longer reaction times (runs 36–41). Each of the homopolymers of 1–6 was quantitatively recovered in every polymerization.

Next, with the use of the styrene as a second addition monomer, complete conversions of styrene were realized with the living polymers of 1–3. The SEC traces of the resulting products always showed two separated peaks which resulted from the virtual homopolymers of 1–3 and the block copolymers having very high molecular weight polystyrene segments, respectively. Figure 4 shows a SEC curve in the polymerization of styrene with living poly(1), typical for the slow initiation with rapid consumption of the second monomer by the newly formed carbanion. We can speculate that only a portion of the living poly(1–3)s reacts (2–10%) slowly with styrene to produce polystyryl anion and the newly formed anion polymerizes rapidly to consume styrene completely. Residual unreacted living polymers remains after the consumption of styrene. Accordingly, the carbanion at the active growing end of 1, 2, or 3 shows only a low reactivity toward styrene. By contrast, no polymerization occurred at all between styrene and the living polymers from 4–6 (runs 45–47).

These observations confirm that the nucleophilicities of the living polymers from 1–6 are much lower than those of living polyisoprene and living polystyrene, possibly due to a reduction of the electron densities on the carbanions by the electron-withdrawing effect of the substituents. It would appear obvious from the crossover reactions with

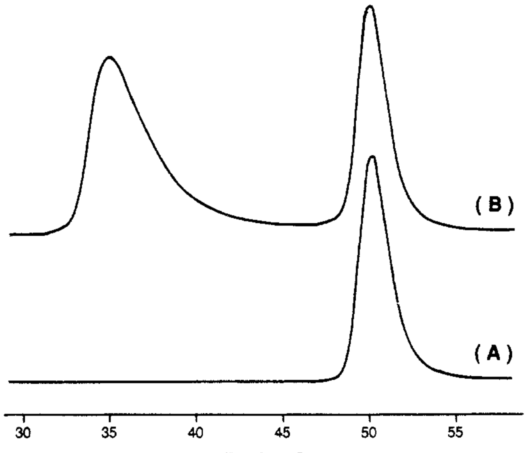


Figure 4. SEC curves (THF) of poly(1) at the first-stage polymerization (A) and of the copolymerization product after the second-stage polymerization of styrene in THF at −78 °C for 2 h (B) (Table IV, run 42): peak A, $\bar{M}_n$(obsd) = 12 000, $\bar{M}_w/\bar{M}_n$ = 1.09.

styrene that the carbanions derived from 1–3 are more reactive than those from 4–6, as might be expected from these monomer reactivities. In any event, a well-defined block copolymer synthesis has not been feasible by this sequential addition order; i.e., 1–6 is added first and isoprene or styrene is then added. The synthesis must be carried out in the reversed addition order as mentioned before in Table III.

Next, the sequential polymerizations using more anionically reactive monomers such as 2VP and tBMA were attempted. The polymerizations of both 2VP and tBMA were found to proceed quantitatively with the living polymers of 1–6. The block copolymers with regulated segments and compositions have been successfully synthesized in any combinations except for 2VP and either living poly(4) or living poly(6).

As mentioned before, no polymerization of 4 was observed with anionic initiators with Li^+.[9] Therefore, we could not carry out the polymerization of living poly(4) bearing Li^+ with 2VP. Instead, we employed the living poly(4) bearing K^+ for the sequential polymerization of 2VP as shown in run 51. Although the polymer yield was quantitative in this case, the molecular weight distribution by SEC was broad. The observed molecular weight was definitely higher than the predicted value. In this case, undesirable side reactions may occur during the second stage of the polymerization of 2VP.

The polymerization of 2VP with living poly(6) for 2 h always gave an insoluble polymeric material quantitatively based on both the monomer weights. It probably involves a cross-linking reaction between the cyano group in poly(6) and the carbanion of the newly produced living poly(2VP). This side reaction might possibly occur slowly, compared to the polymerization, since a soluble polymer was obtained when we terminated a similar polymerization in a short time. In this case, therefore, the first addition should be 2VP and then 6 to achieve the successful synthesis of block copolymer (Table III, run 29).

As mentioned in the preceding section, we have observed that the sequential polymerizations by all the combinations of 1–6 with living poly(2VP) provide the desired block copolymers. It is also found that the well-defined block copolymers are possibly synthesized by the sequential additions of 4–6 to living poly(tBMA), while the carbanion of living poly(tBMA) is not sufficiently nucleophilic to initiate quantitatively the polymerizations of 1–3. Accordingly, among the monomers 1–3, 5, and 2VP as well as the monomers 4–6 and tBMA, "reversible" block copolymerization is possible where both A and B blocks can initiate each other. Either A–B–A or B–A–B triblock copolymers with desired compositions are arbitrarily synthesized only by changing the order of addition of the monomers. On the other hand, in the combination of tBMA and 1–3, there is a restriction. "Unilateral" block copolymerization is only possible where the living polymers of 1–3 can initiate tBMA with quantitative efficiency, but not vice versa.

From the results obtained in this section, it is possible to compare the nucleophiic reactivities of the living polymers. The following is the decreasing order of reactivity: living polyisoprene = living polystyrene > living poly(2VP) = living polymers from 1–3 > living poly(tBMA) = living polymers from 4–6. This reactivity order of living polymer is seen to be almost opposite of the monomer reactivity discussed before. This may be reasonable since the electron-withdrawing nature also reduces the electron densities on the benzylic carbanions to stabilize in a similar manner. It therefore seems possible to predict the nucleophilicity of the propagating carbanion of the living polymers from the reactivity of the employed monomers and vice versa. From the ranking between the living polymers of 1–6, the strength of the electron-withdrawing effect for the substituents introduced is also significant with respect to the reactivity of the living carbanion derived from the monomer.

Sequential Polymerizations of 1–6 with Living Polymers from 1–6. In this section, we establish whether "reversible" or "unilateral" block copolymerization is possible among the six styrenes with electron-withdrawing groups, 1–6. The results are summarized in Table V.

As can be seen in runs 60–64, the block copolymerizations with living poly(1) successfully occur without regard of which monomer from 2 to 6 is added sequentially. Quantitative yields of polymers and the results of good agreement between the calculated and observed $\bar{M}_n$ values as well as the narrow molecular weight distributions were obtained in all combinations. The SEC charts showed that the resulting polymers all had symmetrical unimodal peaks with narrow distributions, the $\bar{M}_w/\bar{M}_n$ values being less than 1.2. These confirm quantitative production of the pure block copolymers with well-defined structures by this sequential route.

Similarly, the living polymers of 2, 3, and 5 initiated quantitatively the polymerizations of 1–6 to afford well-defined block copolymers of the same grade. For example, Figures 5 and 6 show the SEC chromatograms of block copolymers obtained from the reversed addition polymerization of 1 and 3 to oligo(α-methylstyryl)dipotassium in THF at −78 °C. These two SEC curves clearly support that the order of addition of these two monomers does not affect the polymerization results. Thus, the tailor-made A–B–A and B–A–B triblock copolymers, poly(3-*b*-1-*b*-3) and poly(1-*b*-3-*b*-1), can be synthesized only by changing the order of addition of the two comonomers. Consequently, we can demonstrate that the sequential addition is mutually replaceable; i.e., reversible block copolymerization is possible among the monomers 1–3 and 5. This polymerization behavior of 5 is totally unexpected, considering from the observations that the reactivities of monomer and the carbanion can be roughly classified between 1–3 and 4–6, which will be discussed in more detail.

With use of living poly(4) as an initiator, Well-defined block copolymers were obtained by the sequential addition of 1, 5, or 6 to this living polymer. On the other hand, some difficulties were encountered in the cases where 2 and 3 were added to living poly(4). In the first case, no appreciable polymerization of 2 occurred at all the homopoly(4) was recovered quantitatively. The possibilities of side reactions among the carbanions and polar groups may be ruled out from the observations that the red color of living poly(4) remains unchanged after addition of 2 and the block copolymerization by reversed addition takes place without problem. It can be therefore concluded that the carbanion derived from 4 is not capable of initiating the polymerization of 2 under the specific condition at −95 °C. For the latter case, the polymerization of 3 was found to proceed quantitatively, but the resulting block copolymer had a broad molecular weight distribution in this case. A multimodal peak was observed by SEC, indicating that competitive side reactions like ester attack occurred to some extent during the course of the polymerization of 3 with living poly(4).

When living poly(6) was used in block copolymerization, unsatisfactory results were obtained with 1–3 as second monomers. No polymerization of 1 was found to occur at

Table V. Anionic Block Copolymerization of 1–6 with Living Poly(1–6)s at –78 °C in THF[a]

run	countercation	block sequence	1st monomer (A)	2nd monomer (B)	yield,[c] %	block copolymer (homopolymer[b])		
						$10^{-3}\bar{M}_n$		
						calcd[d]	obsd[e]	$\bar{M}_w/\bar{M}_n$
60	K+	B–A–B	1	2	100	17 (7.4)	15 (7.6)	1.12 (1.10)
61	K+	B–A–B	1	3	100	19 (10)	19 (11)	1.07 (1.06)
62	K+	B–A–B	1	4	100	23 (9.1)	17 (8.7)	1.13 (1.08)
63	K+	B–A–B	1	5	100	18 (7.8)	16 (7.8)	1.16 (1.07)
64[f]	K+	B–A–B	1	6	100	17 (9.3)	16	1.05
65	K+	B–A–B	2	1	100	16 (7.7)	16 (8.5)	1.10 (1.10)
66[f]	K+	B–A–B	2	3	100	17 (9.8)	14	1.04
67[f]	K+	B–A–B	2	4	100	21 (11)	17	1.11
68[f]	K+	B–A–B	2	5	100	15 (7.2)	14	1.08
69[f]	K+	B–A–B	2	6	100	19 (10)	16	1.12
70	K+	B–A–B	3	1	100	21 (8.9)	16 (9.0)	1.05 (1.06)
71[f]	K+	B–A–B	3	2	100	17 (7.6)	15	1.04
72[f]	K+	B–A–B	3	4	100	18 (8.3)	16	1.09
73[f]	K+	B–A–B	3	5	100	20 (9.4)	19	1.08
74	K+	B–A–B	3	6	100	19 (9.0)	16 (9.0)	1.07 (1.09)
75	K+	B–A–B	4	1	100	12 (6.7)	13 (6.8)	1.11 (1.18)
76[g]	K+	B–A–B	4	2	0	24 (10)	g (10)	g (1.08)
77[f,h]	K+	B–A–B	4	3	100	17 (10	18[i]	j
78	K+	B–A–B	4	5	100	15 (6.0)	18 (7.1)	1.19 (1.12)
79[f]	K+	B–A–B	4	6	100	21 (12)	20	1.12
80	K+	B–A–B	5	1	100	16 (8.6)	15 (8.5)	1.16 (1.14)
81[f]	K+	B–A–B	5	2	100	22 (9.4)	22	1.19
82[f]	K+	B–A–B	5	3	100	22 (12)	20	1.14
83	K+	B–A–B	5	4	100	14 (6.2)	13 (6.7)	1.22 (1.09)
84[f]	K+	B–A–B	5	6	100	19 (9.0)	18	1.09
85[g]	K+	A–B	6	1	0	18 (10)	g (10)	g (1.10)
86[h]	K+	B–A–B	6	2	24	19 (9.7)	7.4[i] (6.5)	j (1.05)
87[k]	K+	B–A–B	6	3	100	19 (9.3)	k (7.4)	k (1.05)
88[f]	K+	B–A–B	6	4	100	21 (9.2)	16	1.13
89	K+	B–A–B	6	5	100	19 (11)	18 (8.3)	1.07 (1.09)

[a] Polymerization reaction concerning monomer 4 was carried out at –95 °C to avoid the serious side reaction; see ref 9. [b] Homopolymers were quantitatively obtained at the first-stage polymerization in all cases. [c] Yield of the second-stage polymerization. [d] $\bar{M}_n$(calcd) = [monomer] × (MW of monomer) × f/[initiator] + MW of initiator unit. f = 1 or 2, corresponding to the functionality of the initiators. [e] The molecular weights 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. [f] Homopolymer of the first monomer was not isolated in these cases. [g] No polymerization proceeded at the second stage, resulting in a quantitative recovery of the homopolymer of the first monomer. [h] Side reaction may occur during the second-stage polymerization. [i] The molecular weight of the block copolymer was directly estimated from the GPC calibration using polystyrene standards. [j] A multimodal peak or long tailing of the SEC chromatogram of the product was observed. [k] Initiation efficiency of the crossover reaction was moderate (ca. 80%), resulting in a copolymerization product showing a bimodal molecular weight distribution.

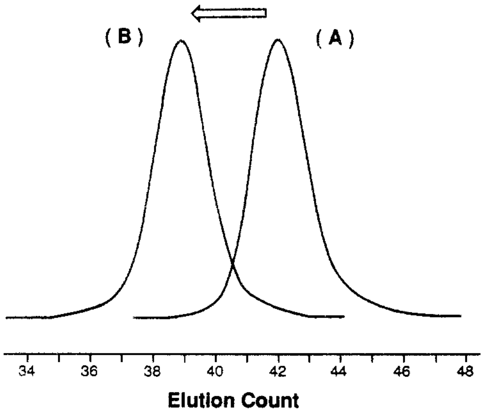


Figure 5. SEC curves (THF) of poly(1) at the first-stage polymerization (A) and of poly(3-*b*-1-*b*-3) (B) (Table V, run 61): peak A, $\bar{M}_n$(obsd) = 11 000, $\bar{M}_w/\bar{M}_n$ = 1.06; peak B, $\bar{M}_n$(obsd) = 19 000, $\bar{M}_w/\bar{M}_n$ = 1.07.

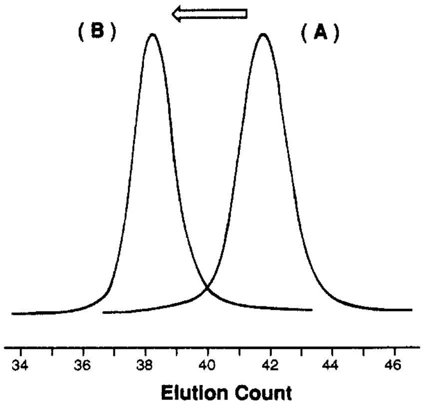


Figure 6. SEC curves (THF) of poly(3) at the first-stage polymerization (A) and of poly(1-*b*-3-*b*-1) (B) (Table V, run 70): peak A, $\bar{M}_n$(obsd) = 9000, $\bar{M}_w/\bar{M}_n$ = 1.06; peak B, $\bar{M}_n$(obsd) = 16 000, $\bar{M}_w/\bar{M}_n$ = 1.05.

all from the fact that the homopolymer at the first stage and the monomer unreacted with quantitatively recovered. A low conversion of 24% could be achieved by the second polymerization of 2 with living poly(6). The SEC chromatogram of the resulting polymer possessed a long low-molecular-weight tailing. Termination was strongly suggested at the second stage of polymerization of 2. Although the polymerization of 3 proceeded quantitatively from living poly(6), the resulting product was a polymer with a bimodal distribution, indicating a mixture of homopoly(6) and the block copolymer. The results clearly indicate low reactivities of living poly(6) toward 1, 2, and 3, respectively. The low reactivity of living poly(6) has thus far prevented the synthesis of well-defined block copolymers by the sequential addition order as shown here. At the sequential addition using living poly(6) as an initiator,

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

	monomer reactivity[b]									
reactivity of living polymer	Isp	St	2VP	1	2	3	4	5	6	tBMA
poly(Isp)$^-$ [c]	+++[d]	+++	+++[e]	+++	+++	+++	+++	+++	+++	+++
poly(St)$^-$ [c]	+++	+++[d]	+++[f]	+++	+++	+++	+++	+++	+++	+++
poly(2VP)$^-$	–	SR[g]	+++[d]	+++	+++	+++	++	+++	+++	++
poly(1)$^-$	–	+	+++	+++[d]	+++	+++	+++	+++	+++	+++
poly(2)$^-$	–	+	++	+++	+++[d]	+++	+++	+++	+++	+++
poly(3)$^-$	–	+	+++	+++	+++	+++[d]	+++	+++	+++	+++
poly(4)$^-$	–	–	SR[g]	+++	–	SR[g]	+++[d]	+++	+++	++
poly(5)$^-$	–	–	+++	+++	+++	+++	+++	+++[d]	+++	+++
poly(6)$^-$	–	–	SR[h]	–	SR[g]	+	+++	+++	+++[d]	+++
poly(tBMA)$^-$	–	–	–	+	+	+	+++	+++	+++	+++[d]

[a] +++: Quantitative initiation efficiency resulting in the block copolymers with narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n < 1.2$). ++: Quantitative initiation efficiency; the polydispersity index ($\bar{M}_w/\bar{M}_n$) of the resulting block copolymer was 1.2–1.4. +: Initiation efficiency of the crossover reaction was not quantitative (2–80%), resulting in a mixture of homopolymer and block copolymer showing a bimodal and broad molecular weight distribution. –: No reaction between the living polymer and the second monomer occurred, resulting in a quantitative recovery of the homopolymer of the first monomer. Most data from Tables II–V. [b] β-Carbon chemical shift of monomer (in ppm): isoprene, 113.5 and 116.7; styrene, 113.8; 2VP, 118.1; **1**, 114.8; **2**, 114.9; **3**, 115.3; **4**, 116.0; **5**, 117.0; **6**, 117.6; tBMA, 124.0. [c] Including the results by using the polymeric carbanion capped with 1,1-diphenylethylene. [d] Postpolymerization. [e] Reference 16. [f] Reference 17. [g] These polymeric products had multimodal and broad molecular weight distributions, probably due to the serious side reaction. [h] An insoluble product was quantitatively obtained from the reaction mixture, probably due to the cross-linking reaction of the polymer.

only combinations of **4** and **5** with living poly(**6**) provide block copolymers having a high degree of block integrity. This is evidenced by the SEC analyses of the resulting polymers which show sharp single peaks eluted on the higher molecular weight sides and the absence of any peaks corresponding to homopolymers.

From the observation at both sequential additions with the living polymers from **4** and **6**, it offers the choice of reversible addition of the following monomer pairs: **1** and **4**, **4** and **5**, **4** and **6**, and **5** and **6**. In the other pairs—**1** and **6**, **2** and **4**, **2** and **6**, **3** and **4**, and **3** and **6**—these types of block copolymers impose the additional restrictions that (a) the low reactive monomer of **1**, **2**, or **3** must be polymerized first and (b) either **4** or **6** is then added to the resulting living polymers. The synthesis of block copolymer must proceed in this order. Furthermore, the reactivities of living poly(**6**) toward monomers **1**–**3** clearly indicate that living poly(**6**) has the lowest nucleophilicity among the living polymers derived from the present six styrene derivatives with electron-withdrawing groups. In comparison with the reactivity of living poly(2VP), living poly(**6**) is evidently much less reactive. Surprisingly, living poly(**6**) appears to have a lower nucleophilicity than living poly(tBMA), which initiates the polymerization of **1** as mentioned before. It can be concluded from the results obtained in this section that reversible block copolymerization among **1**–**6** is possible for most monomer pairs.

Since it is difficult from Tables II–V to see a full view of the block copolymerizations obtained here, we have classified all block copolymerization results[23] into four categories for easy comparison. A summary is listed in Table VI. The first symbol (+++) indicates a successful example of block copolymerization to afford a well-defined block copolymer. The second one (++) means that a sequential block copolymerization occurs with quantitative efficiency, but the resulting block copolymer has a relatively broad distribution of molecular weight ($\bar{M}_w/\bar{M}_n = 1.2$–$1.4$). The third one (+) means that the second-stage polymerization takes place with low initiation efficiency, generally resulting in a mixture of virtual homopolymer and the block copolymer with undesirable structures. The last symbol (–) shows no polymerization at the second stage. From Table VI, the reactivities of monomers and the resulting living polymers are clearly demonstrated. It is especially useful for judgment of the sequential addition order between different monomers in synthesizing a block copolymer.

A wide variety of novel block copolymers have thus been successfully synthesized by using **1**–**6**, isoprene, styrene, 2VP, and tBMA, although the order of addition of monomers is not exchangeable in some combinations. Most of the resulting block copolymers have an excellent degree of block integrity with respect to composition, structure, molecular weight, and molecular weight distribution. The method developed here also is valuable in the synthesis of block copolymers where each or both blocks have polar functional groups in all monomer units.

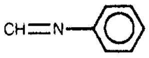
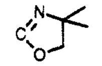
The *N*-cyclohexylimino,[7] oxazolinyl,[8] and *tert*-butyl ester[9] pendant groups on the polymers have been previously reported to be readily deprotected under mild conditions to generate quantitatively more useful formyl and carboxyl functions. The cyano group may also be transformed into many other functional groups, e.g., COOH and CH_2NH_2. Thus, many new block copolymers with other functional groups can be prepared from the block copolymers developed here. The presence of such functionalities in block copolymers may provide practical special advantages in a variety of fields.

Narrow molecular weight distribution is desirable in the synthesis of a block copolymer, although it is not a criterion of living polymerization as emphasized by Quirk.[24] Molecular weight distribution of the resulting polymer is known to be generally sensitive to the polymerization conditions, such as structure and countercation of the initiator, ligand, solvent, and temperature. As mentioned before, we have employed the standard conditions of anionic polymerization as much as possible to compare easily the results of block copolymerization. No attempt was made to optimize the conditions for each of the monomers used here. It would be therefore potentially possible to make the distributions of molecular weight listed in Tables II–V narrower by optimizing the polymerization conditions for each of the cases.

Evaluation of Monomer Reactivity for 1–6 by ^{13}C NMR Measurement. In the preceding sections, the reactivities of new styrene derivatives, **1**–**6**, as well as the resulting living polymers have been evaluated by the results of sequential block copolymerization. Their reactivities are found to be in the range between those of 2VP and tBMA. However, more detailed information on the reactivities of **1**–**6** and their living polymers is not available from the above results.

There have been several previous reports concerning the reactivities of 4-substituted styrenes estimated by

Table VII. Hammett Substituent Parameter and ^{13}C NMR Chemical Shift of the Vinyl β-Carbon for 4-X-Substituted Styrenes

X	C_β[a]	σ_p[b]	X	C_β[a]	σ_p[b]	X	C_β[a]	σ_p[b]
NMe_2	109.3[c]	−0.83	$CONEt_2$ (**1**)	114.8		SO_2NEt_2 (**5**)	117.0	
OMe	111.6	−0.27	 (**2**)	114.9		C≡N (**6**)	117.6	0.66
Me	112.8[c]	−0.17	 (**3**)	115.3		NO_2	118.5	0.78
H	113.8	0.00	COOBut (**4**)	116.0				
Cl	114.4	0.23	COOMe	116.2	0.45			
Br	114.6	0.23	COMe	116.6	0.50			

[a] In $CDCl_3$ in ppm. [b] Reference 29a. [c] Reference 32.

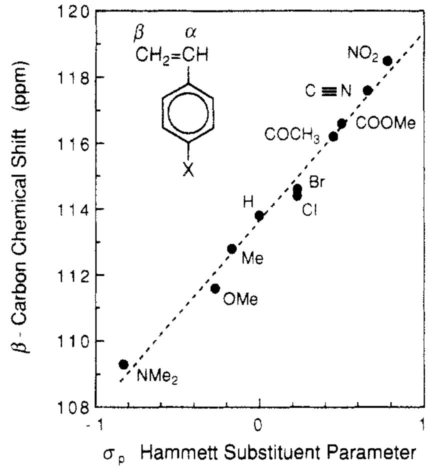


Figure 7. Plot of the β-carbon chemical shifts of the vinyl groups of para-substituted styrenes[32] vs the Hammett σ_p parameters.[29a]

means of various organic reactions such as methoxymercuration,[25] Diels–Alder reaction,[26] free-radical addition reaction,[27] and hydroboration.[28] These reports have revealed the relationship between structure and reactivity and demonstrated that the introduced substituents remarkably affect the reactivities of styrenes. As a generally established parameter to account for the substituent effects, the Hammett σ-value[29] has been effectively employed in these reactions of 4-substituted styrenes.[25–28]

The ^{13}C NMR chemical shifts for aromatic compounds has also been well utilized to determine the electronic effect of the substituent on the phenyl ring for many years. Actually, Dhami and Stothers[30] pointed out a good linear relationship between the Hammett σ-parameter and the β-carbon of the vinyl group of seven 4-substituted styrenes in the range from Me_2N to NO_2 substituents. Figure 7[31] certainly shows a similar linear plot by using the newly reported chemical shifts[32] and substituent values.[29a] More interestingly, Reynolds and co-workers[33] have reported that the chemical shifts of β-carbons of 4-substituted styrenes are precisely related to the π-electron densities at this site calculated by the semiempirical CNDO/2 method. Recent ab initio calculations[34] have again confirmed this linear relationship between the β-carbon chemical shifts and the ab initio π-electron densities. It is therefore possible that the π-electron densities on the carbon–carbon double bonds which might reflect monomer polymerizability of **1**–**6** are estimated from their values of chemical shifts of the β-carbons. This means that the reactivities of **1**–**6** can be evaluated and arranged in reactivity order by measuring the chemical shifts of their β-carbons. The chemical shifts of the β-carbons of **1**–**6** and some styrene derivatives as references are listed in Table VII in addition to the reported Hammett substituent values.[29a]

As can be seen, the values for **1**–**6** (114.8–117.6 ppm) are considerably shifted to lower field than that of styrene (113.8 ppm), as would be expected. This clearly indicates that the π-electron densities on the vinyl bonds of **1**–**6** are decreased to a variety of extents by introducing electron-withdrawing substituents and, in other words, their reactivities increase more than that of styrene under the anionic polymerization condition. The reactivity order increases as follows: styrene < **1** < **2** < **3** < **4** < **5** < **6**.

Similarly, the ^{13}C chemical shift of the terminal benzylic carbanion of the resulting living polymers[35] might indicate the reactivity of the carbabnion, although the data are not currently available. As discussed before, the reactivities of the carbanions from **1**–**6** can be estimated to be in the opposite order of the monomer reactivity. The electron-withdrawing effect of the introduced substituents might contribute to both the enhancement of the monomer reactivity and the stabilization of the propagating carbanion in the same order of strength. Therefore, the reactivity of the carbanion at the growing chain end would be completely opposite to that obtained for the monomer: living polystyrene > living poly(**1**) > living poly(**2**) > living poly(**3**) > living poly(**4**) > living poly(**5**) > living poly(**6**).

As mentioned before, both the reactivities of **1**–**6** and their carbanions were examined by the results of block copolymerization among these and conventional monomers. We have observed that the reactivities of the monomers and the carbanions increase as styrene < **1**–**3** < **4**–**6** and carbanion from **6** < carbanions from **4** and **5** < carbanions from **1**–**3** < styryl anion in these orders, respectively. Evidently, the trends agree very well with those evaluated by the chemical shifts of the β-carbons of **1**–**6** and styrene.

In conclusion, we here recall our synthetic achievement of a series of novel block copolymers with strictly controlled chain architecture by the living block copolymerizations between six 4-substituted styrenes containing electron-withdrawing groups, **1**–**6**, and four conventional monomers. It is evident from the results of crossover reactions that the introduced electron-withdrawing groups play very important roles both in the enhancement of monomer reactivity and in the stabilization of the propagating carbanions of the living polymers. The anionic polymerizabilities of **1**–**6** are apparently higher than that of styrene and are evaluated as being between those of 2VP and tBMA.

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