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Living Anionic Polymerization of 1,4-Diisopropenylbenzene

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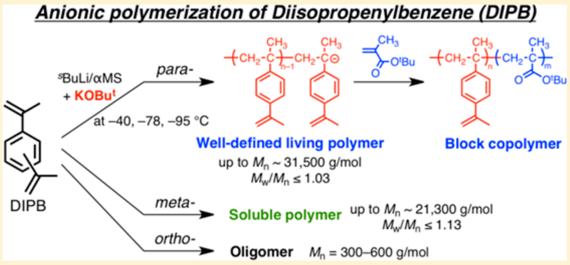
Supporting Information



ABSTRACT: The anionic polymerization of diisopropenylbenzene (DIPB) derivatives was conducted in THF at −78 °C with a specially designed initiator system prepared from oligo(α-methylstyryl)lithium and an excess potassium *tert*-butoxide ($KOBu^t$) (2.7−5.0 equiv to the Li salt). Among the *ortho*-, *meta*-, and *para*-isomers of DIPB derivatives, it was found that the *para*-isomer (*p*-DIPB) successfully underwent the living polymerization in a selective manner through one of the two isopropenyl groups under the above stated conditions. With this living polymerization system, soluble polymers with controllable M_n values ranging from 7620 to 31 500 g/mol and near monodisperse distributions ($M_w/M_n \leq 1.03$) were obtained for the first time. The obtained living polymers were stable at −78 °C even after 168 h and at −40 °C after 6 h, in which the intermolecular addition reaction of the chain-end anion to the pendant isopropenyl group could be completely suppressed. In contrast, the living polymerization of either the *ortho*- or *meta*-isomer was not successful under the same conditions. The block copolymerization of *p*-DIPB with either styrene (S), 2-vinylpyridine (2VP), or *tert*-butyl methacrylate (^{t}BMA) by the sequential addition of such monomers was conducted. Four new PS-*block*-P(*p*-DIPB), P2VP-*block*-P(*p*-DIPB), P(*p*-DIPB)-*block*-P2VP, and P(*p*-DIPB)-*block*-P^{t}BMA containing reactive P(*p*-DIPB) segments were synthesized. On the basis of the block copolymerization results, it is understood that *p*-DIPB is comparable to 2VP and located between S and ^{t}BMA in monomer reactivity. The reactivity increases as follows: S < 2VP ~ *p*-DIPB < ^{t}BMA, while the nucleophilicity of the living chain-end anion decreases in the following order: PS^- > $P2VP^-$ ~ P(*p*-DIPB) $^-$ > P(^{t}BMA) $^-$.

■ INTRODUCTION

It is known that the intermolecular addition reaction of the chain-end anion to the pendant $CH_2{=}CH$ bond significantly occurs during the polymerization of 1,4-divinylbenzene (*p*-DVB). Such the addition reaction results in the formation of highly cross-linked polymers insoluble in solvents. Therefore, *p*-DVB is generally used as a cross-linking agent to prepare micro- and macro-gels, but not considered as a typical monomer.[1−9] In 2011, we successfully found that the oligo(α-methylstyryl)-lithium (αMSLi)-initiated anionic polymerization of *p*-DVB proceeds in a living manner by adding an excess potassium *tert*-butoxide ($KOBu^t$) (10 equiv or more).[10] In this polymerization, one of the two $CH_2{=}CH$ bonds selectively participated the polymerization to quantitatively give the soluble poly(*p*-DVB)s with predictable M_n values up to 60 500 g/mol and near monodisperse distributions ($M_w/M_n \leq 1.05$).[11] The living nature of this system was also guaranteed by the quantitative formation of poly(*p*-DVB)-*block*-poly(2-vinylpyridine) and poly(*p*-DVB)-*block*-poly(*tert*-butyl methacrylate) by the sequential addition of *p*-DVB and then 2-vinylpyridine or *tert*-butyl methacrylate to the above initiator system.[12]

The success of the living anionic polymerization of *p*-DVB may possibly be attributed by the following two issues: First, the ion-dissociation of the chain-end anion may be significantly suppressed by an excess $KOBu^t$ (actually K^+) via the common salt effect. In addition, a steric bulkiness around the chain-end anion may be provided by the coordination of several $KOBu^t$ molecules to the chain-end anion by the ionic interaction. Thus, it is considered that the less dissociate, that is, less reactive and bulkier chain-end anion is formed by the addition of $KOBu^t$. One more important issue is that the reactivity of the pendant $CH_2{=}CH$ bond reduced to some extent by the electron-donating character of the $-CH_2-CH-$ backbone chain formed by the polymerization in comparison to the reactivity of each $CH_2{=}CH$ bond of *p*-DVB. This is clearly evident from the ^{13}C NMR observation that the resonance of 113.9 ppm assigned to the vinyl β-carbon of *p*-DVB is shifted to 113.1 ppm after the polymerization.

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On the basis of the above presumption and observation, the living polymerization of *p*-DVB is considered to proceed in such a way that the less reactive and bulkier chain-end anion preferentially reacts with the more reactive $CH_2{=}CH$ bond (113.9 ppm) of *p*-DVB to initiate the polymerization of *p*-DVB. On the other hand, the less reactive pendant $CH_2{=}CH$ bond (113.1 ppm) incorporated into the backbone chain remains intact during the polymerization.

This success encouraged us to apply the above-designed initiator system, effectively working in the living anionic polymerization of *p*-DVB, to the polymerization of other divinylbenzene derivatives, which were difficult to polymerize in a controlled manner. We now report the possibility of the living anionic polymerization of diisopropenylbenzene (DIPB) derivatives using such an effective initiator system. The DIPB derivatives herein employed involve not only the *para*- but also the *meta*- and *ortho*-isomers to compare the positional effect on the polymerization behavior.

EXPERIMENTAL SECTION

Materials and Instruments. Since all the materials including their syntheses and purification procedures and instruments are the same as those reported in the previous papers,[10−12] they are described in the Supporting Information.

Synthesis of 1,4-Diisopropenylbenzene (*p*-DIPB). After dissolving in 1,4-bis(2-hydroxyisopropyl)benzene in THF, the insoluble portion was removed by filtration. It was further purified by recrystallization from toluene. The reaction mixture of the purified 1,4-bis(2-hydroxyisopropyl)benzene (9.06 g, 46.6 mmol) and *p*-toluenesulfonic acid (10 mg) in toluene (100 mL) was heated at 110 °C for a few hours, while the formed water was removed by a Dean−Stark condenser. After quenching with $NaHCO_3$ aqueous solution, the usual work-up (extraction with diethyl ether, drying over $MgSO_4$, concentration, and column chromatography with hexane) to afford *p*-DIPB as a colorless solid (6.40 g, 40.5 mmol) in 87% yield (mp 62−63 °C). ^1H NMR ($CDCl_3$, 300 MHz; ppm): δ 7.44 (s, 4H, C_6H_4), 5.39 (s, 2H, (*Z*)−$CH_2{=}C(CH_3)\text{-}C_6H_4$), 5.08 (s, 2H, (*E*)−$CH_2{=}C(CH_3)\text{-}C_6H_4$), 2.16 (s, 6H, $CH_2{=}C(CH_3)-$). ^{13}C NMR ($CDCl_3$, 75 MHz; ppm): δ 142.9($CH_2{=}C(CH_3)-$), 140.3, 125.5, 112.4 ($CH_2{=}C(CH_3)-$), and 21.9 ($CH_2{=}C(CH_3)-$).

The syntheses of 1,3-diisopropenylbenzene (*m*-DIPB), 1,2-diisopropenylbenzene (*o*-DIPB), and 1-isopropenyl-3-(α-isopropylethenyl)benzene are described in the Supporting Information.

Polymerization Procedure. All of the polymerizations were conducted according to the usual high vacuum technique with break-seals.[13] Typically, *p*-DIPB was mixed with the initiator prepared from αMSLi and an excess $KOBu^t$ (2.7−5.0 equiv) at −78 °C with vigorous stirring. After allowing to polymerize for a prescribed polymerization time, the usual work-up (quenching with degassed methanol, precipitation in methanol, reprecipitation twice (THF/methanol), and freeze-drying) gave P(*p*-DIPB)s. Since the resulting P(*p*-DIPB)s were not stable in the air for a long time, the freeze-drying was conducted in the dark for overnight. The resulting polymers were stored in ice box (−18 °C) under a N_2 atmosphere to avoid the cross-linking. ^1H NMR ($CDCl_3$, 300 MHz; ppm): δ 7.6−6.2 (br, 4H, $-C_6H_4-$), 5.6−5.2 (br, 1H, (*Z*)−$CH_2{=}C(CH_3)\text{-}C_6H_4\text{-}$), 5.2−4.8 (br, 1H, (*E*)−$CH_2{=}C(CH_3)\text{-}C_6H_4\text{-}$), 2.6 (br, 8H, $-CH_2-C(CH_3)-$). ^{13}C NMR ($CDCl_3$, 75 MHz; ppm): δ 149.7−147.8, 143.2, 137.4, 128.0−123.0, 111.3 ($CH_2{=}C(CH_3)-$), 63.2−58.8, 43.4, 25.6, and 21.8.

The block copolymers were synthesized by the sequential addition of the corresponding monomers to the above-designed initiator system at −78 °C for the times shown in Table 6. The amount of each monomer was also listed in the same table. Typically, the synthesis of P(*p*-DIPB)-*block*-P^{t}BMA was described. Similar to the homopolymerization of *p*-DIPB, *p*-DIPB was polymerized with the above initiator system in THF at −78 °C for 48 h. Then, ^{t}BMA in THF was added to polymerize at −78 °C for 3 h. The same work-up as that used in the homopolymerization gave the expected P(*p*-DIPB)-*block*-P^{t}BMA. The other block copolymers were synthesized by the similar manner as that described above except for the reaction time for each polymerization steps.

RESULTS AND DISCUSSION

In 1978, Okamoto and Mita first reported that *p*-DIPB was anionically polymerized with potassium naphthalenide (K-Naph) in THF at −30 °C to afford a soluble polymer during the early stage of the polymerization.[14] As expected, the gelation by the intermolecular addition reaction of the chain-end anion to the pendant isopropenyl group occurred at the end of the polymerization to afford an insoluble material. Although they indicated that the polymerization was an equilibrium polymerization, no detailed characterization results were available in their paper. Soon after, Lutz, Rempp, and their co-workers also reported the anionic polymerization of *p*-DIPB in THF at −30 °C with 1-phenylethylpotassium.[15] A soluble polymer was obtained in 65% yield after 2 h. The resulting polymer was observed to possess an observed M_n value of 20 900 g/mol by GPC close to that calculated (M_n = 19 500 g/mol) and a somewhat narrow molecular weight distribution (M_w/M_n = 1.25), indicating that the polymerization proceeded in a living manner. However, the broadening of the molecular weight distribution was progressively pronounced as the polymerization proceeded and the insoluble material by cross-linking was formed at the high conversion. The anionic polymerization of the *meta*-isomer (*m*-DIPB) also similarly behaved. Thus, the anionic polymerization of *p*-DIPB or *m*-DIPB could be controlled to a certain extent during the early stage of the polymerization, because of the slow addition reaction, possibly due to the steric bulkier chain-end anion and pendant isopropenyl group.

In 2006, Hirao and his co-workers reported that a structurally analogous 4-isopropenylstyrene substituted with vinyl and isopropenyl groups successfully underwent a selective anionic polymerization through only the vinyl group in a living manner in THF at −78 °C with an initiator bearing K^+ such as K-Naph and cumylpotassium.[16,17] The selective living anionic polymerization was also achieved with αMSLi by the addition of 5 equiv of $KOBu^t$, in which oligo(α-methylstyryl)potassium might be *in situ* formed by exchanging the counteraction from Li^+ to K^+ and work as a real initiator. The soluble poly(4-isopropenylstyrene)s with controllable molecular weights (M_n = 5000−61 000 g/mol) and narrow distributions ($M_w/M_n \leq$ 1.08) were quantitatively obtained. The pendant isopropenyl group completely remained intact for 5 min under the stated conditions. It should be noted that the chain-branching always occurred in the polymerization when used the initiators bearing Li^+ like *sec*-BuLi and αMSLi. Thus, the influence of the countercation on the polymerization behavior is important and critical.

Anionic Polymerization of *p*-DIPB. The anionic polymerization of *p*-DIPB was conducted with αMSLi in the presence of an excess $KOBu^t$, which effectively worked in the living anionic polymerization of both *p*-DVB and 4-isopropenylstyrene, as already mentioned. Although several other potassium alkoxides were found to be also effective in the polymerization of *p*-DVB, $KOBu^t$ was always used throughout this study because it was one of the best additives.[11] The polymerization of *p*-DIPB readily proceeded in THF at −78 °C to afford a soluble polymer in 95% yield after 48 h. The dark red color, characteristic of the living styryl anion derived from *p*-DIPB, remained unchanged during the polymerization. The resulting polymer shows a sharp SEC peak (M_w/M_n = 1.03) without any higher-molecular-weight portion (Figure 1). The observed M_n value (M_n = 7620 g/mol) agreed with that calculated (M_n = 6 750 g/mol) based on the monomer to initiator ratio (Table 1).

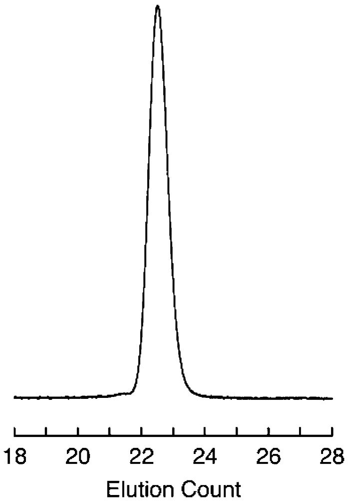


Figure 1. SEC profile of P(*p*-DIPB).

In the ^{1}H NMR spectra of *p*-DIPB and the resulting polymer (see Figure 2, parts a and b), the characteristic resonances at 5.4 and 5.0 ppm to the vinylene ($CH_2{=}C$) protons remained at a 50% intensity, while new peaks (2.0−0.1 ppm) corresponding to the $-CH_2-C-$ protons of the backbone chain appeared, along with two sharp peaks at 2.2−2.0 ppm for the α-CH_3 protons. The ^{13}C NMR spectra also show the similar signal changes before and after the polymerization (see Figure 2, parts c and d). These data clearly demonstrated that *p*-DIPB undergoes the living anionic polymerization in a selective manner through one of the two isopropenyl groups and the thus obtained living polymer is stable at −78 °C for 48 h without occurrence of the intermolecular addition reaction of the chain-end anion to the pendant isopropenyl group. Moreover, the ^{13}C NMR resonance at 112.4 ppm for the vinylene β-carbon of *p*-DIPB was shifted to 111.3 ppm after the polymerization, indicating the lower anionic reactivity of the pendant vinylene group incorporated into the backbone chain as compared to the vinylene group of *p*-DIPB. This is undoubtedly attributed to the electron-donating effect of the $-CH_2-C(CH_3)$- backbone chain.

For the preparation of the high-molecular-weight polymers, a series of polymerizations were conducted by increasing the ratio of monomer to initiator. As shown in Table 1, the M_n value of the polymer could be controlled in the range from 11 200 to 31 500 g/mol. All these polymers possessed near monodisperse distributions ($M_w/M_n \leq 1.03$). The polymerization slowly proceeded and was not complete after 24 h. At the monomer concentration of ca. 0.2 M, the polymer yield was around 90% even after 48 h and nearly quantitative after 168 h. Doubling the monomer concentration (ca. 0.4 M) did not affect the polymerization rate. It was observed under such conditions that the polymerization heterogeneously proceeded because *p*-DIPB was not completely soluble in THF at −78 °C.

The higher-molecular-weight portion was not formed at all in each of the polymers obtained after 24−48 h. A very small amount (~2%) of a dimeric product produced by the same intermolecular 1:1 addition reaction was present in the polymer obtained after 168 h, as shown in Figure 3. We presently consider that this is almost a negligible amount because only 1% of all the polymer chain-end anions may participate in the addition reaction. In contrast to the polymerization of *p*-DVB, in which 10 equiv or more of $KOBu^t$ were required, the use of 2.7 equiv of $KOBu^t$ was sufficient enough to achieve the living polymerization of *p*-DIPB.[18]

Next, the polymerization was conducted by raising the polymerization temperature to −40 °C in order to increase the polymerization rate. In fact, the polymerization rate became much faster at −40 °C and the polymers were obtained in 89 and 92% yields after 2 and 6 h, respectively. The unwanted higher-molecular-weight portion is not formed in each case, as shown in Figure 4, parts 4a and 4b.

The polymer with a M_n value of 15 000 g/mol could also be obtained in 92% yield at −40 °C after 6 h, although a negligible amount (~2%) of the dimeric byproduct was also formed in this case. The amount of the dimer increased up to 15% at −40 °C after 24 h. A very small amount of the trimer was also formed. The deviation of the observed M_n value (M_n = 93 100 g/mol) from that calculated (M_n = 52 100 g/mol) may possibly

Table 1. Anionic Polymerization of *p*-DIPB with Initiators Bearing K$^+$ in THF at −78 or −40 °C

initiator system	temp (°C)	time (h)	conversion (%)[a]	M_n (kg/mol) calcd[b]	SEC[c]	RALLS[d]	M_w/M_n[c]	coupling product[c] (%)
^{s}BuLi/αMS/$KOBu^t$ (4.2 equiv)[e]	−78	48	95	6.75	6.53	7.62	1.03	0
^{s}BuLi/αMS/$KOBu^t$ (4.0 equiv)	−78	24	91	8.82	9.00	11.2	1.03	0
^{s}BuLi/αMS/$KOBu^t$ (5.0 equiv)	−78	48	86	16.7	16.6	19.2	1.02	0
^{s}BuLi/αMS/$KOBu^t$ (4.7 equiv)	−78	168	98	33.7	22.9	31.5	1.02	~ 2
^{s}BuLi/αMS/$KOBu^t$ (4.7 equiv)	−78	24	69	7.66	5.23	7.22	1.05	0
^{s}BuLi/αMS/$KOBu^t$ (4.5 equiv)	−40	2	89	6.76	6.00	7.83	1.04	0
^{s}BuLi/αMS/$KOBu^t$ (4.4 equiv)	−40	6	92	7.79	7.20	8.96	1.07	0
^{s}BuLi/αMS/$KOBu^t$ (4.6 equiv)	−40	6	92	17.3	19.1	15.0	1.03	~2
^{s}BuLi/αMS/$KOBu^t$ (4.1 equiv)	−40	24	94	52.1	70.9	93.1	1.10	15
K-Naph[f]/$KOBu^t$ (6.2 equiv)	−78	24	91	19.0	13.9	15.0	1.08	0
K-Naph	−78	24	91	18.6	15.3	16.5	1.06	9.3

[a] Determined by ^{1}H NMR. [b] M_n(calcd) = (MW of monomer) × (convn)/100 × [monomer]/[initiator] + (MW of initiator fragment). [c] Evaluated by SEC calibrated with polystyrene standards. [d] Evaluated by SEC equipped with triple detectors. [e] Oligo(α-methylstyryl)lithium was prepared from *sec*-BuLi (^{s}BuLi) and a 3-fold excess of α-methylstyrene (αMS).

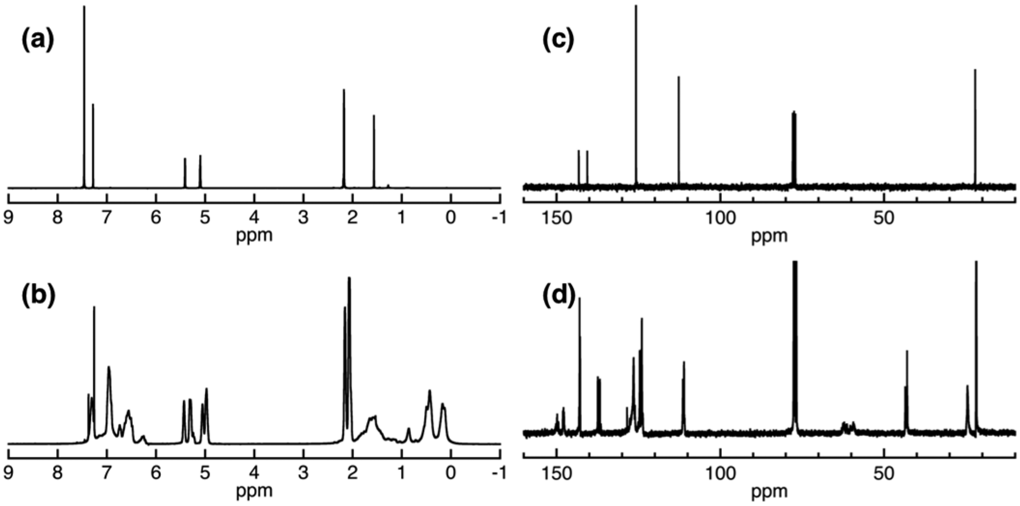


Figure 2. ^{1}H NMR spectra of *p*-DIPB (a) and P(*p*-DIPB) (b) and ^{13}C NMR spectra of *p*-DIPB (c) and P(*p*-DIPB) (d).

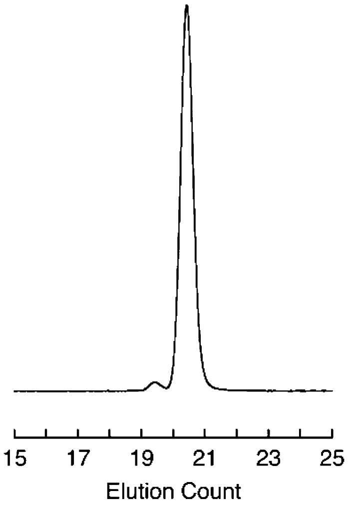


Figure 3. SEC profile of the P(*p*-DIPB) obtained after 168 h.

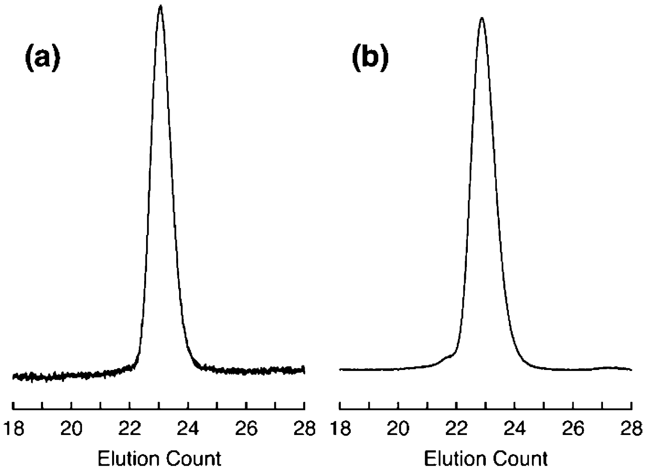


Figure 4. SEC profiles of P(*p*-DIPB)s obtained after 2 h (a) and after 6 h (b).

be due to the impurities in *p*-DIPB. Accordingly, the living polymer was almost stable at −40 °C for 6 h, but the unwanted addition reaction gradually occurred for the longer time of 24 h.

The polymerization of *p*-DIPB also proceeded with K-Naph in the presence of 6.2 equiv of KOBu^t. As also listed in Table 1, a soluble polymer with a narrow molecular weight distribution and a predictable molecular weight was obtained in 91% yield. No higher-molecular-weight portion was present in the resulting polymer. Under the same conditions, a polymer was obtained in 91% yield by the polymerization with K-Naph without KOBu^t. In this case, the dimeric product was formed in 9.3% yield. Once again, the use of excess KOBu^t was found to be essential to suppress the unwanted addition reaction.

The polymerization of *p*-DIPB with *sec*-BuLi at −78 °C was observed to proceed faster than that with the above-prepared initiator. A soluble polymer with a M_n value of 21 500 g/mol was obtained in 98% yield after 15 h as listed in Table 2. However, the higher-molecular-weight portion including not only dimer, but also oligomers, was observed in the resulting polymer (see Figure 5). The higher-molecular-weight portion of 8.5% was already formed in the polymer yield of 50% for 3 h. This clearly indicated that the addition reaction competitively occurs during the polymerization under such conditions. As also seen in Table 2, the addition of either LiOBu^t or LiCl was not effective to suppress the formation of the higher-molecular-weight portion even at −95 °C. Thus, the resulting polymers always included the higher-molecular-weight portions in the polymerization with the initiators bearing Li$^+$, but were completely soluble.

In conclusion, *p*-DIPB underwent living anionic polymerization in a selective manner through one of the two isopropenyl group with the designed initiator system prepared from *α*MSLi and an excess KOBu^t in THF at −78 °C. The polymerization was slow and complete after 168 h. Under such conditions, the living anionic polymer was stable at −78 °C. It was observed that raising the polymerization temperature to −40 °C increased the polymerization rate. The resulting living polymer was stable for 6 h at −40 °C, but the addition reaction gradually occurred after 6 h. The presence of KOBu^t is of course essential to suppress the addition reaction and 2.7 equiv of KOBu^t are sufficient enough in the living polymerization of *p*-DIPB. This is in sharp contrast to the polymerization of *p*-DVB, in which 10 equiv or more of KOBu^t are required to suppress the similar addition reaction even within a few minutes.

Table 2. Anionic Polymerization of *p*-DIPB with Initiators Bearing Li$^+$ in THF at −78 or −95 °C

initiator system	temp (°C)	time (h)	conversion (%)^a	M_n (kg/mol) calcd^b	SEC^c	RALLS^d	M_w/M_n^{c}	coupling product^c (%)
^{s}BuLi	−78	3	50	9.39	8.74	9.91	1.18 (1.03)^e	8.5
^{s}BuLi	−78	15	98	16.4	18.9	21.5	1.11 (1.02)^e	11
^{s}BuLi/LiOBu^t (4.1 equiv)	−78	24	98	16.5	14.8	19.3	1.16 (1.05)^e	11
^{s}BuLi/LiCl (4.4 equiv)	−78	24	99	14.8	15.7	21.9	1.26 (1.02)^e	11
^{s}BuLi	−95	24	27	5.51	4.71	5.00	1.16 (1.04)^e	7.5

^{a}Determined by ^{1}H NMR. $^b M_n$(calcd) = (MW of monomer) × (convn)/100 × [monomer]/[initiator] + (MW of initiator fragment). ^{c}Evaluated by SEC calibrated with polystyrene standards. ^{d}Evaluated by SEC equipped with triple detectors. $^e M_w/M_n$ of main peak.

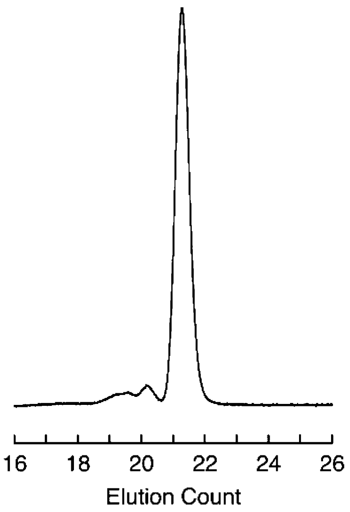


Figure 5. SEC profile of P(*p*-DIPB) obtained with *sec*-BuLi.

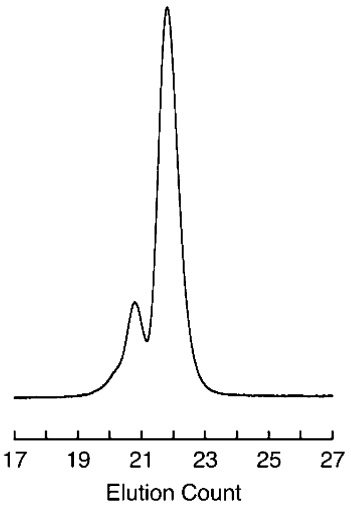


Figure 6. SEC profile of P(*m*-DIPB).

It should be noted that higher-molecular-weight portions gradually increased in the obtained P(*p*-DIPB)s when the polymers were allowed to stock in the air at room temperature. In contrast, they were completely stable even after one year at −18 °C under a nitrogen atmosphere.

Anionic Polymerizations of 1,3- and 1,2-Diisopropenylbenzenes. To study the influence of the substituent position on the polymerization, the polymerizations of 1,3- and 1,2-diisopropenylbenzenes, that is, the *meta*-isomer (*m*-DIPB) and *ortho*-isomer (*o*-DIPB), were conducted under the above-mentioned conditions (Table 3). In the polymerization of *m*-DIPB, the polymer having a controllable M_n value (M_n = 3310 g/mol) and a narrow distribution (M_w/M_n = 1.07) was obtained in 43% yield after 2.5 h. After 24 h, the polymer (M_n = 21 300 g/mol) was obtained in 80% yield. Although the main peak was very narrow (M_w/M_n = 1.04), a dimeric product was formed in 19% yield, as shown in Figure 6. Increasing the amount of KOBu^t to an 11-fold excess slightly decreased the dimer formation to 11%.

Thus, the unwanted addition reaction cannot be suppressed in the polymerization of *m*-DIPB. As illustrated in Scheme 1, the chain-end anion of *p*-DIPB takes five resonance structures, including the pendant isopropenyl group (10π system), while four resonance structures are taken in the case of *m*-DIPB (8π system). Thus, the less stabilized and more reactive chain-end anion may facilitate the addition reaction leading to the chain-branching, like *m*-DVB previously reported.[11]

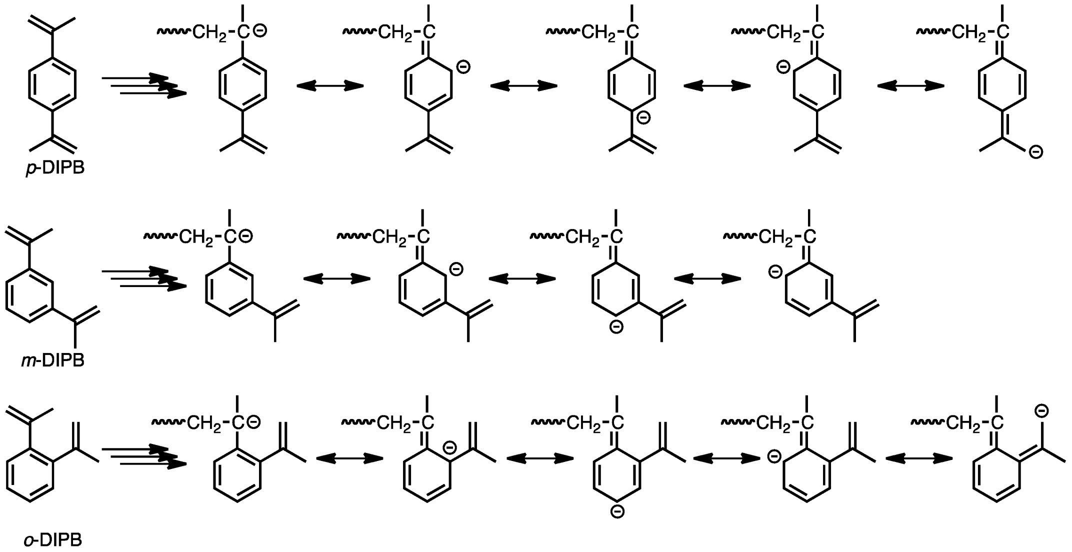
The polymerization of *o*-DIPB was also carried out under the identical conditions. In this case, only a small amount of oligomer (average molecular weight = ca. 600 g/mol) was obtained in 5.9% yield after 24 h. The polymerization was performed by changing the conditions using K-Naph or *sec*-BuLi as the initiator at −78, −40, or even 0 °C. Similar molecular weight oligomers were always obtained in 4−14% yields. The intramolecular cyclization was suggested to partly occur by a ^{1}H NMR analysis of the resulting oligomers, as illustrated in Scheme 2. We initially thought that *o*-DIPB behaved similar to *p*-DIPB during the polymerization, since the intermediate chain-end anion might take five resonance

Table 3. Anionic Polymerization of *m*-DIPB in THF at −78 °C

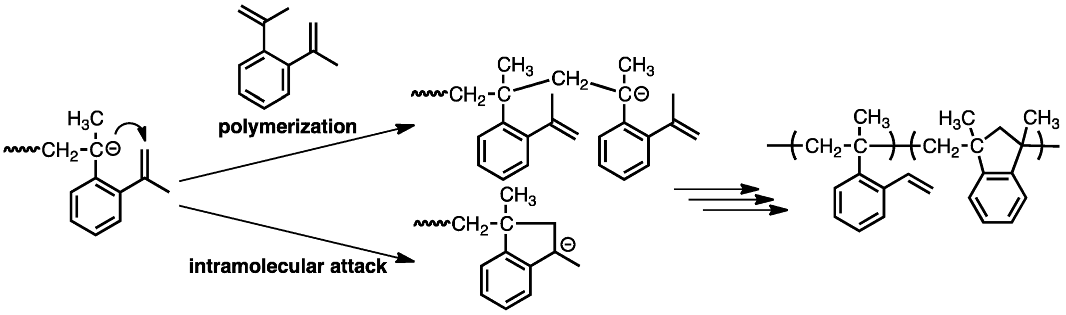
initiator system	time (h)	conversion (%)^a	M_n (kg/mol) calcd^b	SEC^c	RALLS^d	M_w/M_n^{c}	coupling product^c (%)
^{s}BuLi/αMS/KOBu^t (3.7 equiv)	2.5	43	3.41	2.74	3.31	1.07	0
^{s}BuLi/αMS/KOBu^t (5.1 equiv)	24	80	19.0	15.4	21.3	1.10 (1.04)^e	19
^{s}BuLi/αMS/KOBu^t (11 equiv)	24	81	16.4	13.7	16.2	1.13 (1.06)^e	11

^{a}Determined by ^{1}H NMR. $^b M_n$(calcd) = (MW of monomer) × (convn)/100 × [monomer]/[initiator] + (MW of initiator fragment). ^{c}Evaluated by SEC calibrated with polystyrene standards. ^{d}Evaluated by SEC equipped with triple detectors. $^e M_w/M_n$ of main peak.

Scheme 1. Resonance Structures of Chain-End Anions Derived from *p*-, *m*-, and *o*-DIPB



Scheme 2. Intramolecular Cyclization during the Polymerization of *o*-DIPB



structures (see Scheme 1) like the case derived from *p*-DIPB. However, no polymerization occurred after 24 h. The steric hindrance of the *o*-isopropenyl group may be responsible for this, although the reason is not understood at the present time. Thus, the polymerizations of both *m*-DIPB and *o*-DIPB have not yet been successfully controlled.

A new *meta*-substituted monomer with isopropenyl and *α*-isopropylethenyl groups, as shown in Figure 7, was synthesized and polymerized under the similar conditions for 48 h. This monomer underwent the selective polymerization via the polymerizable isopropenyl group in a living manner (see Figure 8 and Table 4). Thus, the introduction of a bulkier isopropyl substituent at the *α*-position of the *m*-vinyl group makes it possible to achieve the living anionic polymerization.

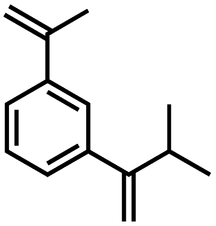


Figure 7. 1-Isopropenyl-3-(*α*-isopropylethenyl)benzene.

Block Copolymerization. Block copolymers are usually synthesized by the sequential addition of two or more different monomers to an anionic initiator.[19] Among the monomers having similar reactivities, the resulting living chain-end anions also show similar reactivities and, therefore, the crossover block copolymerization is possible. In practice, almost all block copolymers can be synthesized by sequentially adding the corresponding monomers according to the block sequences. On the other hand, the synthesis of block copolymers is significantly limited in block type when monomers with

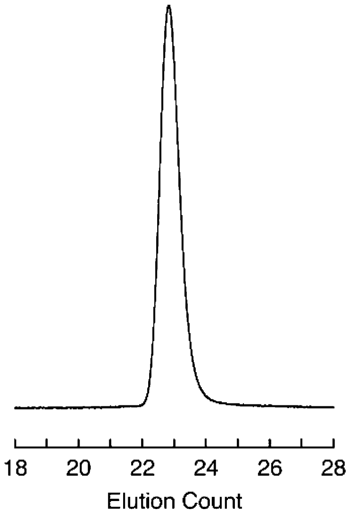


Figure 8. SEC profile of poly(1-isopropenyl-3-(*α*-isopropylethenyl)-benzene).

Table 4. Anionic Polymerization of 1-Isopropenyl-3-(α-isopropylethenyl)benzene in THF at −78 °C

			M_n (kg/mol)			
initiator system	time (h)	conversion[a] (%)	calcd[b]	SEC[c]	RALLS[d]	M_w/M_n[c]
^{s}BuLi/αMS/KOBu^t (4.2 equiv)	48	97	11.3	13.1	14.4	1.04

[a] Determined by ^{1}H NMR. [b] M_n(calcd) = (MW of monomer) × (convn)/100 × [monomer]/[initiator] + (MW of initiator fragment). [c] Evaluated by SEC calibrated with polystyrene standards. [d] Evaluated by SEC equipped with triple detectors.

different reactivities are employed. The success of the block copolymer synthesis strongly depends on the addition order of the monomers, since a more reactive monomer generally produces a less reactive living chain-end anion and vice versa. A serious problem often arises such that the less reactive monomer cannot be polymerized with the less reactive living chain-end anion. The synthesis of the target block copolymer is not possible by this combination. Accordingly, the monomer must be sequentially added in such a way that the less reactive monomer is the first to polymerize, followed by the polymerization of the more reactive monomer.

In order to synthesize new block copolymers containing reactive P(p-DIPB) segments, the sequential polymerization of p-DIPB with either of S, 2VP, or ^{t}BMA was performed under the similar conditions to those used in the homopolymerization of p-DIPB. As already known, the above three monomers in addition to p-DIPB undergo the living anionic polymerization and these three monomers show different monomer reactivities. Both the reactivities of the three monomers and their living chain-end anions are examined based on the previously reported crossover block copolymerization results. With regard to the monomer reactivity, S is the least reactive monomer among them, while ^{t}BMA is the most reactive one. The reactivity of 2VP is positioned between these two monomers. Thus, the monomer reactivity increases as follows: S < 2VP < ^{t}BMA. In contrast, the living chain-end anion reactivity increases in the opposite direction, that is, living poly(^{t}BMA) (P^{t}BMA$^-$) < living poly(2VP) (P2VP$^-$) < living polystyrene (PS$^-$).[19−22] Since PS$^-$ is the most reactive living chain-end anion, both 2VP and ^{t}BMA are readily polymerized with PS$^-$ to afford the well-defined PS-*block*-P2VP and PS-*block*-P^{t}BMA.[23] On the other hand, the least reactive P^{t}BMA$^-$ is not capable of polymerizing the least reactive S and even the less reactive 2VP. As expected, P2VP$^-$ polymerizes the most reactive ^{t}BMA to give a P2VP-*block*-P^{t}BMA. The polymerization of S with P2VP$^-$ occurs only with an insufficient initiation efficiency, followed by the rapid propagation of S. As a result, most of the starting P2VP is recovered and a high-molecular-weight and high PS content P2VP-*block*-PS is obtained. In addition, the generated PS$^-$ was added to some extent to the pyridine C=N moiety. Thus, both the reactivities of the monomers and their chain-end anions are evaluated by the block copolymerization results summarized in Table 5.

Table 5. Summary of Block Copolymerization among S, 2VP, p-DIPB, and ^{t}BMA[a]

	monomer			
polymer anion	S	2VP	p-DIPB	^{t}BMA
PS$^-$	++[b]	++	++	++
P2VP$^-$	+	++[b]	++	++
P(p-DIPB)$^-$	+	++	++[b]	++
P(^{t}BMA)$^-$	−	−	−	++[b]

[a] Key: ++, living polymerization; +, insufficient initiation efficiency; −, no polymerization. [b] Homopolymerization.

The first series block copolymerization, in which S, 2VP, or ^{t}BMA was polymerized, followed by addition of p-DIPB, was conducted. With this series block copolymerization, not only the synthetic possibility of block copolymers, but also the monomer reactivity of p-DIPB will be understood. For the block copolymerization of S with p-DIPB, S was first polymerized for 30 min and then p-DIPB was polymerized with the resulting PS$^-$ for 48 h. The polymer yield was quantitative based on the total weights of S and p-DIPB, indicating that the second-stage polymerization of p-DIPB quantitatively proceeded. The SEC profile exhibited a sharp monomodal peak, while the peak of the starting PS almost disappeared (Figure 9). The characterization results listed in Table 6 and the SEC observation clearly show the successful synthesis of the expected PS-*block*-P(p-DIPB). Similarly, P2VP$^-$ was prepared using the same initiator system, followed by addition of p-DIPB. The polymer yield was quantitative. The SEC peak of the resulting polymer completely moved to the higher-molecular-weight side and the peak of the starting P2VP almost disappeared. Agreements of the M_n values and compositions are satisfactory between the values measured and the calculated ones. Thus, P2VP$^-$ quantitatively initiated the polymerization of p-DIPB to give the expected P2VP-*block*-P(p-DIPB). On the other hand, the polymerization of P^{t}BMA$^-$ with p-DIPB did not occur at all at −78 °C for 48 h and both the p-DIPB monomer and deactivated P(^{t}BMA) were quantitatively recovered. The SEC of the polymer obtained after the second-stage polymerization exhibited the same shape and elution count as that of the starting P^{t}BMA.

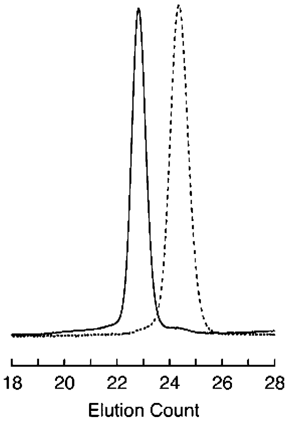


Figure 9. SEC profile of PS-*block*-P(p-DIPB).

With the first series block copolymerization, two new PS-*block*-P(p-DIPB) and P2VP-*block*-P(p-DIPB) were successfully synthesized, while the synthesis of P^{t}BMA-*block*-P(p-DIPB) was not possible because P^{t}BMA$^-$ could not initiate the polymerization of p-DIPB. On the basis of these results, it can be concluded that p-DIPB polymerizable with P2VP$^-$ is more reactive than styrene and appears to be comparable to 2VP in

Table 6. Anionic Block Copolymerization of *p*-DIPB with S, 2VP, or ^{t}BMA with Oligo(α-methylstyryl)lithium and a 3.5-Fold Excess of KOBu^t in THF at −78 °C

monomers				M_n (kg/mol)			composition first/second (mol %)	
first	second	time (h)	conversion (%)[a]	calcd[b]	RALLS[c]	M_w/M_n[d]	calcd	^{1}H NMR
S		0.5	100	6.65	5.89	1.04		
	p-DIPB	48	91	13.9	15.3	1.03	56/44	59/41
2VP		1	100	5.74	6.53	1.18		
	p-DIPB	48	91	14.6	13.8	1.08	47/53	47/53
^{t}BMA		3	100	11.8	9.88	1.09		
	p-DIPB	48	0	29.7	10.3	1.12	41/59	100/0
p-DIPB		48	96	6.32	6.67	1.04		
	S	0.5	100	14.2	15.4	1.22	36/64	31/69
p-DIPB		48	90	5.76	6.38	1.07		
	2VP	1	100	16.9	16.8	1.07	24/76	24/76
p-DIPB		48	95	6.16	7.47	1.04		
	^{t}BMA	3	100	12.9	15.5	1.10	45/55	44/56

[a] Determined by ^{1}H NMR. [b] M_n(calcd) = (MW of monomer) × (convn)/100 × [monomer]/[initiator] + (MW of initiator fragment). [c] Evaluated by SEC equipped with triple detectors. [d] Evaluated by SEC.

monomer reactivity. The reactivity of *p*-DIPB is definitely less reactive than that of ^{t}BMA because *p*-DIPB cannot be polymerized with P^{t}BMA$^-$.

Next, the second series block copolymerization, in which *p*-DIPB was first polymerized to prepare the P(*p*-DIPB)$^-$, followed by addition of S, 2VP, or ^{t}BMA, was conducted under the same conditions as those employed in the first series block polymerization. In the second-stage polymerization of S with P(*p*-DIPB)$^-$, S was quantitatively polymerized at −78 °C for 30 min. The peak of the resulting polymer moved to the higher-molecular-weight side, but rather broad and asymmetric in shape and tailed to the lower-molecular weight side (Figure 10). In addition, the same peak as that of the starting P(*p*-DIPB) remained to a certain extent. This strongly indicated the slow initiation of S with P(*p*-DIPB)$^-$ with an insufficient efficiency in the second-stage polymerization. Thus, a well-defined P(*p*-DIPB)-*block*-PS could not be obtained by this sequential order of the two monomers. This result also indicated that the anionic reactivity of P(*p*-DIPB)$^-$ is somewhat lower than that of PS$^-$, which rapidly and quantitatively initiated the polymerization of S. Two other block copolymers of P(*p*-DIPB)-*block*-P2VP and P(*p*-DIPB)-*block*-P(^{t}BMA) were synthesized without any difficulty by the sequential addition of *p*-DIPB and then 2VP or ^{t}BMA to the initiator under the same conditions.

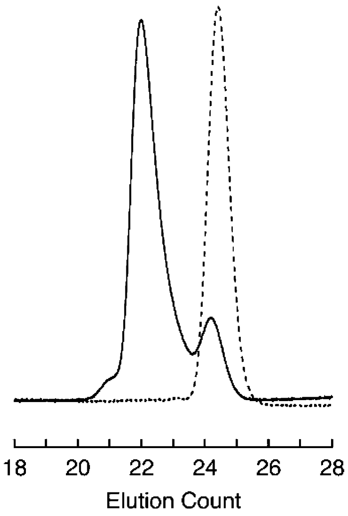


Figure 10. SEC profile of P(*p*-DIPB)-*block*-PS.

The two block copolymers of P(*p*-DIPB)-*block*-P2VP and P(*p*-DIPB)-*block*-P(^{t}BMA) were newly synthesized by the second series sequential polymerization. Their successful syntheses also support the living nature of the polymerization of *p*-DIPB. On the basis of the results, the anionic reactivity of P(*p*-DIPB)$^-$ is slightly lower than that of PS$^-$ and comparable to that of P2VP$^-$ because P(*p*-DIPB)$^-$ can initiate the polymerization of S with an insufficient efficiency and quantitatively polymerizes both 2VP and ^{t}BMA. In our previous study, the living anionic polymer of *p*-DVB could not polymerize S at all under very similar conditions.[12] Accordingly, P(*p*-DIPB)$^-$ appeared to be appreciably higher than P(*p*-DVB)$^-$ in anionic reactivity, possibly to due to the electron-donating character of the α-methyl substituent of the isopropenyl group to increase the electron-density on the chain-end anion.

In conclusion, four block copolymers, that is, PS-*block*-P(*p*-DIPB), P2VP-*block*-P(*p*-DIPB), P(*p*-DIPB)-*block*-P2VP, and P(*p*-DIPB)-*block*-P(^{t}BMA), were successfully synthesized by developing the sequential polymerization procedure. All of them are new block copolymers containing reactive P(*p*-DIPB) segments and well-defined in structure. Throughout the block copolymerization study, as listed in Table 5, *p*-DIPB was understood to be comparable to 2VP and located between S and ^{t}BMA in monomer reactivity, namely, S < 2VP ~ *p*-DIPB < ^{t}BMA. On the other hand, the anionic reactivity of the chain-end anion is shown as follows: PS$^-$ > P2VP$^-$ ~ P(*p*-DIPB)$^-$ > P^{t}BMA$^-$. The newly obtained data on *p*-DIPB by the block copolymerization were added to Table 5.

■ CONCLUSIONS

We have successfully demonstrated that *p*-DIPB undergoes the living anionic polymerization in a selective manner through one of the two isopropenyl groups by the initiator system prepared from αMSLi and excess KOBu^t. The unwanted intermolecular addition reaction of the chain-end anion to the pendant isopropenyl group was almost suppressed at −78 °C for 168 h and at −40 °C for 6 h. Soluble polymers were obtained under such conditions. The molecular weight was precisely controlled in the range from 7 620 to 31 500 g/mol and narrowly distributed, the M_w/M_n values being ≤ 1.03.

In contrast, the anionic polymerization of the corresponding *meta*-isomer proceeded to afford soluble polymers with about 90% yields after 24 h under the same conditions as already stated. However, in all of the polymerizations, the formation of higher-molecular-weight-portions was not avoided. The polymerization of the *ortho*-isomer was more problematic, possibly due to the steric hindrance of the *o*-isopropenyl group. Only small amounts of oligomers (M_n = 300−600 g/mol) were obtained after 24 h.

The block copolymerization was conducted by the sequential addition of *p*-DIPB with either S, 2VP, or ^{t}BMA. With the block copolymerization, in which *p*-DIPB was added as either the first or second monomer, four new well-defined PS-*block*-P(*p*-DIPB), P2VP-*block*-P(*p*-DIPB), P(*p*-DIPB)-*block*-P2VP, and P(*p*-DIPB)-*block*-P^{t}BMA containing reactive P(*p*-DIPB) segments were successfully synthesized. On the basis of the block copolymerization results, it is understood that *p*-DIPB is comparable to 2VP and located between S and ^{t}BMA in monomer reactivity, namely, S < 2VP ∼ *p*-DIPB < ^{t}BMA, while the anionic reactivity of the chain-end anion increases as follows: PS^- > $P2VP^-$ ∼ P(*p*-DIPB)$^-$ > P(^{t}BMA)$^-$.

Finally, it should be mentioned that the anionic polymerization behavior of *p*-DIPB was different from that of *p*-DVB with respect to the stability of the chain-end anion. Under very similar polymerization conditions at −78 °C, P(*p*-DIPB)$^-$ was stable even after 168 h and, on the other hand, P(*p*-DVB)$^-$ retained its stability within a few minutes, although it was stable at least for 30 min at the extremely low temperature of −95 °C. The anionic reactivity of P(*p*-DIPB)$^-$ was appreciably higher than that of P(*p*-DVB)$^-$ from the viewpoint of the possible polymerization of styrene with P(*p*-DIPB)$^-$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and ^{1}H NMR spectra (Figure S1−S12). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.5b00575.

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Notes

The authors declare no competing financial interest.

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