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Living Anionic Polymerization of 4-(α-Alkylvinyl)styrene Derivatives

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Summary. The anionic polymerization of four bis-functionalized styrene derivatives with α-alkylvinyl groups have been carried out in *THF* at $-78°C$ with the initiator prepared from oligo(α-methylstyryl)-lithium and potassium *tert*-butoxide. The four monomers herein used are 4-isopropenylstyrene (**4**), 3-isopropenylstyrene (**5**), 2-isopropenylstyrene (**6**), and 4-(α-isopropylvinyl)styrene (**7**). It was found that under such polymerization conditions, the vinyl groups of both **4** and **7** are selectively polymerized and the isopropenyl and α-isopropylvinyl groups remain completely intact to afford stable living anionic polymers. As expected, the resulting polymers possessed precisely controlled chain lengths and narrow molecular weight distributions. More importantly, they also possessed the pendant isopropenyl and α-isopropylvinyl group in each monomer unit possible for further modification. On the other hand, the anionic polymerization of either **5** or **6** proceeded more or less along with the unwanted side reactions leading to chain-branching, followed by cross-linking. The positional effect of isopropenyl group on the polymerization and the cause of possible side reactions were discussed.

Keywords. Anions; Alkenes; Block copolymerization; Carbanions; Controlled molecular weight.

Introduction

It is known that gelling occurs immediately in the anionic polymerization of 1,4-divinylbenzene (**1**) or its isomers of representative bis-functionalized monomers, resulting in the formation of highly cross-linked materials insoluble in all solvents [1–5]. On the other hand, treatment of 1,3-diisopropenylbenzene (**2**) or 1,4-diisopropenylbenzene (**3**) with an anionic initiator leads to a soluble polymer with a pendant isopropenyl group at up to 50% or even higher conversions [6–8]. In practice, the polymerization proceeded homogeneously and the resulting polymers

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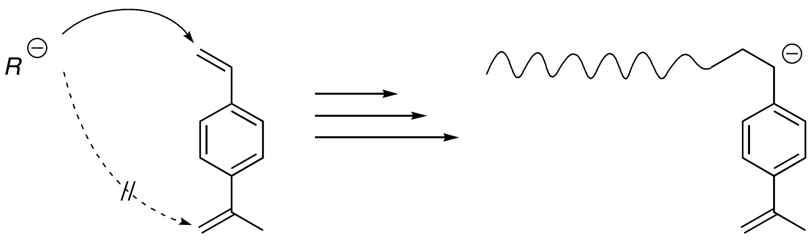
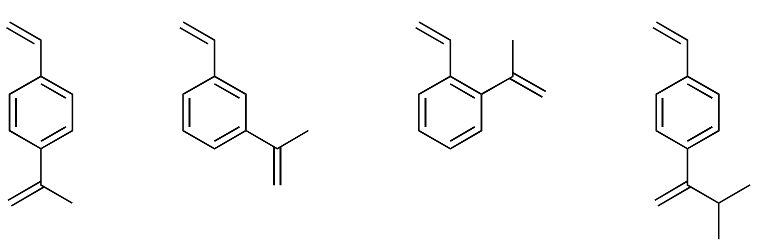


Scheme 1

were essentially linear polymers with relatively narrow molecular weight distributions, their M_w/M_n values being less than 1.3. Thus, diisopropenylbenzenes appear to be different from divinylbenzenes in the anionic polymerization behavior. This may possibly be because the reactivity of isopropenyl group becomes lower than that of vinyl group presumably due to electron donating ability and steric bulkiness of the α-methyl group, although the propagating chain-end anions derived from diisopropenylbenzenes seem more reactive than those derived from divinylbenzenes by the same electronic effect. However, the occurrence of branching, followed by cross-linking was not avoidable at the final stage of the polymerization of diisopropenylbenzenes.

Herein, the question has been raised how the anionic polymerization of a bis-functionalized monomer substituted with both vinyl and isopropenyl groups proceeds. We speculated that if this monomer was treated with an anionic initiator, the vinyl group would be predominantly polymerized and the isopropenyl group would remain as such, since the vinyl group is more reactive than the isopropenyl group and the generated styryl-type anion similar to the **1**-derived anion seems less reactive than the **3**-derived α-methylstyryl-type anion as mentioned above. It is therefore expected that a new living polystyrene functionalized with a pendant isopropenyl group can be produced as illustrated in Scheme 1.

In this study, we report on the anionic polymerization of a series of bis-functionalized monomers substituted with both vinyl and isopropenyl groups in order to examine the possibility of living anionic polymerization. These monomers herein examined are 4-isopropenylstyrene (**4**) and its *meta*- and *ortho*-isomers, 3-isopropenylstyrene (**5**) and 2-isopropenylstyrene (**6**), and one more similar styrene derivative, 4-(α-isopropylvinyl)styrene (**7**), as shown below (Formulae).



4 **5** **6** **7**

monomers

Needless to say, the practical significance of this polymerization lies in the fact that the pendant C=C bonds activated by phenyl groups are available for further modification. This is a part of our program to study the living anionic polymerization of a series of functionalized styrene derivatives [9–12].

Results and Discussion

Anionic Polymerization of ***4***

The anionic polymerization of **4** was first carried out in *THF* at −78°C with *sec-Bu*Li as an initiator. Under such conditions, the polymerization of **4** was very rapid and complete within 5 min. No gelling occurred at all and a soluble polymer was quantitatively obtained. The addition of the first aliquot of **4** to *sec-Bu*Li turns instantaneously to reddish violet in color, indicating the generation of the anion derived from **4**. This color disappeared immediately by quenching with degassed methanol. The polymer was precipitated in methanol and purified by reprecipitation twice from *THF* to methanol and freeze-drying.

The ^{1}H NMR spectrum of the resulting polymer showed that the vinyl group had completely reacted and the signals for the isopropenyl group remained in more than 95%. This indicates that the vinyl group is predominantly polymerized under the conditions employed here. However, the SEC profile exhibits a multimodal distribution broadening from 10^3 to 10^5 in the molecular weight as shown in Fig. 1.

The sharp single peak (A) ($M_{\mathrm{n\ SEC}} = 9.2\,\mathrm{kg/mol}$, $M_w/M_n = 1.06$) corresponds nearly to the molecular weight ($M_n = 8.5\,\mathrm{kg/mol}$) assuming that **4** polymerizes in a living manner. On the basis of these analytical results, we can explain what happens in the anionic polymerization of **4** as follows: At first, **4** undergoes living

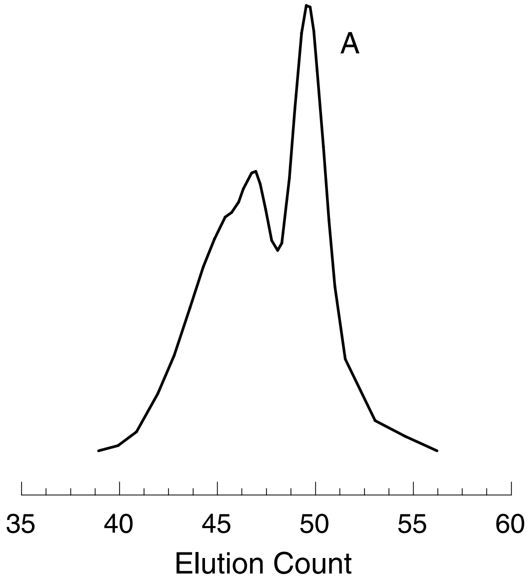


Fig. 1. SEC curve of poly(**4**) obtained with *sec-Bu*Li

polymerization, followed by the attacking of the propagating chain-end anion gradually on the pendant isopropenyl group in another polymer chain, thus leading to chain-branching. A similar result was obtained by the anionic polymerization in *THF* at −78°C with oligo(α-methylstyryl)lithium as an initiator.

In contrast to such results, the treatment of oligo(α-methylstyryl)lithium with potassium *tert*-butoxide (^{t}*Bu*OK) can be very effective to suppress the unwanted side reactions leading to the chain-branching. With this treatment, the counter cation of the initiator was changed from Li^+ to K^+ by shifting the equilibrium. The initiator was prepared by the addition of a 5-fold excess of ^{t}*Bu*OK to oligo(α-methylstyryl)lithium, followed by allowing the mixture to stand for additional

Table 1. Anionic polymerization of **4** in *THF* at −78°C for 5–10 min[a]

Initiator type[b], mmol	**4** mmol	M_n (kg/mol)		
		calcd	obsd[c]	M_w/M_n[c]
*sec-Bu*Li, 0.0751	4.41	8.46	14.9	1.44
*sec-Bu*Li/α-*MeSt*, 0.0578	3.79	9.44	12.1	1.45
*sec-Bu*Li/α-*MeSt*/^{t}*Bu*OK, 0.105	14.5	20.7	21.3 (20.4)[d]	1.02
*sec-Bu*Li/α-*Me*St/^{t}*Bu*OK, 0.104	6.25	9.33	9.24	1.03
*sec-Bu*Li/α-*Me*St/^{t}*Bu*OK, 0.0402	7.33	27.5	25.9	1.02
*sec-Bu*Li/α-*Me*St/^{t}*Bu*OK, 0.0200	8.42	61.4	61.4	1.02
Cumyl-K, 0.0447	5.50	17.7	19.8	1.03
K-Naph, 0.0774	2.88	10.7	16.3	1.06

[a] Yields of polymer were quantitative in all cases; [b] α-*MeSt*: α-methylstyrene, ^{t}*Bu*OK: potassium *tert*-butoxide, Cumyl-K: cumyl potassium, K-Naph: potassium naphthalenide; [c] determined by SEC relative to polystyrene; [d] end-group analysis by ^{1}H NMR (see Ref. [13])

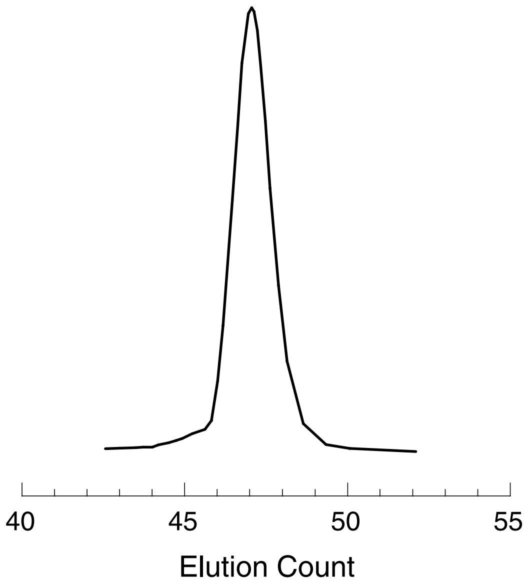


Fig. 2. SEC curve of poly(**4**) obtained with *sec-Bu*Li/α-*MeSt*/^{t}*Bu*OK

10 min. Then, **4** was added to polymerize in *THF* at −78°C for 5 min. The color was immediately changed from orange red to the characteristic reddish violet and remained unchanged until the quenching with degassed methanol. The polymer was obtained quantitatively. The results are summarized in Table 1.

As shown in Fig. 2, the resulting polymer exhibits a sharp monomodal SEC distribution, the M_w/M_n value being 1.02. No higher molecular weight shoulder was present. The M_n value measured by SEC is in good agreement with the calculated value from the ratio of [**4**] to [initiator]. The M_n value determined by the end-group analysis with ^{1}H NMR also agreed well with that calculated [13].

The ^{1}H NMR spectra of **4** and the resulting polymer show that the signals at 6.75, 5.79, and 5.28 ppm (signals (a), (b), and (d) in Fig. 3) corresponding to the vinyl protons completely disappear, while those at 5.43 and 5.12 ppm (signals (c) and (e) in Fig. 3) assignable to the isopropenyl vinylene protons remain in expected intensities (see Fig. 3).

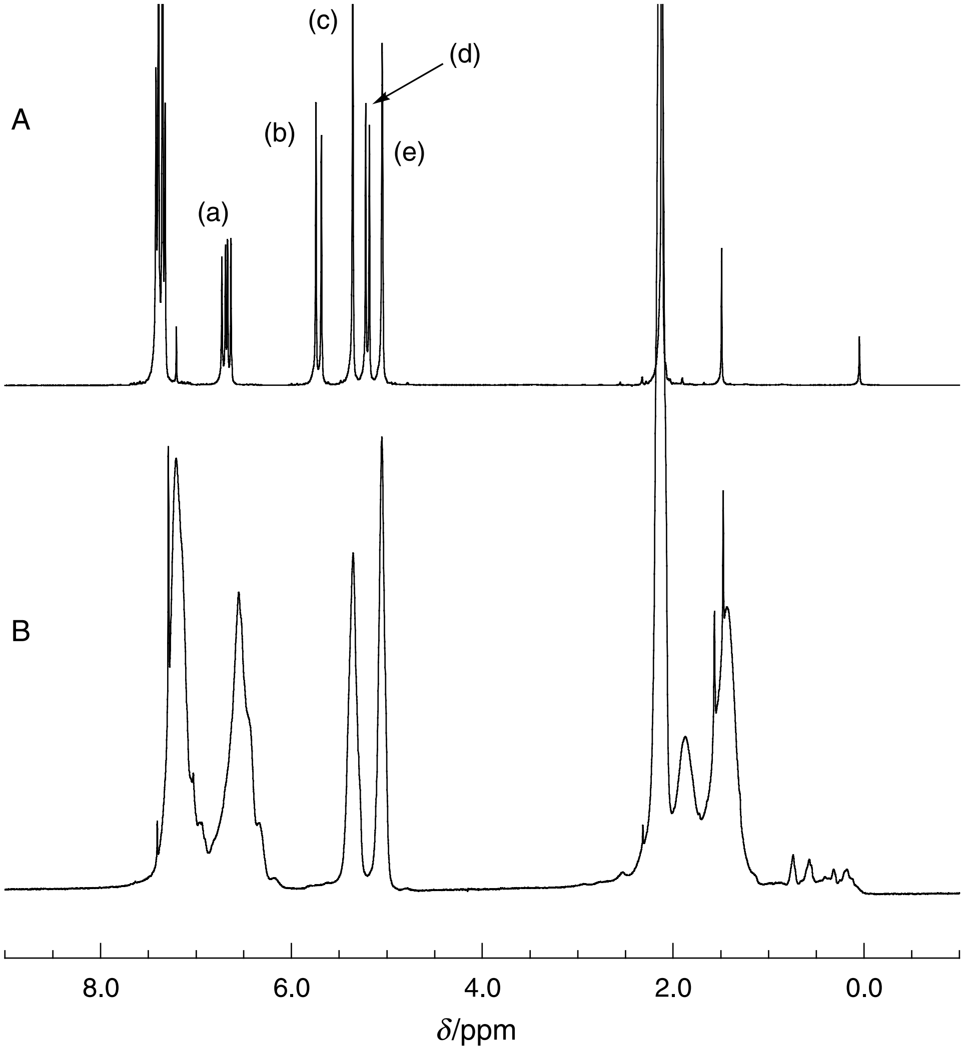


Fig. 3. ^{1}H NMR spectra of **4** (A) and poly(**4**) (B)

Likewise, the ^{13}C NMR analysis also indicates the same conclusion. Thus obviously, all analytical results confirm that the vinyl group of **4** is selectively polymerized in a living manner and the pendant isopropenyl group remained completely intact during and after the conclusion of the polymerization. Thus, the living anionic polymerization of **4** is achieved by using the initiator system prepared from *^{t}Bu*OK and oligo(α-methylstyryl)lithium. In order to further evaluate the usefulness of the initiator system in the polymerization of **4**, three more sets of the polymerization of **4** were carried out at different monomer to initiator ratios under the same conditions. As was seen in Table 1, the difference between predicted and observed molecular weights is less than 10% in each of all instances. Their molecular weight distributions were found to be extremely narrow, the M_w/M_n values being less than 1.03. These results again confirm the living nature of the selective anionic polymerization of **4**. The success of the living anionic polymerization of **4** is undoubtedly resulted from the combination of the less reactive isopropenyl group and the styryl-type anion stabilized *via* resonance of the *para*-substituted isopropenyl group.

The effectiveness of the initiator bearing K^+ as a counter cation was also demonstrated by the successful results of the living anionic polymerization of **4** with either cumylpotassium or potassium naphthalenide as shown in Table 1. This can be explained that the chain-end carbanion with K^+ as a counter cation is more stable than that with Li^+ which is dissociated from the carbanion due to strong coordination by a few *THF* molecules. Thus the anion attack on the pendant isopropenyl group was prevented.

One of the most advantageous features of the living polymerization is to be able to synthesize the block copolymers with precisely controlled structures. The synthesis of two kinds of block copolymers was carried out by a two-step sequential monomer addition, styrene followed by **4** and *vice-versa* with the initiator prepared from *^{t}Bu*OK and oligo(α-methylstyryl)lithium. The first and second polymerization times were 5 min and 5 min, respectively. Yields of the polymers were quantitative in both cases. The results are summarized in Table 2.

Figure 4 shows SEC profiles of the polymers obtained at the first- and second-stages of the block copolymerization where styrene and **4** were added in this order. One can see that the peak (A) of the first-stage polymer disappears completely and moves toward higher molecular weight after the addition of **4**. The molecular weight distribution of the second-stage polymer remains narrow. Agreement between the M_n value as well as the composition observed and those calculated

Table 2. Block copolymerization of **4** and styrene in *THF* at −78°C[a]

Initiator[b] mmol	1st monomer type, mmol	2nd monomer type, mmol	M_n (kg/mol)		
			calcd	obsd[c]	M_w/M_n[d]
0.103	Styrene, 5.25	**4**, 6.95	15.6	16.2	1.04
0.103	**4**, 11.9	Styrene, 6.48	21.4	21.6	1.17

[a] Yields of polymer were quantitative in all cases; [b] *sec-Bu*Li/α-*Me*St/*^{t}Bu*OK; [c] determined by SEC and ^{1}H NMR; [d] determined by SEC

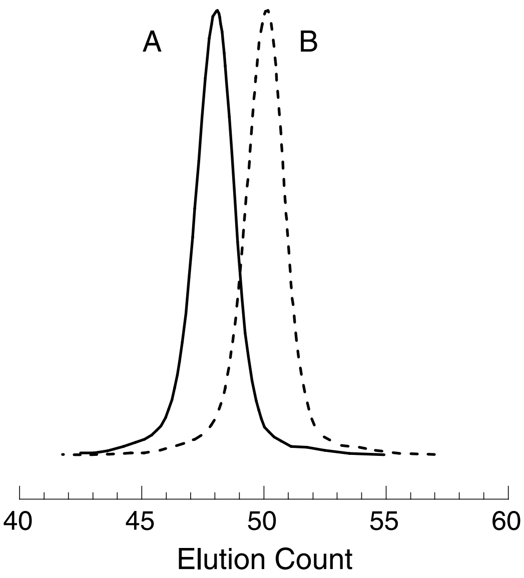


Fig. 4. SEC curves of polystyrene-*block*-poly(**4**) (A) and base polystyrene (B)

is quite satisfactory in the second-stage polymer. Thus, the block copolymerization of styrene followed by **4** proceeded as desired to afford the expected AB diblock copolymer of polystyrene-*block*-poly(**4**). The success of this block copolymerization further confirms the living nature of the polymerization of **4** under the employed conditions.

On the other hand, the block copolymerization by reversing the sequence of monomer addition, namely **4** followed by styrene, was not completely successful under the same conditions. As can be seen in Fig. 5, the formation of a small higher molecular weight shoulder is observed in addition to the main sharp peak corre-

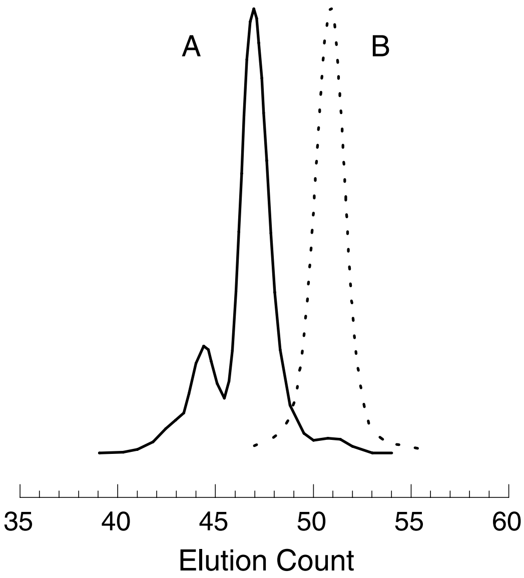


Fig. 5. SEC curves of poly(**4**)-*block*-polystyrene (A) and base poly(**4**) (B)

sponding to the expected BA diblock copolymer. Since a styrene-derived anion generated at the second-stage polymerization seems more reactive than the **4**-derived anion stabilized by the resonance effect *via* the *para*-substituted isopropenyl group, the styrene-derived anion may react gradually with the pendant isopropenyl group. Thus, the addition order of the two monomers is important in the block copolymerization, although the styrene-derived anion can initiate the polymerization of **4** and *vice-versa*.

*Anionic Polymerization of **5** and **6***

In order to elucidate the positional effect of isopropenyl group on the polymerization, the *meta*- and *ortho*-isomers, **5** and **6**, were newly synthesized and polymerized under the same conditions. The anionic polymerization of **5** was similarly carried out in *THF* at −78°C with the initiator prepared from ^{t}*Bu*OK and oligo(α-methylstyryl)lithium. Upon addition of **5** to the initiator, an immediate color change for orange red to dark red occurred. The polymerization of **5** was also rapid and complete within 5 min. A soluble polymer was obtained quantitatively. The ^{1}H NMR analysis of the resulting polymer indicated that the vinyl group of **5** was selectively polymerized. However, a certain amount of higher molecular weight fraction is formed as can be seen in the SEC profile (Fig. 6(A)). By termi-

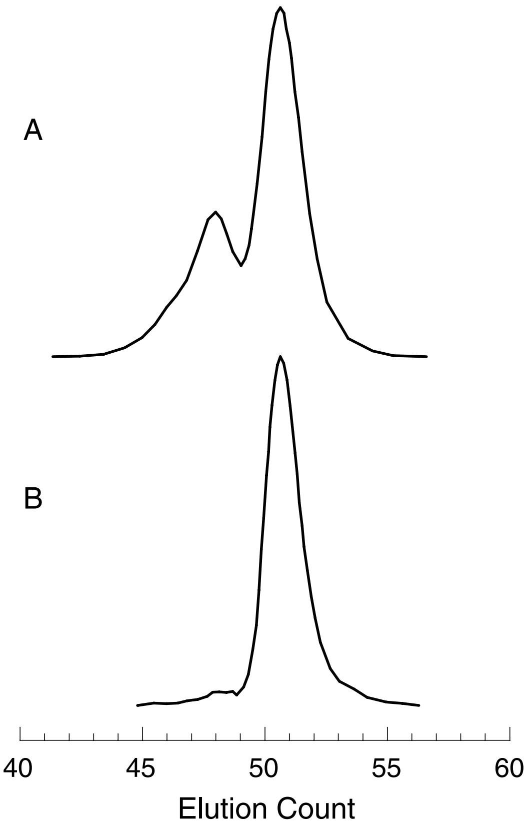
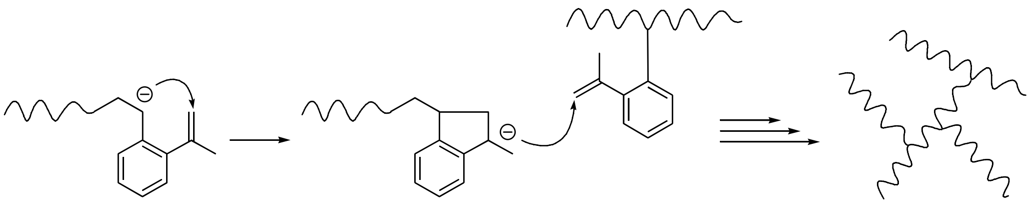


Fig. 6. SEC curves of poly(**5**) terminated after 5 min (A) and 1 min (B)



Scheme 2

nating the polymerization after 1 min, a polymer with a narrow monomodal SEC distribution was obtained in 82% yield (see Fig. 6(B)). The M_n value of this polymer measured by SEC is in good agreement with that calculated. Accordingly, it may be concluded that the anionic polymerization of **5** proceeds in a living manner, followed by the reaction of the living chain-end anion gradually with the pendant isopropenyl group in another polymer chain.

In the anionic polymerization of **6** under the same conditions, turbidity appeared immediately following the addition of **6**, and the precipitate was found within a few second to cause gelation. After 5 min polymerization time, the gel-like insoluble polymer was obtained in 43% yield. By extending the reaction time to 3 h, the insoluble polymer was quantitatively obtained.

As mentioned above, the **4**-derived anion is stabilized by the resonance *via* the *para*-substituted isopropenyl group. On the other hand, the same resonance effect can not be expected for the **5**-derived anion whose isopropenyl group is placed at the *meta*-position. Accordingly, the **5**-derived anion is more reactive than the **4**-derived anion and thereby reacted with the pendant isopropenyl group in the polymer to a certain extent under the same conditions. The **6**-derived anion, similar to the **4**-derived anion, can be stabilized by the resonance *via* the *ortho*-placed isopropenyl group. However, gelling occurred in this polymerization. Therefore, we speculate that the **6**-derived anion once generated reacts intramolecularly with the *ortho*-isopropenyl group to generate a more reactive α-methylstyrene-derived anion, followed by attack of the anion on the pendant isopropenyl group, as illustrated in Scheme 2. Thus, the influence of substitution position of the isopropenyl group is of significance on the anionic polymerization behavior. The *para*-substitution of isopropenyl group is essential to achieve the living anionic polymerization.

Anionic Polymerization of 7

As mentioned in the preceding section, the living anionic polymerization of **4** was successfully demonstrated. It was however observed that the propagating chain-end anion reacted gradually with the pendant isopropenyl group and a small high molecular weight shoulder was produced by allowing the polymerization mixture to stand for additional 20 min under the same conditions. Accordingly, the **4**-derived chain-end anion was not completely stable toward the isopropenyl group in *THF* even at −78°C. In order to suppress such unwanted side reactions, we have synthesized a new styrene derivative **7** in which α-methyl group of the isopropenyl group is replaced by a more sterically bulky isopropyl group.

Table 3. Anionic polymerization of **7** in *THF* at −78°C[a]

Initiator[b] mmol	**7** mmol	time min	M_n (kg/mol)		
			calcd	obsd[c]	M_w/M_n[d]
0.0681	5.29	5	11.7	12.9	1.03
0.0508	6.98	10	20.6	25.2	1.08
0.0916	3.58	60	7.19	7.53	1.04

[a] Yields of polymer were almost quantitative; [b] *sec-Bu*Li/*α-MeSt*/^{t}*Bu*OK; [c] determined by RALLS; [d] determined by SEC

The anionic polymerization of **7** was carried out with the initiator from ^{t}*Bu*OK and oligo(α-methylstyryl)lithium in *THF* at −78°C for 5 min. As expected, the selective living anionic polymerization of **7** was achieved without problem. The ^{1}H NMR analysis of the resulting polymer showed that all the vinyl groups reacted and the α-isopropylvinyl group remained completely intact. In order to examine the stability of the living polymer, the polymerization times were extended to 10 min and 60 min, respectively. Any higher molecular weight shoulder was not observed in the polymer obtained after 10 min or even after 60 min, indicating that the living anionic polymer derived from **7** is much more stable than that derived from **4**. As can be seen in Table 3, a comparison of the calculated and observed M_n values shows good agreement in each instance. These polymers all possessed sharp monomodal SEC distributions. The replacement of methyl group by isopropyl one is thus very effective.

Conclusions

The anionic polymerization of four bis-functionalized styrene derivatives **4**–**7** was investigated under the conditions in *THF* at −78°C mainly with use of the initiator prepared from oligo(α-methylstyryl)lithium and ^{t}*Bu*OK. These monomers herein used were 4-isopropenylstyrene (**4**), 3-isopropenylstyrene (**5**), 2-isopropenylstyrene (**6**), and 4-(α-isopropylvinyl)styrene (**7**). Under such conditions, both **4** and **7** underwent living polymerization where their vinyl groups were selectively polymerized and the isopropenyl and α-isopropylvinyl groups remained completely intact. The resulting polymers possessed precisely controlled chain lengths and narrow molecular weight distributions ($M_w/M_n < 1.08$) as well as the pendant isopropenyl and α-isopropylvinyl groups in all monomer units possible for further modification. In contrast to the successful living polymerization of **4** and **7**, the polymerization of **5** and **6** proceeded more or less along with the unwanted side reactions, resulting in the formation of polymers with chain-branching or insoluble cross-linked polymers. The positional effect of the isopropenyl group is thus crucial to achieve the living anionic polymerization and the *para*-substitution is essential for this purpose.

It was also found that the replacement of the α-methyl group of **4** by a sterically bulkier isopropyl group is effective to stabilize the living anionic polymer derived. In fact, the living polymer derived from **7** was stable and no side reactions occurred at all in *THF* at −78°C even after 1 h. In forthcoming study, the anionic polymerization of a series of structural similar bis-functionalized monomers will be reported in the very near future.

Experimental

Materials

All chemicals (>98%) were purchased from Aldrich, Japan, and used as received unless otherwise stated. 4-Chlorostyrene (>99%, Hokko Chemical Industry Co., Ltd.) was distilled over CaH_2 under reduced pressure. Acetone was distilled over K_2CO_3 under nitrogen. Isobutyric anhydride was distilled over CaH_2 under reduced pressure. Both 2- and 3-bromostyrenes were prepared by the *Wittig* reaction of the corresponding bromobenzaldehyde with methylenetriphenylphosphorane. The resulting styrenes were distilled over CaH_2 under reduced pressures. *THF* was refluxed over Na wire, distilled over $LiAlH_4$ under nitrogen, and then distilled from its sodium naphthalenide solution on a vacuum line. Potassium *tert*-butoxide (^{t}*Bu*OK) was prepared by reacting a stoichiometric amount of *tert*-butanol with potassium naphthalenide in *THF* at -78°C under a high vacuum condition (10^{-6} Torr). Potassium naphthalenide was prepared by the reaction of naphthalene with potassium in *THF*. Cumylpotassium was prepared by the reaction of cumyl methyl ether with K/Na alloy in *THF* according to the previous method [14]. Both oligo(α-methylstyryl)lithium and potassium were prepared by the reaction of *sec-Bu*Li or potassium naphthalenide with a 3-fold excess of α-methylstyrene in *THF* at 25°C for 30 s and subsequently by allowing to stand at -78°C for 15 min.

Measurements

Both ${}^{1}H$ and ${}^{13}C$ NMR spectra were recorded on a Bruker DPX300 in $CDCl_3$. Chemical shifts were recorded in ppm downfield relative to tetramethylsilane ($\delta = 0$) for ${}^{1}H$ NMR and relative to $CDCl_3$ ($\delta = 77.1$) for ${}^{13}C$ NMR. Size exclusion chromatography (SEC) was performed on a Tosoh HLC-8020 with ultraviolet (254 nm) and refractive index detection using *THF* as a carrier solvent at a flow rate of $1.0\,cm^3/min$ at 40°C. Calibration curves were made to determine number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) with standard polystyrene samples. Vapor pressure osmometry (VPO) measurements were made with a Corona 117 instrument in benzene at 40°C with a highly sensitive thermoelectric couple (TM-32K: sensitivity 35 000 $\mu V \pm 10\%/1\,M$) and with equipment of very exact temperature control. Right angle laser light scattering (RALLS) was performed by an Asahi Techneion AT-2002 equiped with a Viscotek TDA model 301 triple detector array using *THF* as a carrier solvent at a flow rate of $1.0\,cm^3/min$ at 30°C.

4-Isopropenylstyrene (**4**)

Under nitrogen, the *Grignard* reagent was prepared by adding slowly 4-chlorostyrene (20.0 g, 144 mmol) to magnesium (4.80 g, 196 mmol) in *THF* ($140\,cm^3$) at 70°C for 1 h, followed by allowing to react at 70°C for additional 2 h. The *Grignard* reagent thus prepared was cooled to 0°C and acetone (11.6 g, 200 mmol) was added dropwise and the reaction mixture was allowed to react at 25°C for additional 15 h. The reaction mixture was then neutralized with 2 *N* HCl, extracted with ether, washed with brine, and dried over $MgSO_4$. Removal of the solvent under reduced pressure yielded crude 4-(2-hydroxy-2-propyl)styrene (23.2 g, 99%). It was used in the next reaction without purification. 4-(2-Hydroxy-2-propyl)styrene (23.2 g, 113 mmol) and a small amount of *p*-toluenesulphonic acid were dissolved in benzene ($80\,cm^3$) and the reaction mixture was refluxed for 3 h. It was then neutralized with $NaHCO_3$, extracted with ether, and dried over $MgSO_4$. Removal of the solvent under reduced pressure followed by column chromatography and fractional distillation (51°C/1 mm Hg) yielded 4-isopropenylstyrene (10.3 g, 50%) as a white crystal (mp 34–35°C). ${}^{1}H$ NMR (300 MHz, $CDCl_3$): $\delta = 7.40$–7.49 (m, 4H, Ar), 6.75 (dd, 1H, $J = 10.9$ and 19.0 Hz, $CH_2{=}C\underline{H}{-}Ar$), 5.28 and 5.79 (2d, 2H, $J = 10.8$ and 17.5 Hz, $C\underline{H}_2{=}CH{-}Ar$), 5.12 and 5.43 (2s, 2H, $C\underline{H}_2{=}C(Ar)CH_3$), 2.19 (s, 3H, $-CH_3$) ppm; ${}^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta = 142.9$ ($CH_2{=}\underline{C}(Ar)CH_3$), 140.7, 136.5, 126.1, 125.7

(Ar), 136.8 ($CH_2{=}\underline{C}H$–Ar), 113.7 ($\underline{C}H_2{=}CH$–Ar), 112.4 ($\underline{C}H_2{=}C(Ar)CH_3$), 21.8 (–$CH_3$) ppm; Anal ($C_{11}H_{12}$): calcd C 91.61, H 8.39; found C 91.62 H 8.39.

3-Isopropenylstyrene (**5**)

The title monomer **5** was similarly synthesized by the reaction of the *Grignard* reagent of 3-bromostyrene with acetone, followed by dehydration. After usual work-up, **5** was purified by column chromatography, followed by fractional distillation at 48°C/2 mm Hg to give 5.83 g (47%) of **5** as a colorless liquid. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.31$–7.43 (m, 4H, Ar), 6.76 (dd, 1H, $J = 10.9$ and 19.0 Hz, $CH_2{=}C\underline{H}$–Ar), 5.19 and 5.70 (2d, 2H, $J = 10.8$ and 17.6 Hz, $C\underline{H}_2{=}CH$–Ar), 5.04 and 5.33 (2s, 2H, $C\underline{H}_2{=}C(Ar)CH_3$), 2.10 (s, 3H, –$CH_3$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 143.2$, 141.6, 128.4, 125.2, 125.1, 123.7 (Ar), 137.5 ($CH_2{=}\underline{C}(Ar)CH_3$), 137.0 ($CH_2{=}\underline{C}H$–Ar), 113.9 ($\underline{C}H_2{=}CH$–Ar), 112.7 ($\underline{C}H_2{=}C(Ar)CH_3$), 22.1 (–$CH_3$) ppm; Anal ($C_{11}H_{12}$): calcd C 91.61, H 8.39; found C 91.63, H 8.39.

2-Isopropenylstyrene (**6**)

The title monomer **6** was similarly synthesized by the reaction of the *Grignard* reagent of 2-bromostyrene with acetone, followed by dehydration. After usual work-up, **6** was purified by column chromatography and fractional distillation twice at 49°C/2 mm Hg to give 2.11 g (21%) of **6** as a colorless liquid. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.06$–7.46 (m, 4H, Ar), 6.84 (dd, 1H, $J = 10.9$ and 19.0 Hz, $CH_2{=}C\underline{H}$–Ar), 5.14 and 5.59 (2d, 2H, $J = 10.8$ and 17.6 Hz, $C\underline{H}_2{=}CH$–Ar), 4.80 and 5.16 (2s, 2H, $C\underline{H}_2 = C(Ar)CH_3$), 1.97 (s, 3H, –$CH_3$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 144.9$ ($CH_2{=}\underline{C}(Ar)CH_3$), 143.0, 134.9, 128.1, 127.6, 127.1, 125.5 (Ar), 135.7 ($CH_2{=}\underline{C}H$–Ar), 123.7 ($\underline{C}H_2{=}CH$–Ar), 112.7 ($\underline{C}H_2{=}C(Ar)CH_3$), 21.9 (–$CH_3$) ppm; Anal ($C_{11}H_{12}$): calcd C 91.61, H 8.39; found C 91.62, H 8.41.

4-(1-Isopropylvinyl)styrene (**7**)

Under nitrogen, the *Grignard* reagent prepared from 4-chlorostyrene (24.7 g, 178 mmol) and magnesium (5.30 g, 218 mmol) in *THF* (100 cm^3) was added dropwise to isobutyric anhydride (43.7 g, 276 mmol) dissolved in *THF* (40 cm^3) at 0°C. The reaction mixture was stirred at 25°C for additional 15 h and neutralized with 2 *N* HCl, extracted with ether, and dried over $MgSO_4$. Removal of the solvent, followed by flash column chromatography (hexanes) yielded 4-vinylisobutyrophenone (17.1 g, 56%) as a viscous yellowish liquid.

Under nitrogen, 4-vinylisobutyrophenone (9.00 g, 51.7 mmol) dissolved in *THF* (40 cm^3) was added dropwise to a *THF* (50 cm^3) solution of methylenetriphenylphosphorane prepared from methyltriphenylphosphonium bromide (22.7 g, 63.6 mmol) and potassium *tert*-butoxide (7.92 g, 70.6 mmol) at 0°C. The reaction mixture was stirred at 25°C overnight and quenched with water. The organic layer was extracted with ether and dried over $MgSO_4$. It was concentrated and poured into hexane to remove triphenylphosphine oxide. After removal of solvents, flash column chromatography (hexanes), followed by fractional distillation twice at 65°C/1 mm Hg gave **7** as a colorless liquid (5.16 g, 61%). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.71$ (dd, 1H, $J = 10.8$ and 17.5 Hz, $CH_2{=}C\underline{H}$–Ar), 5.23 and 5.47 (2d, 2H, $J = 10.8$ Hz, $C\underline{H}_2{=}CH$–Ar), 5.03 and 5.21 (2s, 2H, $C\underline{H}_2{=}C(Ar)CH(CH_3)_2$), 2.77–2.90 (m, 1H, –$C\underline{H}(CH_3)_2$), 1.10 (d, 6H, $J = 6.9$ Hz, –$CH(C\underline{H}_3)_2$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 155.3$ ($CH_2{=}(Ar)CH(CH_3)_2$), 142.3, 130.4, 126.8, 126.1 (Ar), 136.6 ($CH_2{=}\underline{C}H$–Ar), 113.6 ($\underline{C}H_2{=}CH$–Ar), 110.0 ($\underline{C}H_2{=}C(Ar)CH(CH_3)_2$), 32.1 (–$\underline{C}H(CH_3)_2$), 22.1 (–$CH(\underline{C}H_3)_2$) ppm; Anal ($C_{13}H_{16}$): calcd C 90.64, H, 9.31; found C 90.81, H 9.31.

Anionic Polymerization

All the monomers **4**–**7** thus synthesized were distilled over CaH_2 under reduced pressure and finally distilled over dibutylmagnesium (*ca.* 3 mol%) on the vacuum line.

The anionic polymerization was carried out by adding the monomer to an appropriate initiator, followed by allowing to polymerize in *THF* at −78°C under high vacuum conditions in a glass apparatus equipped with break-seals. The polymerization was then carefully terminated with a 5-fold excess of degassed methanol in *THF* at −78°C and the reaction mixture was poured into a large amount of methanol to precipitate the polymer. The polymer was collected by filtration, purified by two reprecipitations from *THF* to methanol, and then freeze-dried from its benzene solution. A typical procedure is as follows: The anionic initiator was prepared by mixing oligo(α-methylstyryl)lithium (0.104 mmol) with ^{t}*Bu*OK (0.625 mmol) in *THF* (20.0 $\mathrm{cm^3}$) at −78°C, followed by allowing the reaction mixture to stand for additional 10 min. To this initiator, **4** (0.901 g, 6.25 mmol) in *THF* solution (10.5 $\mathrm{cm^3}$) chilled to −78°C was added at once with vigorous shaking and the polymerization mixture was allowed to react at −78°C for 5 min. The polymerization was terminated with degassed methanol and the resulting mixture was poured into a large amount of methanol (300 $\mathrm{cm^3}$) to precipitate the polymer. The resulting polymer was reprecipitated twice from its *THF* solution into methanol and freeze-dried from its benzene solution for 24 h.

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[13] The anionic polymerization of **4** was carried out with the initiator prepared from ^{t}*Bu*OK and oligo(α-methylstyryllithium) under the conditions in *THF* at −78°C for 5 min. The living polymer produced was then end-capped with a 1.5-fold excess of 1,1-bis(4-trimethylsilylphenyl)ethylene in *THF* at −78°C for 1 h. The resulting polymer was carefully purified and characterized by ^{1}H NMR (end-group analysis) to determine the M_n value by comparing two signal areas at 6.1–7.6 and 0.2–0.3 ppm assignable to aromatic protons of the main chain and the terminal silylmethyl protons, respectively.

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