

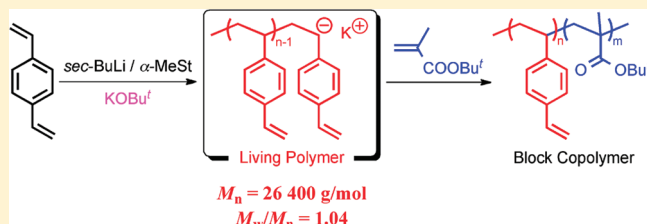
Living Anionic Polymerization of 1,4-Divinylbenzene

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Supporting Information

ABSTRACT: We have successfully realized for the first time the living anionic polymerization of 1,4-divinylbenzene (**1**) with the use of a specially designed initiator system prepared from oligo(α -methylstyryl)lithium and a 11-fold or more excess of potassium *tert*-butoxide. The polymerization was very fast and complete at $-78\text{ }^{\circ}\text{C}$ for 1 min. Soluble polymers having a pendant vinyl group in each monomer unit were always quantitatively obtained under such conditions. The resulting poly(**1**)s possessed predictable molecular weights ($M_n = 11\,000\text{--}26\,400\text{ g/mol}$) and narrow molecular weight distributions ($M_w/M_n < 1.05$). Furthermore, a new well-defined diblock copolymer, poly(**1**)-*block*-poly(*tert*-butyl methacrylate), was also successfully synthesized with the same initiator system by the anionic block copolymerization where **1** and *tert*-butyl methacrylate were sequentially added in this order.



In usual vinyl polymerization, 1,4-divinylbenzene (**1**) and its isomers are widely used as cross-linking agents. In fact, the radical or anionic copolymerization of **1** with other vinyl monomer(s) generally leads to gel formation at an early stage of polymerization, giving cross-linked materials insoluble in all solvents. These cross-linked materials are often utilized as various ion-exchange resins and reactive micro- and macro-gels. By reacting living anionic polymers of styrene, 1,3-butadiene, or isoprene with **1**, many-armed star-branched polymers are readily prepared via addition reaction followed by cross-linking reactions.¹

Surprisingly, soluble lightly branched polymers having a pendant vinyl group can be obtained under appropriate conditions in the anionic polymerization of **1** or the anionic copolymerization of **1** and styrene or 1,3-diene monomers.^{2–11} The formation of a soluble polymer is undoubtedly attributed to the fact that the pendant vinyl group in the polymer chain is much lower in reactivity than the vinyl group(s) in **1** activated by a long conjugation system ranging from the vinyl group to the other one via the phenyl group. Accordingly, the initiation, followed by the propagation reaction, may precede the pendant vinyl group attack by the chain-end anion leading to the cross-linking. Different reactivity between the vinyl groups in **1** and the pendant one is indicated by kinetic studies of the polymerization of **1** and ¹H NMR analysis of the resulting polymers and model compounds.^{2–4,10–12} However, cross-linking among polymers usually occurs at the final stage of the polymerization to result in insoluble polymers even in such polymerizations.

A particular case was reported by Tsuruta, Nagasaki, and their co-workers where soluble polymers were obtained in high yields ($\sim 90\%$) by the anionic polymerization of **1** with lithium diisopropylamide with an excess of diisopropylamine.^{12–16} The

authors suggested that the excess diisopropylamine would play an important role in stabilizing the chain-end carbanion enough to become inactive toward the pendant double bond. However, termination reactions between the excess diisopropylamine and the chain-end anion often occurred during polymerization and, therefore, this system was far from living polymerization.

In this communication, we report on the first successful demonstration of the living anionic polymerization of **1**. In order to examine the polymerization behavior, the polymerization of **1** was carried out under a typical condition of anionic polymerization of styrene derivatives in THF at $-78\text{ }^{\circ}\text{C}$ with *sec*-BuLi. When **1** was mixed with *sec*-BuLi, an orange red color, characteristic of the styryl carbanion derived from **1**, immediately appeared. As expected, an insoluble polymer was quantitatively obtained after 30 min under such conditions. On the other hand, relatively surprisingly, a soluble polymer was produced in 100% yield when the polymerization was quenched after 1 min. As shown in Figure 1a, a SEC profile of the resulting polymer exhibits a multimodal distribution, strongly indicating that the polymer is highly branched in structure, but not a cross-linked product.

The polymerization behavior was not influenced by the addition of a 24-fold excess of LiCl to the polymerization system. In sharp contrast, a remarkable effect was observed by the addition of a 12-fold excess of potassium *tert*-butoxide (KOBu^t) to the same system except for the use of oligo(α -methylstyryl)lithium as the initiator instead of *sec*-BuLi. A soluble polymer having a sharp monomodal SEC distribution ($M_w/M_n = 1.04$) was quantitatively obtained, as shown in Figure 1b. ¹H and ¹³C NMR

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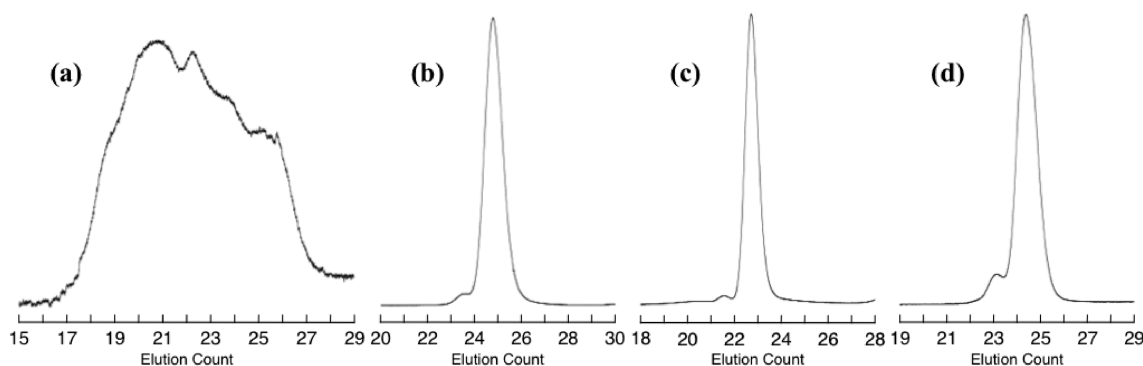


Figure 1. SEC profiles of polymers: (a) DVB-1, (b) DVB-3, (c) DVB-4, and (d) DVB-5.

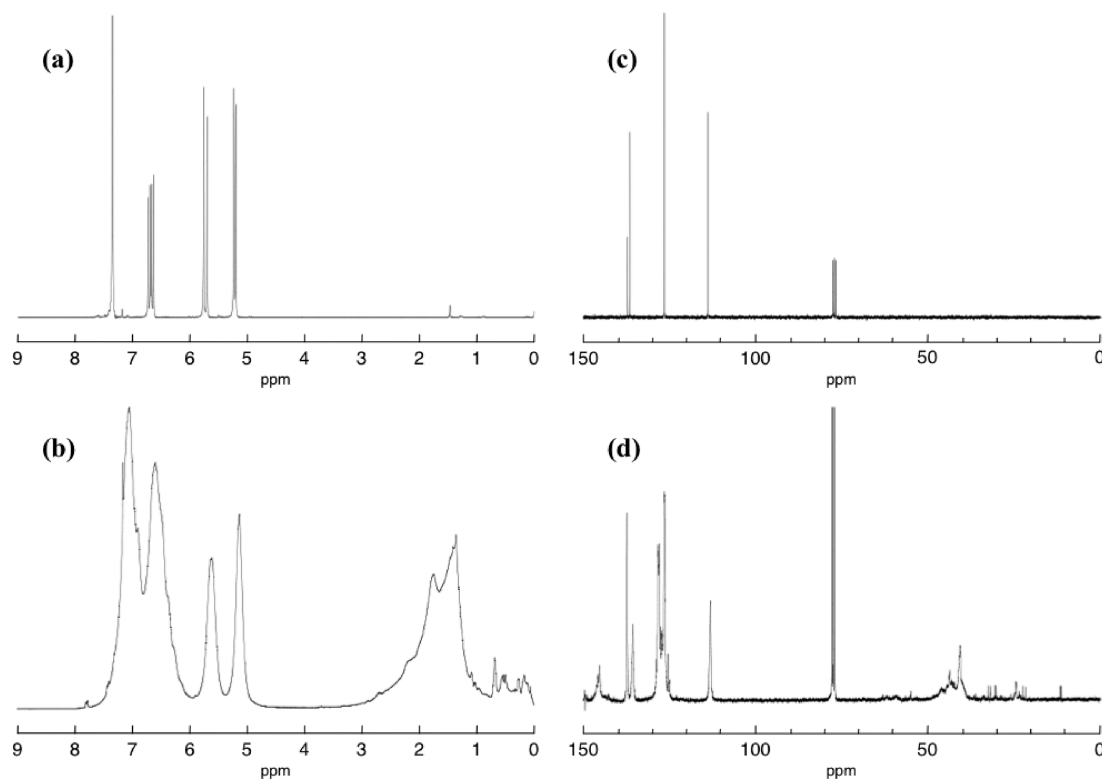


Figure 2. ^1H and ^{13}C NMR spectra of **1** and poly(**1**): (a) ^1H NMR of **1**, (b) ^1H NMR of poly(**1**), (c) ^{13}C NMR of **1**, and (d) ^{13}C NMR of poly(**1**).

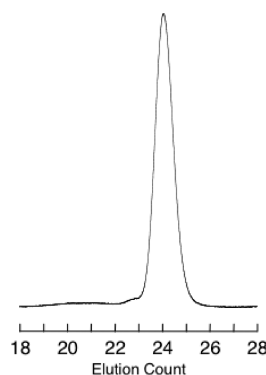
spectra of the resulting polymer as well as **1** are shown in Figure 2, parts a–d. In the ^1H NMR spectrum of the resulting polymer, characteristic signals at 5.61 and 5.13 ppm assigned to methylene ($\text{CH}_2=\text{CH}$) protons of the vinyl groups remained in 50% intensity, while a new broad multimodal peak appeared in the range from 3.0 to 0.80 ppm corresponding to $-\text{CH}_2-\text{CH}-$ protons of the backbone chain. Similar signal changes were also observed in the ^{13}C NMR spectra. These clearly demonstrate that **1** undergoes vinyl polymerization to afford a poly(**1**) having a pendant vinyl group. Furthermore, the resonance of the vinyl β -carbon (in poly(**1**)) was considerably shifted from 113.9 to 113.1 ppm after the polymerization, indicating the lower reactivity (or electrophilicity) of the pendant vinyl group as compared with that of **1**. The characterization results are summarized in Table 1.

The molecular weight determined by SEC-RALLS ($M_n = 11\,300$ g/mol) was in good agreement with that ($M_n = 11\,100$ g/mol) predicted from the ratio of $[\textbf{1}]/[\text{oligo}(\alpha\text{-methylstyryl})\text{lithium}]$ (see run DVB-3). Under the same conditions, a relatively high-molecular-weight polymer with a narrow molecular weight distribution ($M_n = 26\,400$ g/mol and $M_w/M_n = 1.04$) was obtained at a higher monomer to initiator ratio (see Figure 1(c) and run DVB-4 in Table 1). Each of these analytical results is strong proof that the anionic polymerization of **1** proceeds in a living manner and that the pendant vinyl group in the poly(**1**) remains intact during the course of the polymerization. As a matter of fact, the amount of KO^tBu is critical. For instance, a soluble polymer was obtained in 100% yield under similar conditions with a 5.0-fold excess of KO^tBu . However, a SEC trace of the resulting polymer exhibits

Table 1. Anionic Polymerization of **1** in THF at $-78\text{ }^{\circ}\text{C}$ for 1 min^a

run	initiator system	M_n (g/mol)			M_w/M_n^b	
		calcd	SEC ^b	SEC-RALLS ^c	SEC	SEC-RALLS
DVB-1	<i>sec</i> -BuLi	10 600	22 200	—	3.53 ^d	
DVB-2	<i>sec</i> -BuLi/LiCl (24 equiv)	10 600	12 700	25 000	2.22 ^d	
DVB-3	<i>sec</i> -BuLi/ α MS ^e /KO ^t Bu (12 equiv)	11 100	9300	11 300	1.04	1.01 ^c
DVB-4	<i>sec</i> -BuLi/ α MS ^e /KO ^t Bu (12 equiv)	26 000	24 900	26 400	1.04	1.01 ^c
DVB-5	<i>sec</i> -BuLi/ α MS ^e /KO ^t Bu (5.0 equiv)	13 000	11 900	14 300	1.04 ^f	1.01 ^c

^aYields of polymer were almost quantitative in all cases. ^bUsing polystyrene standards calibration curve. ^cDetermined by SEC-RALLS equipped with triple detectors. ^dMultimodal distribution. ^e α -Methylstyrene. ^fA small high molecular weight polymer (*ca.* 7%) was present.

**Figure 3.** SEC profile of AB diblock copolymer, poly(**1**)-*block*-poly(¹BMA).**Table 2.** Anionic Block Copolymerization of **1** and ¹BMA in THF at $-78\text{ }^{\circ}\text{C}$ with Oligo(α -methylstyryl)lithium and KOBu^t for 1 min and 3 h^a

M_n (g/mol)			M_w/M_n^b	composition (w/w)	
calcd	SEC ^b	SEC-RALLS ^c		poly(1)/poly(¹ BMA)	
			SEC	calcd	obsd ^d
17 900	13 100	18 200	1.05 (1.01) ^c	57/43	55/45

^aYield of polymer was quantitative. ^bUsing polystyrene standard calibration curve. ^cDetermined by SEC-RALLS equipped with triple detectors. ^dDetermined by ¹H NMR.

a sharp main peak ($M_w/M_n = 1.04$) together with a peak (*ca.* 7%) as twice the molecular weight, as shown in Figure 1d. The formation of this higher-molecular-weight polymer may result from the addition reaction of the living poly(**1**) to the pendant vinyl group in another polymer chain after the conclusion of the polymerization. Although very small peaks could be observed in Figure 1, parts b and 1c, they were almost negligible (<2%).

The living nature of the polymerization of **1** was further examined using sequential block copolymerization with *tert*-butyl methacrylate (¹BMA). After a complete conversion of **1**, *tert*-butyl methacrylate was added to the polymerization mixture to continue the polymerization at $-78\text{ }^{\circ}\text{C}$ for 3 h. The orange red color of the polymerization mixture turned to almost colorless immediately after the addition of ¹BMA. The polymerization was terminated with degassed methanol and the polymer was precipitated in water. The polymer yield was

quantitative. The resulting polymer, as shown in Figure 3, exhibits a narrow monomodal SEC distribution without the presence of a homopolymer of **1**. The molecular weight and composition of the resulting polymer determined by SEC-RALLS and ¹H NMR agreed well with those calculated, as listed in Table 2. These results clearly confirm that the resulting polymer is the requisite AB diblock copolymer, poly(**1**)-*block*-poly(¹BMA), with expected and well-defined structures. Thus, the living nature of the polymerization of **1** was also supported by the successful formation of the AB diblock copolymer.

In the polymerization of **1** with oligo(α -methylstyryl)lithium having an excess KOBu^t, the counteraction of the resulting living polymer is considered to replace Li⁺ with K⁺ by the presence of excess K⁺. It is also considered that the chain-end anion is considerably shifted to an ion-pair via equilibrium. An additional steric hindrance around the chain-end anion may be provided by the coordination of several KOBu^t molecules. Accordingly, the chain-end anion may possibly be much less reactive than that in the absence of KOBu^t, since the latter chain-end anion bearing Li⁺ is shifted to a highly reactive solvent-separated ion-pair or even a free ion by strongly coordinating several THF molecules to Li⁺. This enables selective living anionic polymerization of **1** under the employed conditions, in which the less reactive chain-end anion may predominately react with the most reactive vinyl group of **1** activated by the long conjugation system but not with the least reactive pendant vinyl group in the polymer chain.

In conclusion, we have realized the living anionic polymerization of **1** with a specially designed initiator system using excess KOBu^t, in which one of the two vinyl groups selectively undergoes polymerization, while the other one remains as such in the side chain. As a result, soluble polymers of **1** with predictable molecular weights and narrow molecular weight distributions as well as a pendant vinyl group in each monomer unit were successfully synthesized. Furthermore, a new well-defined diblock copolymer, poly(**1**)-*block*-poly(¹BMA), could also be synthesized. A more detailed polymerization study of **1** and related divinyl monomers is now under investigation.

■ ASSOCIATED CONTENT

S Supporting Information. Text giving the details for the synthesis of **1**, the anionic polymerization of **1**, and the block copolymerization of **1** and *tert*-butyl methacrylate. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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