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Notes

Preparation of a Polystyrene Macromonomer with a Novel Anionic Initiator Containing an Olefinic Vinyl Group

Atsushi Takano,* Takahiro Furutani, and Yoshinobu Isono

Department of Chemistry, Nagaoka University of Technology, Nagaoka, Niigata 940-21, Japan

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Introduction

Macromonomers are a useful building block to prepare branched polymers such as star-shaped and graft (co)polymers. Various methods, e.g., radical, condensation, and ionic polymerizations, have been applied to the preparation of macromonomers.[1,2] Incidentally, it is well-known that anionic polymerization offers a beneficial method to obtain a "tailor-made polymer" having a definite molecular structure, predictable molecular weight, and narrow molecular weight distribution.[3–12] Hence, an anionic polymerization technique may be useful to prepare a "tailor-made macromonomer".

A macromonomer having an olefinic vinyl group at the chain end may be beneficial. For example, polystyrene having a terminal, olefinic vinyl group can be expected to be copolymerized with olefinic monomer by a Ziegler–Natta catalyst, resulting in formation of polyolefin-*graft*-polystyrene. Olefinic vinyl groups can be modified to another functional group with various reactions, e.g., hydroboration,[13] hydrosilation,[14] and halogenation.[15]

There are two ways to prepare the aimed macromonomer by anionic polymerization: One is to use an initiator having a vinyl group (preintroduction of a vinyl group) and the other is to use a quencher having a vinyl group (postintroduction of a vinyl group). On the one hand, the latter method has the advantage that established anionic polymerization techniques can be applied but has the disadvantage that the degree of introduction of the end group is not necessarily unity.[16,17] On the other hand, the former has the advantage of quantitative introduction of the vinyl group.

The present objective is to prepare polystyrene having one olefinic vinyl group at the chain end, a predictable molecular weight in the range from 1000 and up, and a narrow molecular weight distribution. Hence, the former method is adequate for our purpose. Waack et al. have reported the anionic polymerizations of styrene and similar monomers with vinyllithium and allyllithium as initiators.[18,19] These initiators gave, however, low rate constants in the initiation reactions, which led to broad molecular weight distributions. This may be due to the resonance stabilization of the carbanions. Such a stabilization effect can be avoided by the insertion of some methylene groups as a spacer between the vinyl group and the carbanion. Taking these facts and speculations into consideration, we have synthesized a new initiator, 4-pentenyllithium (**I**).

Table 1. Synthesis of 4-Pentenyllithium[a]

5-bromo-1-pentene (mol)	lithium (mol)	solvent	temp (K)	convn (%)
0.042	0.42	Hp[b]	293	0
0.094	0.65	Hp/ether[c]	195	4
0.055	0.48	Hp/ether[c]	253	38
0.048	0.51	Hp/ether[c]	273	88

[a] Conditions of reaction: time, 24 h; concentration, 2.2–5.4%. [b] *n*-Heptane. [c] Mixture of *n*-heptane/diethyl ether (3/1 in volume ratio).

To obtain a sample having a narrow molecular weight distribution, we need the condition $k_i \gg k_p$, where k_i and k_p are rate constants of initiation and propagation reactions, respectively, particularly in the preparation of a low molecular weight sample.[5] Such a condition can be obtained more easily in a nonpolar solvent such as benzene than in a polar solvent such as tetrahydrofuran.[20] Hence, we adopt benzene as the polymerization solvent in this study.

This paper briefly shows the initiation ability and efficiency of the initiator **I** for styrene in benzene and the preparation of the tailor-made polystyrene having one olefinic vinyl group at the chain end.

Experimental Section

Initiator. 4-Pentenyllithium (**I**) was prepared by the reaction between 5-bromo-1-pentene (**II**) and metallic lithium in an all-glass apparatus equipped with break-seals under a pressure of 1 × 10^{-3} Pa or lower. **II** was purchased from Aldrich Chemical Co., Ltd. (purity 97%). After being purified by fractional distillation and dried over calcium hydride, **II** was transferred to a vacuum apparatus and purified again by distillation in vacuo. The purified **II** and *n*-heptane were introduced into a vacuum apparatus where metallic lithium had been placed. After being vigorously stirred at room temperature for 3 days until the metallic lithium was converted into a dispersible powder, diethyl ether was added and stirred at a given temperature for 1 day to give the initiator. After the mixture solvent, *n*-heptane/diethyl ether, was distilled away, part of the product was removed for ^{1}H NMR measurement. The removed one was dissolved in benzene-d_6 and transferred into an NMR tube followed by being sealed off.[8,9] The remainder was diluted with purified *n*-heptane. The concentration of the initiator was determined by the method of Gilmann et al.[21]

Monomer, Solvents, and Quencher. Styrene was purified in the same way as previously reported.[10] Benzene and tetrahydrofuran (THF) were purified in the same ways as previously reported.[9,10] Trimethylchlorosilane was dried over calcium hydride.

Polymerization of Styrene. Anionic polymerization of styrene with **I** as the initiator was carried out at 293 K in benzene in a sealed glass apparatus under 1 × 10^{-3} Pa or lower, using essentially the same procedure as previously reported.[8–12] After being quenched with trimethylchlorosilane, the polystyrene was precipitated from benzene solution into an excess of methanol. The purified polymer was freeze-dried from the benzene solution for 24 h.

Molecular Characterization. Number-average molecular weights, $\bar{M}_n$, were determined by vapor pressure osmometry (VPO) in toluene at 308 K with a Corona type 117 instrument.

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* To whom correspondence should be addressed.

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Table 2. Anionic Polymerization of Styrene with I in Benzene[a]

no.	I[b] (mmol)	styrene (mmol)	yield (%)	$10^{-3}M_k$[c]	GPC: $10^{-3}\bar{M}_n$	GPC: $\bar{M}_w/\bar{M}_n$	VPO: $10^{-3}\bar{M}_n$	no. of vinyl groups per molecule, N_v: phenyl[d]	no. of vinyl groups per molecule, N_v: trimethylsilyl[e]
1	1.9_4	$33._2$	100	1.9_2	1.9	1.0_7	1.8	0.98 ± 0.04	0.96 ± 0.04
2	1.3_1	$37._4$	100	3.1_1	3.3	1.0_5	3.2	0.97 ± 0.04	0.99 ± 0.04
3	1.8_9	565	100	$31._2$	31	1.0_7			

[a] Conditions of polymerization: temp, 293 K; time, 1 h (no. 1), 3 h (no. 2), 12 h (no. 3); concn, 1.4% (no. 1), 2.1% (no. 2), 3.3% (no. 3). [b] 4-Pentenyllithium. [c] M_k was calculated from the ratio of the amounts of styrene to 4-pentenyllithium. [d] Estimated from the ^{1}H NMR signal intensity ratio of the vinyl to the phenyl protons and the value of M_n by VPO. [e] Estimated from the ^{1}H NMR signal intensity ratio of the vinyl to the CH_3Si protons.

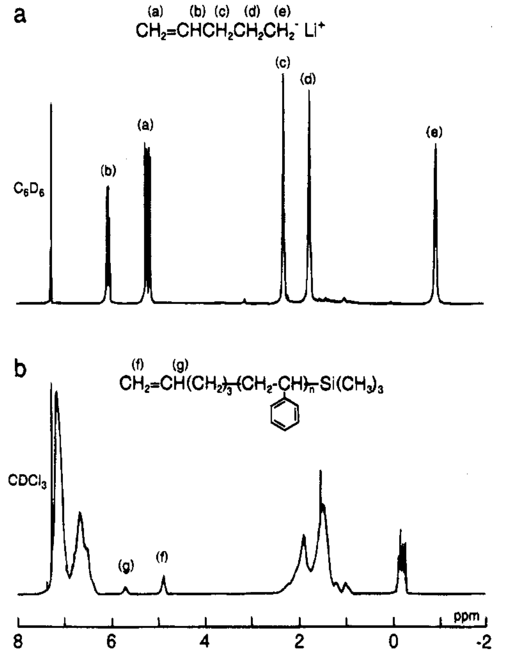

Figure 1. ^{1}H NMR spectra: (a) 4-pentenyllithium in C_6D_6; (b) polystyrene, no. 1, in $CDCl_3$.

Molecular weight heterogeneities, $\bar{M}_w/\bar{M}_n$, where obtained by gel permeation chromatography (GPC) at 298 K using a refractive index detector, RI-8012 (Tosoh Ltd.). The columns were a set of G2000H$_{XL}$, G2500H$_{XL}$, and GMH$_{XL}$ (Tosoh Ltd.) for the lower molecular weight samples ($\bar{M}_n$ < 5000) and a set of three GMH$_{XL}$ for the higher molecular weight sample ($\bar{M}_n$ > 5000). THF was used as an eluent.

^{1}H NMR spectra were obtained with a JEOL EX-400 FT-NMR spectrometer (399.65 MHz). Chemical shifts were referenced to benzene (7.20 ppm) in benzene-d_6 or chloroform (7.26 ppm) in chloroform-d.

Results and Discussion

Synthesis and Characterization of 4-Pentenyllithium. The results of the preparation of 4-pentenyllithium were summarized in Table 1. The reaction between 5-bromo-1-pentene and lithium did not proceed in *n*-heptane at 293 K. However, the reaction products were obtained in a mixture of *n*-heptane/diethyl ether (3/1 in volume ratio). The yield increased with a rise in temperature; 88% at the highest at 273 K.

The ^{1}H NMR spectrum of the product in benzene-d_6 is shown in Figure 1a. The final product was confrimed to be 4-pentenyllithium: 400-MHz ^{1}H NMR (C_6D_6) δ −0.90 (t, 2H, $-CH_2Li$), 1.77 (quint, 2H, $-CH_2-CLi$), 2.48 (quad, 2H, $-CH_2C{=}C$), 5.19 (m, 1H, $^{H}{>}C{=}C{<}_{C-}$), 5.27 (m, 1H, $_{H}{>}C{=}C{<}_{C-}$), 6.08 (m, 1H, $-CH{=}C{<}$).

Polymerization of Styrene with 4-Pentenyllithium. 4-Pentenyllithium has a primary carbanion as *n*-butyllithium has. Hence, the initiation of styrene polymerization by 4-pentyllithium in benzene is rather slow.[22] After styrene was added to 4-pentenyllithium dissolved in benzene, it took several minutes before the color of the solution began to change from the original pale yellow. Over 1/2 h the color gradually changed to deep yellow, which is a characteristic color of poly(styryllithium). This means the initiation in benzene is very slow as presumed. When a small amount of THF, which is known as an initiation promoter,[23] was added to the solution, the color of the solution immediately changed to deep yellow, showing the quick initiation. The color remained unchanged and disappeared instantly upon addition of the quencher, trimethylchlorosilane.

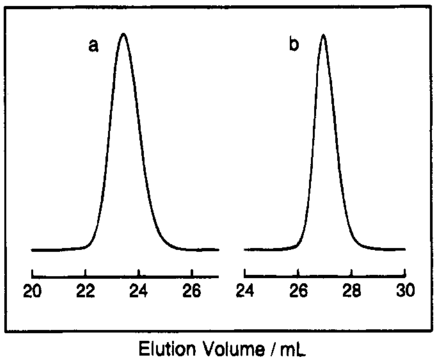

Figure 2. GPC chromatograms of polystyrenes: (a) sample no. 1; (b) sample no. 3. Conditions: eluent, THF at 298 K; flow rate, 1 mL/min; concentration, 0.1 g/dL; RI detector; columns (see text).

The results of the polymerization of styrene with 4-pentenyllithium are listed in Table 2. The polymer yields were quantitative. In all the samples, the values of $\bar{M}_n$ determined by VPO and/or GPC were in agreement with or very close to those of the kinetic molecular weight, M_k, which is calculated from the molar ratio of styrene to 4-pentenyllithium. Hence, it is clear that 4-pentenyllithium has initiation ability and quantitative initiation efficiency for styrene in benzene, where THF is effective as promoter of the initiation reaction.

Figure 2 shows the GPC chromatograms of samples nos. 1 and 3. Sample no. 2 also showed a similar curve. All the samples showed single and narrow peaks, indicating successful living polymerizations of styrene with 4-pentenyllithium. The ^{1}H NMR spectrum of sample no. 1 is shown in Figure 1b. Other samples showed similar spectra. The signals at 4.9 and 5.7 ppm are assigned to vinyl protons. Hence, it is clear that there exists an end vinyl group.

The average number of vinyl groups per molecule, N_v, can be estimated from the signal intensity ratio, i.e., the intensity ratio of the vinyl to the phenyl protons or that of the vinyl to the CH_3-Si protons, and the value of $\bar{M}_n$ by VPO. These values are also listed in Table 2. The estimated values of N_v for both sample nos. 1 and 2 were unity within experimental error.

The results confirm that the resulting polystyrenes have one vinyl group at the end of the chain. Hence, it can be concluded that 4-pentenyllithium can be used as the initiator to obtain a vinyl-ended polystyrene having a predictable molecular weight and a narrow molecular weight distribution.

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