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Protection and Polymerization of Functional Monomers. 19. Synthesis of Well-Defined Poly(ethynylstyrene)s by Means of Anionic Living Polymerization of (Trimethylsilyl)ethynylstyrenes

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ABSTRACT: The anionic polymerizations of the three ethynylstyrenes protected with a trimethylsilyl group have been carried out in THF at −78 °C with a variety of initiators. The monomers involve 4-(trimethylsilyl)-ethynylstyrene (1), 3-(trimethylsilyl)ethynylstyrene (2), and 2-(trimethylsilyl)ethynylstyrene (3) that are isomers with different substituent positions. They are found to undergo anionic living polymerization. The polymers from 1 and 3 were observed to have molecular weights predictable from [M]/[I] ratios and narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n < 1.14$). From the meta isomeric monomer, 2, on the other hand, the polymers with somewhat broad molecular weight distributions ($\bar{M}_w/\bar{M}_n = 1.22$–$1.39$) were obtained, although their observed molecular weights agreed with those predicted. Complete deprotection of the silyl groups from the polymers provides the poly(2-, 3-, and 4-ethynylstyrene)s with well-regulated chain lengths, identical to those of the parents poly(1), poly(2), and poly(3). The poly(4-ethynylstyrene) thus obtained can be quantitatively brominated to give a poly[4-(1,2-dibromoethenyl)styrene] which still retains a narrow distribution of the molecular weight. Some novel block copolymers with a high degree of block integrity are synthesized by using these new living polymers. They are poly[(2-vinylpyridine)-*b*-1-*b*-(2-vinylpyridine)], poly(1-*b*-styrene-*b*-1), poly(1-*b*-isoprene-*b*-1), poly(2-*b*-styrene-*b*-2), poly[(methyl methacrylate)-*b*-3-*b*-(methyl methacrylate)], and poly(3-*b*-styrene-*b*-3).

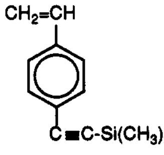
Introduction

In order to synthesize well-defined functional polymers with precisely regulated polymer chain lengths, we have been recently developing a new strategy which combines both the methods of protection and anionic living polymerization of functional monomers.[1] The reason to protect the functional groups is that conventional anionic living polymers from styrene and 1,3-dienes do not tolerate most functional groups. Our strategy involves protection of the functional group of a monomer and the anionic living polymerization of the protected monomer, followed by deprotection to regenerate the original functional group. If this route could successfully be executed, the resulting polymer would have a functional group in each monomer unit and desirable characteristics of the parent living polymer with respect to the main-chain structure.

Through our pioneering work, we have successfully synthesized a variety of polystyrene derivatives mainly para-substituted with functional groups such as OH,[2,3] CH_2CH_2OH,[4,5] NH_2,[6,7] CH_2NH_2 and $CH_2CH_2NH_2$,[8] CHO,[9–11] $COCH_3$,[12] COOH,[13,14] and poly(2-hydroxyethyl methacrylate).[15] Similarly, other research groups also have synthesized poly(4-vinylphenol)[16,17] and poly(methacrylic acid).[18,19] Clearly, this protection–anionic living polymerization–deprotection strategy becomes generally and versatilely used for synthesizing such functional polymers.

As a part of our program to investigate the more general applicability of the above-mentioned strategy, we have focused here on ethynylstyrenes. For the attempted synthesis of poly(ethynylstyrene)s, both the C–H and the $C{\equiv}C$ bonds of ethynyl functions may require protection before their anionic polymerizations. It is known that the proton of the $C{\equiv}CH$ bond is relatively acidic to destroy the highly nucleophilic anionic initiators used for styrene derivatives.[20] Moreover, the $C{\equiv}C$ bond is believed to be susceptible to addition reactions as well as polymerization.[21] Among a number of known protecting groups,[22] the trimethylsilyl group would be the most suitable one for our purpose, since it was reported that the $SiC{\equiv}C$ bonds were stable toward carbanionic species[23] but readily cleaved with F^-[24] or OH^-. In addition, the introduction of a trimethylsilyl group into the β position of the ethynyl function may become more resistant to undesirable nucleophilic addition reaction and anionic polymerization.

In our previous paper,[25] we demonstrated the first successful synthesis of poly(4-ethynylstyrene) with a predictable molecular weight and a narrow molecular weight distribution by the anionic living polymerization of 4-(trimethylsilyl)ethynylstyrene, followed by deprotection of the silyl protecting group. In this paper we report the details of the anionic living polymerization of 4-(trimethylsilyl)ethynylstyrene (1). In addition, the corresponding meta and ortho isomers (2 and 3) are newly synthesized and their anionic polymerizations are attempted, with the ultimate goal of examining the general effectiveness of silyl protection under the anionic polymerization conditions.



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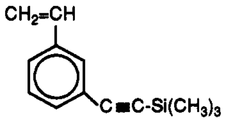

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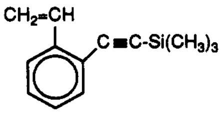

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Experimental Section

Materials. (Trimethylsilyl)acetylene and bis(triphenylphoshine)palladium(II) chloride were kindly supplied by Shinetsu Chemical Industry and N. E. Chemcat, respectively. They were used without further purification. Piperidine was distilled over CaH_2 under an atmosphere of nitrogen. Styrene, α-methylstyrene, methyl methacrylate, and isoprene were washed with 10% NaOH and water and were dried over $MgSO_4$ overnight. After filtration, they were dried over CaH_2 and distilled under a nitrogen atmosphere. Styrene and α-methylstyrene were distilled on a high-vacuum line after addition of appropriate amounts of benzylmagnesium chloride. Methyl methacrylate was distilled over trihexylaluminum on a high-vacuum line. Isoprene was distilled from its *n*-butyllithium solution on a high-vacuum line. 2-Vinylpyridine was distilled twice over KOH and then over CaH_2 under a nitrogen atmosphere. It was distilled on a high-vacuum line after addition of a small amount of *n*-butyllithium. These monomers were diluted with tetrahydrofuran and divided into several ampules with break-seals on the vacuum line. Tetrahydrofuran (THF) was refluxed over a sodium wire and distilled from its $LiAlH_4$ solution under a nitrogen atmosphere. It was distilled from its sodium naphthalenide solution on the vacuum line. Commercially available *n*- and *sec*-butyllithiums were used without further purification. Metal naphthalenides were prepared by the reactions of naphthalene with the corresponding alkali metals in THF at room temperature for 10 h in a sealed reactor with break-seals on the vacuum line. A slightly excess naphthalene was generally used in the reaction. After filtration, their concentrations were determined by colorimetric titration using 1-octanol from a characteristic green to a colorless end point in the sealed reactors via break-seals. Living oligomers of α-methylstyrene were prepared just prior to the polymerization from the metal naphthalenides or butyllithium and a 2–5 times molar excess of α-methylstyrene in THF at 25 °C for 30 s and −78 °C for 10–30 min.

4-(Trimethylsilyl)ethynylstyrene (1). 1 was synthesized by modifying the reaction previously reported.[26] A dry piperidine (730 mL) solution of 2-bromostyrene (33.20 g, 181 mmol), bis(triphenylphosphine)palladium(II) chloride (4.14 g, 5.89 mmol), and copper(I) iodide (0.14 g, 0.73 mmol) was prepared, and nitrogen was then bubbled through this solution for 2 h. (Trimethylsilyl)acetylene (21.41 g, 218 mmol) was added dropwise to the solution at 50 °C, and the mixture was stirred at 50 °C for an additional 6 h under an atmosphere of nitrogen. After filtration of the precipitated piperidinium salt, the solvent was evaporated. The residue was washed with water and extracted with hexane (200 mL × 5). The extract was dried over Na_2SO_4. After filtration and evaporation, column chromatography on silica gel with hexane as an eluent yielded the desired product of 1. It was further purified by fractional distillation at 69–69 °C (0.33 mmHg) to give 16.20 g (80.9 mmol, 45%) of 1 as a colorless liquid: ^1H NMR (90 MHz, $CDCl_3$) δ 7.48–7.25 (m, 4H, Ar), 6.69 (dd, 1H, $CH=$), 5.75, 5.28 (2d, 2H, $J = 17$ and 11 Hz, $CH_2=$), 0.25 (s, 9H, $SiCH_3$); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 137.8 (Ar, C1), 136.3 ($=CH$), 132.2 (Ar, C3), 126.1 (Ar, C2), 122.5 (Ar, C4), 114.8 ($CH_2=$), 105.2 ($ArC\equiv$), 94.8 ($\equiv CSi$), 0.07 ($SiCH_3$); IR (neat, cm^{-1}), 760, 866, 1250 (CSi), 912 ($CH=CH_2$), 2156 ($C\equiv C$).

3-(Trimethylsilyl)ethynylstyrene (2). 2 was obtained by the reaction of 3-bromostyrene (12.1 g, 66.0 mmol) with (trimethylsilyl)acetylene (7.78 g, 7.92 mmol) by a method similar to that in the case of 1. After 2 was isolated by column chromatography, it was further purified by fractional distillation at 91.0–91.5 °C (3.5 mmHg) to give 10.1 g (76%) of 2 as a colorless liquid: ^1H NMR (90 MHz, $CDCl_3$) δ 7.52–7.30 (m, 4H, Ar), 6.67 (dd, 1H, $CH=$), 5.75, 5.27 (2d, 2H, $J = 18$ and 11 Hz, $CH_2=$), 0.26 (s, 9H, $SiCH_3$); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 137.8 (Ar, C1), 136.2 ($=CH$), 131.3 (Ar, C4), 129.9 (Ar, C2), 128.5 (Ar, C6), 123.5 (Ar, C3), 114.7 ($CH_2=$), 105.1 ($ArC\equiv$), 94.3 ($\equiv CSi$), 0.10 ($SiCH_3$); IR (neat, cm^{-1}) 759, 842, 1250 (CSi), 920 ($CH=CH_2$), 2150 ($C\equiv C$).

2-(Trimethylsilyl)ethynylstyrene (3). 3 was obtained by the reaction of 2-bromostyrene (12.1 g, 66.0 mmol) with (trimethylsilyl)acetylene (7.78 g, 7.92 mmol) by a method similar to that in the case of 1. After 3 was isolated by column chromatography, it was further purified by fractional distillation at 84.5–86.0 °C (3.5 mmHg) to give 5.84 g (44%) of 3 as a colorless liquid: ^1H NMR (90 MHz, $CDCl_3$) δ 7.62–7.02 (m, 5H, Ar and $CH=$), 5.85, 5.35 (2d, 2H, $J = 18$ and 11 Hz, $CH_2=$), 0.26 (s, 9H, $SiCH_3$); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 139.4 (Ar, C1), 135.0 ($=CH$), 132.9 (Ar, C3), 128.7 (Ar, C5), 127.4 (Ar, C4), 124.6 (Ar, C6), 121.9 (Ar, C2), 115.6 ($CH_2=$), 103.5 ($ArC\equiv$), 99.2 ($\equiv CSi$), 0.10 ($SiCH_3$); IR (neat, cm^{-1}) 843, 868, 1250 (CSi), 914 ($CH=CH_2$), 2156 ($C\equiv C$).

Homopolymerization. The monomers 1–3 were degassed and stirred over finely ground CaH_2 overnight and were distilled on a vacuum line into a round-bottomed flask equipped with break-seals. After adding 3–5 mol % of benzyl chloride free benzylmagnesium chloride in THF into the monomer through the break-seal, the mixture was stirred for 1 h at room temperature and then distilled on a vacuum line into the break-seal-attached round-bottomed flask prewashed with sodium naphthalenide in THF. The monomer was diluted to 0.2–0.5 M solutions with THF and stored at −30 °C until ready for polymerization. All polymerizations were carried out at −78 °C for 0.5–1 h with shaking under high-vacuum conditions (10^{-6} mmHg) in an all-glass apparatus equipped with break-seals in the usual manner. The desired charge of monomer in THF was added to the THF solution of the initiator with strong shaking. Both the solutions must be kept at −78 °C. The polymerization was terminated with a few drops of degassed methanol after an appropriate time. The polymer was then precipitated by pouring the mixture into a large amount of methanol. It was purified by reprecipitation twice from THF solution to methanol and freeze-dried from the benzene solution. The polymers thus obtained were characterized by ^1H and ^{13}C NMR and IR. Poly(1): ^1H NMR (90 MHz, $CDCl_3$) δ 7.35–7.00 (br s, 2H, Ar), 6.60–6.10 (br s, 2H, Ar), 2.10–0.90 (m, 3H, CH_2CH), 0.24 (s, 9H, $SiCH_3$); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 145.3 (Ar, C1), 132.1 (Ar, C3), 127.6 (Ar, C2), 120.8 (Ar, C4), 105.5 ($ArC\equiv$), 93.7 ($\equiv CSi$), 43.6 (CH), 40.6 (CH_2), 0.2 ($SiCH_3$); IR (KBr, cm^{-1}) 759, 868, 1250 (CSi), 2159 ($C\equiv C$). Poly(2): ^1H NMR (90 MHz, $CDCl_3$) δ 7.55–6.05 (m, 4H, Ar), 2.30–0.80 (m, 3H, CH_2CH), 0.21 (s, 9H, $SiCH_3$); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 144.8 (Ar, C1), 130.9 (Ar, C2), 130.0 (Ar, C4 and C5), 128.2 (Ar, C6), 123.0 (Ar, C3), 105.7 ($ArC\equiv$), 93.6 ($\equiv CSi$), 43.0 (CH), 40.4 (CH_2), 0.3 ($SiCH_3$); IR (KBr, cm^{-1}) 759, 842, 1250 (CSi), 2156 ($C\equiv C$). Poly(3): ^1H NMR (90 MHz, $CDCl_3$) δ 7.65–6.25 (br s, 4H, Ar), 3.25–2.10 (m, 1H, CH), 1.90–0.80 (m, 2H, CH_2), −0.03 (br s, 9H, $SiCH_3$); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 147.5 (Ar, C1), 133.3 (Ar, C3), 128.5 (Ar, C5), 126.9 (Ar, C6), 125.1 (Ar, C4), 122.5 (Ar, C2), 104.7 ($ArC\equiv$), 97.2 ($\equiv CSi$), 47.0 (CH), 40.8 (CH_2), 0.3 ($SiCH_3$); IR (KBr, cm^{-1}) 841, 868, 1250 (CSi), 2154 ($C\equiv C$).

Block Copolymerization. Block copolymerizations were carried out by the sequential addition of two different monomers. The first-stage polymerization was carried out in THF at −78 °C in a manner similar to the homopolymerization and somewhat sampled to determine the characteristics. The second block was prepared by adding an appropriate amount of second monomer to the living polymer produced in the first-stage polymerization. After quenching with degassed methanol, the polymer was precipitated in methanol, purified by reprecipitation twice, and then freeze-dried. Yields were quantitative in all runs. They were characterized by IR, ^1H and ^{13}C NMR, SEC, and VPO.

Deprotection of Poly[(trimethylsilyl)ethynylstyrene]s. Poly(1) (0.320 g, 1.6 mmol based on a (trimethylsilyl)ethynylstyrene unit) was dissolved in dry THF (10 mL), and the solution was cooled at 0 °C. $(C_4H_9)_4NF$ in THF (1 M, 3.3 mL) was added to the solution, and the mixture was stirred at 0 °C for 1 h. The polymer was precipitated in methanol and purified twice by reprecipitation using a THF–methanol system. The yield of polymer was quantitative. The polymer was identified as poly(4-ethynylstyrene) from the following analyses: ^1H NMR (90 MHz, $CDCl_3$) δ 7.40–6.20 (m, 4H, Ar), 3.04 (s, 1H, $C\equiv CH$), 2.30–0.70 (m, 3H, CH_2CH); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 145.8 (Ar, C1), 132.1 (Ar, C3), 127.6 (Ar, C2), 119.9 (Ar, C4), 83.8 ($ArC\equiv$), 77.1 ($\equiv CH$), 43.0 (CH), 40.8 (CH_2); IR (KBr, cm^{-1}) 2109 ($C\equiv C$), 3294 ($\equiv CH$).

Similarly, the deprotection of trimethylsilyl groups from poly(2) and poly(3) was carried out. Yields of polymers were quantitative in both cases. They were identified as poly(3-ethynylstyrene) and poly(2-ethynylstyrene), respectively. The analytical results are as follows.

Poly(3-ethynylstyrene): ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.55–5.95 (m, 4H, Ar), 3.01 (s, 1H, C≡CH), 2.30–0.60 (m, 3H, CH_2-CH); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 144.7 (Ar, C1), 131.2 (Ar, C2), 130.1 (Ar, C4 and C5), 128.3 (Ar, C6), 122.0 (Ar, C3), 84.0 (ArC≡), 77.1 (≡CH), 43.0 (CH), 40.5 (CH_2); IR (KBr, cm^{-1}) 2108 (C≡C), 3293 (≡CH). Poly(2-ethynylstyrene): ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.10–6.20 (m, 4H, Ar), 3.35–2.00 (m, 1H, CH), 2.54 (s, 1H, C≡CH), 2.00–0.80 (br s, 2H, CH_2); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 148.8 (Ar, C1), 132.4 (Ar, C3), 128.6 (Ar, C5), 127.2 (Ar, C6), 125.2 (Ar, C4), 121.6 (Ar, C2), 82.6 (ArC≡), 80.5 (≡CSi), 41.6 (CH), 37.7 (CH_2); IR (KBr, cm^{-1}) 2104 (C≡C), 3296 (≡CH).

Bromination of Poly(4-ethynylstyrene). The reaction was carried out in a manner similar to the previous method reported.[27] To a stirred solution of poly(4-ethynylstyrene) (0.120 g, 0.94 mmol based on the ethynylstyrene unit) in $CHCl_3$ (12 mL) was added dropwise bromine in $CHCl_3$ (0.09M, 12 mL) at 25 °C. The mixture was stirred for an additional 30 min at room temperature. The polymer was precipitated in methanol and purified by thrice reprecipitation using a THF–methanol system. A yield of polymer was quantitative. The polymer was identified to be poly[4-(1,2-dibromoethenyl)styrene] by IR, ^{1}H and ^{13}C NMR, and elemental analysis: ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.80–5.80 (overlapping m, 5H, Ar and =CHBr), 2.70–0.80 (m, 3H, CH_2-CH); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 146.1 (Ar, C1), 136.0 (Ar, cis C4), 134.8 (Ar, trans C4), 131.1 (cis ArCBr=), 129.5 (Ar, C3), 127.8 (Ar, C2), 121.7 (trans ArCBr=), 108.5 (cis =CHBr), 102.7 (trans =CHBr), 43.2 (CH), 40.7 (CH_2); IR (KBr, cm^{-1}) 689 (CBr), 1582 (=CBr), 1654 (C=CH). Anal. Calcd for $(C_{10}H_8Br_2)_{3.08}(C_9H_{10})_{0.322}$: C, 43.75; H, 3.04; Br, 53.22. Found: C, 43.71; H, 3.10; Br, 53.21. The C_9H_{10} shown here was the residue of the initiator.

Measurements. Infrared (IR) spectra were recorded on a JEOL JIR-AQS20M FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (89.6 MHz for ^{1}H and 22.53 MHz for ^{13}C). Chemical shifts were reported in ppm downfield relative to tetramethylsilane (δ 0.00) for ^{1}H NMR and to $CDCl_3$ (δ 77.1) for ^{13}C NMR as standard, respectively. Size-exclusion chromatograms (SEC) were obtained at 40 °C with a Toyo Soda HLC-8020 instrument equipped with three polystyrene gel columns (TOSOH G5000H$_{XL}$, G4000H$_{XL}$, G3000H$_{XL}$) with ultraviolet (254 nm) or refractive index detection. THF was the carrier solvent at a flow rate of 1.0 mL/min. Vapor-pressure osmometry (VPO) measurement was made with a Corona 117 instrument in benzene solution with a highly sensitive thermoelectric couple and equipment of very exact control of temperature. The number-average molecular weights ($\bar{M}_n$) up to 10^5 were obtained within an analytical error of ±5%. Laser light scattering measurements for weight-average molecular weight ($\bar{M}_w$) determination were performed at 25 °C with an Ootsuka Electronics SLS-600R instrument in a benzene solution. The glass transition temperature (T_g) was measured by differential scanning calorimetry using a Seiko Instruments SSC/5200. The samples were first heated to 200 °C, cooled rapidly to room temperature, and then scanned again at a rate of 20 °C/min.

Results and Discussion

Anionic Polymerization of 1. In our previous paper,[25] we demonstrated that 1 is quantitatively polymerized with either oligo(α-methylstyryl)lithium or the corresponding potassium salt to afford new living polymers with a $C{\equiv}CSiMe_3$ function. Here, to examine the anionic polymerizability of 1 in detail, the polymerization of 1 was carried out with a variety of anionic initiators. They included oligo(α-methylstyryl)lithium, *n*- and *sec*-butyllithium (*n*-BuLi and *s*-BuLi), and potassium naphthalenide.

The reaction mixtures always exhibit a brownish red in the case of lithium salt or a dark red in the case of potassium salt, respectively, which indicate production of polystyryl anions from 1. The characteristic colors remained unchanged at −78 °C even after 24 h but immediately disappeared by quenching a few drops of degassed methanol. The polymers were obtained quantitatively in all runs under the conditions. From the analytical results of ^{1}H and ^{13}C NMR and IR, it is obvious that the anionic polymerization of 1 proceeds in a vinyl polymerization mode exclusively to afford the expected poly[4-(trimethylsilyl)ethynylstyrene]. Furthermore, no cleavage of the Si–C bond was observed by the same analyses after purification of the polymer by reprecipitation thrice using a THF–methanol system. The purified polymers were therefore directly characterized by SEC and VPO in the form of poly[4-(trimethylsilyl)ethynylstyrene].

Table I. Anionic Polymerization of 1 in THF at −78 °C for 0.5–1 h[a]

1	initiator		α-methylstyrene	$10^{-3}\bar{M}_n$		
(mmol)	type	mmol	(mmol)	calcd[b]	obsd[c]	$\bar{M}_w/\bar{M}_n$[d]
3.08	K-Naph[e]	0.105	0.322	12	10	1.04
3.14	K-Naph	0.0998		13	14	1.09
3.72	K-Naph	0.0633	0.319	25	25	1.04
3.17	*s*-BuLi[f]	0.0572		11	12	1.10
3.09	*n*-BuLi[g]	0.0497		12	17	1.09
3.69	*n*-BuLi	0.0456	0.304	17	15	1.04
5.04	Li-Naph[h]	0.0915	0.327	23	21	1.13
2.85	*s*-BuLi	0.0241	0.356	25	28	1.03
2.91	*s*-BuLi	0.0196	0.246	31	39	1.04
4.93	*s*-BuLi	0.0245	0.317	42	40 (39)[i]	1.08
3.38	*s*-BuLi	0.00921	0.257	77	99 (98)[i]	1.07

[a] Yields of polymers wer quantitative in all runs. [b] $\bar{M}_n$(calcd) was calculated from the [M] to [I] ratio. [c] $\bar{M}_n$(obsd) was obtained by VPO. [d] $\bar{M}_w/\bar{M}_n$ was determined by SEC using polystyrene calibration. [e] Potassium naphthalenide. [f] *s*-Butyllithium. [g] *n*-Butyllithium. [h] Lithium naphthalenide. [i] Values were $\bar{M}_w$s obtained by light scattering in benzene at 25 °C.

Table I summarizes the molecular weights and molecular weight distributions from by $\bar{M}_w/\bar{M}_n$ values of the resulting polymers. The SEC analyses revealed unimodal and symmetrical peaks with narrow distributions for all polymer samples. The $\bar{M}_w/\bar{M}_n$ values were less than 1.1. As can be seen in Table I, the number-average molecular weights ($\bar{M}_n$) measured by VPO are in fair agreement with those values predicted from [M] to [I] ratios in most cases. However, a polymer with a higher $\bar{M}_n$ value was obtained in the case of *n*-BuLi initiation. This probably may be explained by the insufficient dissociation of *n*-BuLi.

The higher molecular weights tend to have more deviation from the calculated values. For example, a $\bar{M}_n$ was obtained to be 99 000 by VPO in the polymer with $\bar{M}_n$ calculated as 77 000. Since it still possessed a narrow molecular weight distribution, trace impurities in the monomer would cause some loss of initiator before propagation reaction, so that the molecular weight would be somewhat higher than expected. More rigid purification of 1 may possibly require the obtainment of polymers with $\bar{M}_n$ values of 10^5 order.

It is of great importance to elucidate the stability of the growing chain for proof of livingness of the polymerization. For this purpose, postpolymerization is one of the most suitable methods. After the first polymerization of 1 with oligo(α-methylstyryl)dipotassium at −78 °C for 30 min, the second feed of 1 was then added to the reaction mixture. It was allowed to stand an additional 30 min to complete further polymerization. Both pre- and postpolymers were obtained quantitatively. As shown in Figure 1, the peak of the postpolymer shifts completely to a higher molecular weight side and no peak is observed at all in the molecular weight region of the prepolymer. Both the pre- and postpolymers are found to possess the desirable $\bar{M}_n$ values and narrow molecular weight distributions. Evidently, the propagating polymer chain end is stable at −78 °C at least for 30 min and is capable of initiating further polymerization quantitatively. This result as well as the

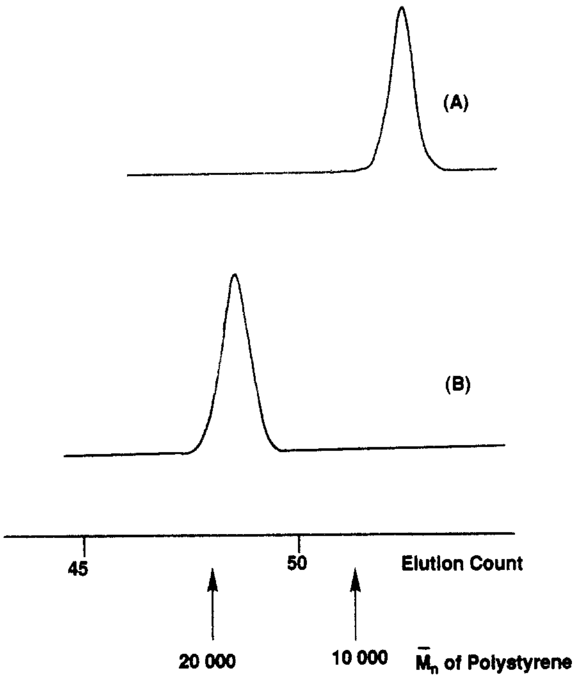

Figure 1. SEC charts of pre- (A) and postpolymers (B). (A) $\bar{M}_n$(obsd) = 7000; (B) $\bar{M}_n$(obsd) = 17 000.

Table II. Anionic Polymerizations of 2 and 3 in THF at −78 °C for 0.5 h[a]

monomer (mmol)	initiator		α-methylstyrene (mmol)	$10^{-3}\bar{M}_n$		$\bar{M}_w/\bar{M}_n$[d]
	type	mmol		calcd[b]	obsd[c]	
2 (2.86)	K-Naph	0.111	0.310	11	13	1.22
2 (3.80)	Li-Naph	0.161	0.358	10	11	1.28
2 (3.32)	Li-Naph	0.0635	0.351	22	21	1.39
3 (2.73)	K-Naph	0.113	0.332	10	10	1.08
3 (3.88)	K-Naph	0.101	0.270	16	15	1.10
3 (3.03)	K-Naph	0.0568	0.295	23	19	1.10
3 (2.35)	*s*-BuLi	0.0458	0.314	11	13	1.10
3 (2.86)	Li-Naph	0.0969	0.255	12	10	1.14

[a] Yields of polymers were quantitative in all runs. [b] $\bar{M}_n$(calcd) was calculated from the [M] to [I] ratio. [c] $\bar{M}_n$(obsd) was obtained by VPO. [d] $\bar{M}_w/\bar{M}_n$ was determined by SEC using polystyrene calibration.

results on molecular weight and the distribution clearly confirms the living character of the anionic polymerization of **1**. Accordingly, the trimethylsilyl group perfectly protects the terminal ethynyl function of 4-ethynylstyrene during the course of the anionic living polymerization. Furthermore, narrow distributions of molecular weight offer convincing evidence that the initiation reaction must be sufficiently rapid under these conditions.

Anionic Polymerizations of 2 and 3. In order to examine the effectiveness of the trimethylsilyl protecting group for other ethynylstyrenes, we have newly synthesized the corresponding meta- and ortho-substituted monomers, **2** and **3**, and attempted their anionic polymerizations under exactly the same conditions.

The anionic polymerization of the meta isomeric monomer, **2**, was carried out in THF at −78 °C with either oligo(α-methylstyryl)dilithium or the dipotassium salt. A characteristic brownish-red color was observed in each of the polymerization mixtures. Yields of polymers were quantitative after 30 min. Occurrence of the vinyl polymerization of **2** was clearly ascertained by the IR and ^{1}H and ^{13}C NMR analyses. The $Me_3Si–C$ bond was observed to be stable and intact after a purification workup.

The results are summarized in Table II, which includes the $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values. A comparison for the $\bar{M}_n$ value of each polymer shows that the values observed are in good agreement with those calculated within experimental error. The SEC traces of polymers all show unimodal and quite symmetrical peaks, although the molecular weight distributions are observed to be somewhat broad, the $\bar{M}_w/\bar{M}_n$ values being in the range from 1.22 to 1.39. To ascertain the living character of the polymerization of **2**, the postpolymerization was carried out similar to the case of **1**. Yields of pre- and postpolymers were quantitative. The SEC analyses of both polymers showed that the peak of the postpolymer shifted to a higher molecular weight side, although the peaks of pre- and postpolymers were relatively broad and therefore overlapped each other to some extent. Both the pre- and postpolymers were found to possess predictable molecular weights. The result of postpolymerization suggests that the active propagating chain end from **2** appears stable and initiates further polymerization. These results as well as the red coloration in the polymerization systems indicate that the anionic polymerization of **2** is living.

As will be mentioned in the section on the synthesis of block copolymerization, the resonance effect and electron-withdrawing nature[28] of a (trimethylsilyl)ethynyl group may significantly influence both the reactivities of **1**–**3** and the active growing chain ends of the resulting living polymers. Moreover, those effects must be different by the position of the substituent. We believe that somewhat broad molecular weight distributions of the poly(**2**)s can be due to a slow initiation compared to the propagation reaction, since both the reaction rates may be caused by the above-mentioned effects.

Similarly, the anionic polymerization of the ortho-substituted monomer, **3**, was carried out at −78 °C in THF on oligo(α-methylstyryl)lithium, -dilithium, or -dipotassium. Upon addition of **3** to the initiator solutions, an immediate and characteristic color change from dark red to dark violet occurred in all the cases. Yields of polymers were quantitative after 30 min. The expected vinyl polymerization and no cleavage of the Si–C bond are clearly demonstrated by the analyses of IR and ^{1}H and ^{13}C NMR. The results of the polymerization are summarized again in Table II.

As can be seen, there is a fair agreement between the $\bar{M}_n$ values calculated and observed by VPO. Narrow molecular weight distributions for all samples are realized by the SEC measurement. The $\bar{M}_w/\bar{M}_n$ values were observed to be 1.08–1.14. These results indicate the living polymerization of **3** under the conditions. The success of the postpolymerization of **3** also provides direct evidence of the living polymerization. The effectiveness of trimethylsilyl protection for *p*-, *m*-, and *o*-ethynylstyrenes is thus evident in their anionic living polymerizations.

The success of anionic living polymerization of the ortho-substituted monomer is of particular interest, because it is possible to obtain the stereoregulated polymers with well-regulated chain lengths. In fact, the splitting of C1 carbon of the aromatic ring of the 2-ethynylstyrene unit appears different from those of the meta and para derivatives, although more detailed information by high-resolution NMR will be needed to discuss this.

Block Copolymerizations of 1–3 with Isoprene, Styrene, 2-Vinylpyridine, and Methyl Methacrylate. One of the most characteristic advantages of living polymerization is to provide the best method for creating block copolymers with precisely controlled chain structures and compositions. In addition to such a synthetic utility, the block copolymerization by using living polymers has another important aspect, that relative reactivities of monomers and the living growing chain ends can be elucidated from the effectiveness of copolymerization.

Table III. Block Copolymerization of 1–3 with Isoprene, Styrene, 2-Vinylpyridine (2VP), and Methyl Methacrylate (MMA) in THF at −78 °C[a]

initiator	block type	monomer A	monomer B	block copolymer (homopolymer[b]) $10^{-3}\bar{M}_n$(calcd)[c]	$10^{-}\bar{M}_n$(obsd)[d]	$\bar{M}_w/\bar{M}_n$[e]
K-Naph	A–B–A	1	isoprene	23 (14)	26 (15)	1.05 (1.05)
K-Naph	A–B–A	1	styrene	21 (12)	22 (10)	1.06 (1.03)
s-BuLi/DPE	B–A	1	2VP	22 (8.4)	*h* (7.8)	*h* (1.04)
Li-Naph	B–A–B	1	2VP	21 (9.7)	19 (6.7)	1.09 (1.10)
K-Naph	A–B–A	2	styrene	30 (9.3)	28 (8.2)	1.24 (1.09)
K-Naph	A–B–A	3	styrene	19 (9.6)	18 (9.8)	1.06 (1.10)
Li-Naph/α-MeSt[g]	B–A–B	3	MMA	20 (7.5)	24 (9.0)	1.18 (1.12)

[a] Yields of polymers were quantitative in all runs. [b] Homopolymers were obtained by the first-stage polymerization. [c] $\bar{M}_n$(calcd) was calculated from the [M] to [I] ratio. [d] $\bar{M}_n$(obsd) was obtained by VPO. [e] $\bar{M}_w/\bar{M}_n$ was determined by SEC using polystyrene calibration. [f] 1,1-Diphenylethylene. [g] α-Methylstyrene. [h] Bimodal distribution.

Furthermore, the result may also give direct information on the stability of the living polymer at the first stage. In this section, the block copolymerizations of 1–3 with isoprene, styrene, 2-vinylpyridine (2VP), and methyl methacrylate (MMA) have been performed to examine the synthetic possibility of novel block copolymers with poly(ethynylstyrene) block segments. The reactivities of 1–3 and their living polymers are also discussed from the results of the block copolymerizations.

At first, an ABA triblock copolymer of 1 (A monomer) with styrene (B monomer) was synthesized by the addition of 1 to the difunctional living polystyrene initiated with potassium naphthalenide in THF at −78 °C. The polymerization proceeded quantitatively to yield the expected block copolymer having a predictable molecular weight and composition and a narrow molecular weight distribution as shown in Table III. The SEC trace also demonstrated the successful block copolymerization by the observation that the peak of the block copolymer shifted completely to the higher molecular weight side and it was a symmetrical unimodal peak with a narrow distribution. Similarly, a well-defined ABA block copolymer of poly(1-*b*-isoprene-*b*-1) was synthesized. Furthermore, novel ABA triblock copolymers containing poly(2) and poly(3) segments as terminal A blocks were also successfully synthesized by the addition of 2 and 3 to the difunctional living polystyrene in a manner similar to the case of 1. Their well-defined and regulated structures are demonstrated by VPO, SEC, and ^{1}H NMR analyses. Poly(2-*b*-styrene-*b*-2) was observed to possess a somewhat broad molecular weight distribution, the $\bar{M}_w/\bar{M}_n$ being 1.24, as would be expected from the result of homopolymerization of 2.

An attempt to synthesize the block copolymer failed by the sequential addition of 1 to the living polymer of 2-vinylpyridine (2VP) initiated with 1,1-diphenyl-3-methylpentyllithium from *s*-BuLi and 1,1-diphenylethylene. The yield of polymer was 100% in this case. However, a bimodal distribution curve was observed in the chromatogram of SEC. The first peak eluted at the low molecular weight region was consistent with that of the homopolymer of 2VP polymerized at the first stage. There appeared a second peak at the high molecular weight region which resulted from the polymerization of 1 initiated with the living poly(2VP). This peak may correspond to a block copolymer of 2VP and 1 with a higher molecular weight poly(1) segment than expected. We can speculate that the carbanion produced from 2VP is not nucleophilic enough to polymerize 1 quantitatively but still has the ability to initiate the polymerization of 1 very slowly. As soon as the initiation of 1 starts only a small extent from the living poly(2VP), the newly formed polystyryl anion from 1 polymerizes to consume rapidly 1. Residual unreacted living poly(2VP) remains even after the conclusion of the second-stage polymerization of 1. It is obvious from the result that the living poly(2VP) shows low reactivity toward 1.

Next, the synthesis of the block copolymer with reversed sequence was attempted by addition of isoprene, styrene, or 2VP to the difunctional living polymer of 1. The living poly(1) could not initiate the polymerization of isoprene, and the homopolymer of 1 was quantitatively recovered. Styrene was polymerized with the living poly(1) with low efficiency, resulting in a mixture of virtual homopolymer and the block copolymer having a polystyrene segment of very high molecular weight. Thus, the synthesis of BAB block copolymers failed by the sequential addition of either isoprene or styrene to the living poly(1). These results indicate that the living polymer from 1 is not sufficiently nucleophilic enough to initiate the polymerization of either isoprene or styrene, although the latter appears to react slowly with the living polymer. On the other hand, the polymerization of a more anionically reactive 2VP occurred quantitatively to produce the poly(2VP-*b*-1-*b*-2VP) with a predictable molecular weight and a narrow molecular weight distribution. The SEC analysis showed that the peak of the starting poly(1) shifted completely to a higher molecular weight side. No peak corresponding to the homopolymer was observed.

We also attempted to synthesize a BAB triblock copolymer by using the living poly(3) with styrene or MMA as a second monomer. Again, difficulty was encountered in polymerizing styrene with living poly(3). A low initiation efficiency of the living polymer toward styrene was indicated by the analytical results of the resulting polymer. This phenomenon is very similar to the one which occurs in the living poly(1)-initiated polymerization of styrene as mentioned before. On the other hand, MMA was quantitatively polymerized with the difunctional living polymer of 3. The VPO and ^{1}H NMR analyses of the resulting polymer strongly confirm a formation of poly(MMA-*b*-3-*b*-MMA) with desirable segment lengths. This is further supported by the observation of SEC that the resulting polymer possesses a symmetrical unimodal peak and no peak corresponding to the homopolymer.

Thus, we have successfully synthesized some novel block copolymers with poly(ethynylstyrene) segments. However, it is observed that the sequential addition with certain combinations of 1, 2, or 3 and conventional monomers imposes the restriction to "reversible" block copolymerization where both the A and B blocks can initiate each other. For example, the living polymer of 1 has little or less ability to initiate the polymerization of isoprene or styrene but not vice versa. From the results of block copolymerizations obtained here, it is definite that 1 is an anionically more reactive monomer than isoprene and styrene, while the living poly(1) is less reactive than those living polymers from isoprene and styrene. The anionic

Table IV. Solubilities of Poly(1), Poly(2), Poly(3), and Poly(4-, 3-, or 2-ethylnylstyrene)[a]

solvent	poly(1)	poly(2)	poly(3)	poly(4ESt)[b]	poly(3ESt)[c]	poly(2ESt)[d]
hexane	S	S	S	I	I	I
benzene	S	S	S	S	S	S
diethyl ether	S	S	S	S	S	S
ethyl acetate	S	S	S	S	S	S
chloroform	S	S	S	S	S	S
acetone	S	S	S	S	S	S
1,4-dioxane	S	S	S	S	S	S
tetrahydrofuran	S	S	S	S	S	S
N,N-dimethylformamide	S	S	I	S	S	S
dimethyl sulfoxide	I	I	I	S	S	S
ethanol	I	I	I	I	I	I
methanol	I	I	I	I	I	I
water	I	I	I	I	I	I

[a] S, soluble; I, insoluble. [b] Poly(4-ethynylstyrene); $\bar{M}_n$ = 12 000. [c] Poly(3-ethynylstyrene); $\bar{M}_n$ = 13 000. [d] Poly(2-ethynylstyrene); $\bar{M}_n$ = 13 000.

reactivities of 1 and the living polymer seem to be roughly located near that of 2VP, although a low reactivity of living poly(2VP) toward 1 has been demonstrated. This may be caused by the electron-withdrawing nature of the (trimethylsilyl)ethynyl group,[28] which enhances the reactivity of the monomer by reducing the electron density of the vinyl bond and, on the other hand, reduces the nucleophilicity of the resulting living polymer by a similar effect. The resonance effect may also play an important role in determining their reactivities. On the reactivities among 1–3, it can be concluded from the results that they are approximately the same, but a more detailed experiment is necessary for this discussion.

Deprotection of the Trimethylsilyl Group from Polymers of 1–3. As mentioned in the preceding section, the (trimethylsilyl)ethynyl functions of the polymers of 1–3 stayed intact during the purification step of polymers. These polymers can therefore be directly characterized in their forms by SEC, VPO, and NMR analyses. On the other hand, it was found that the Si–C bonds of the polymers were readily and completely cleaved by treating with $(C_4H_9)_4NF$ in THF in a manner similar to that previously reported in the case of the low molecular weight analog.[29] For example, the poly(1) was treated with $(C_4H_9)_4NF$ in THF at 0 °C for 1 h and the mixture was poured into methanol to precipitate the polymer. The yield was quantitative, assuming complete conversion to poly(4-ethynylstyrene).

The IR spectrum of the resulting polymer showed new bands at 2109 and 3294 cm^{-1} characteristic of $\nu_{C\equiv C}$ and ν_{C-H} and complete disappearance of the absorptions at 759, 868, 1250, and 2159 cm^{-1} due to δ_{Si-Me} and $\nu_{C\equiv CSiMe}$, respectively. Examination of the resulting polymer by ^{1}H NMR spectroscopy clearly showed resonances assigned to poly(4-ethynylstyrene). A resonance of the trimethylsilyl group at 0.24 ppm was no longer present in the spectrum, whereas the terminal ethynyl proton appeared instead at 3.04 ppm. It was found that the integral ratio of ethynyl to aromatic protons was exactly 1:4 as expected. The ^{13}C NMR also gave the same analytical result. It is clear from these results that complete deprotection is achieved to afford poly(4-ethynylstyrene) under the conditions employed.

The SEC profile of the resulting poly(4-ethynylstyrene) demonstrated that the shapes of the peaks before and after deprotection were indeed identical. The sample still possessed a narrow molecular weight distribution (M_w/M_n = 1.04) and eluted in a slightly lower molecular weight side than that of the parent polymer. This indicates no detectable side reactions leading to main-chain degradation and/or chain branching during the deprotection step. Similarly, complete conversion of either poly(2) or poly(3) was achieved into poly(3-ethynylstyrene) or poly(2-ethynylstyrene). Again their molecular weight distributions remained unchanged after deprotection, indicating no side reactions during the deprotection process.

Table V. Glass Transition Temperatures (T_g) of Poly(1), Poly(2), Poly(3), and Poly(4-, 3-, or 2-ethynylstyrene)

polymer	$10^{-3}\bar{M}_n$(obsd)	$\bar{M}_w/\bar{M}_n$	T_g (°C)
poly(1)	10	1.04	156.6
poly(1)	14	1.09	159.2
poly(1)	21	1.13	165.0
poly(2)	13	1.22	115.1
poly(2)	21	1.39	118.9
poly(3)	10	1.08	111.7
poly(3)	19	1.10	118.4
poly(4-ethynylstyrene)	14	1.13	89.5
poly(3-ethynylstyrene)	14	1.39	69.2
poly(2-ethynylstyrene)	13	1.10	81.9

Table IV summarizes the solubilities of poly(1), poly(2), and poly(3) and the three poly(ethynylstyrene)s thus obtained. It is generally observed that these polymers show a solubility similar to that of polystyrene and are soluble in common organic solvents such as benzene, diethyl ether, 1,4-dioxane, THF, ethyl acetate, chloroform, and acetone but insoluble in ethanol, methanol, and water. Interestingly, solubility changed from the protected polymers to deprotected ones. For example, the polymers from 1–3 are soluble in hexane but insoluble in dimethyl sulfoxide. By contrast, the deprotected polymers showed the opposite solubility in both solvents, e.g., soluble in dimethyl sulfoxide but insoluble in hexane. Little difference in the solubility was observed among the polymers with different substituent positions.

The glass transition temperatures (T_g) of all polymer samples were measured by differential scanning calorimetry, since most were new polymers and no data on their T_g values were available. The results are summarized in Table V. The values of T_g of poly(1) were higher than those of poly(2) and poly(3). As expected, the T_g values tend to increase with an increase of the molecular weight of the polymer. With poly(ethynylstyrene)s, their T_g values are found to decrease to a large extent in comparison with their parent polymers.

Bromination of Poly(4-ethynylstyrene). Since many reactions of the ethynyl group are known in organic synthesis, further chemical modifications of the poly(ethynylstyrene)s by means of these reactions are expected to derive other new functional polymers. Among the known reactions, we have chosen here the electrophilic bromination reaction by which bromine is added to the carbon–carbon triple bond of poly(4-ethynylstyrene). The dibromo adducts are usually formed, but bromoalkynes are sometimes produced in the bromination of terminal acetylenes.[30]

The poly(4-ethynylstyrene) was allowed to react with a slight excess of bromine in chloroform at room temperature. The polymer was isolated by precipitation in methanol. The yield of the polymer was almost quantitative based on the formation of dibromo adduct. The IR spectrum of the polymer obtained showed that the two sharp bands at 3294 and 2109 cm^{-1} characteristic of $\nu_{\mathrm{C-H}}$ and $\nu_{\mathrm{C\equiv C}}$ disappeared completely, while new absorptions at 1654 cm^{-1} for $\nu_{\mathrm{C=CH}}$, 1582 cm^{-1} for $\nu_{\mathrm{=CBr}}$, and 689 cm^{-1} for $\nu_{\mathrm{C-Br}}$ appeared. In the ^{1}H NMR spectrum, a resonance for the ethenyl proton appeared at 7.80–5.80 ppm, although it was overlapped by aromatic protons. As expected, the signal at 3.04 ppm corresponding to the terminal ethynyl proton completely disappeared. It was found that the integral ratio of ethenyl and aromatic protons to methylene and methine protons of the main chain was exactly 5:3. ^{13}C NMR spectral analysis did not show the signals due to ethynyl carbons at 83.8 and 77.1 ppm at all but the newly appeared resonances responsible for the dibromoethenyl group at 131.1 and 108.5 ppm and at 121.7 and 102.7 ppm for cis and trans ArCBr=CHBr, respectively. All signals assigned in the spectrum are clearly consistent with the expected structure of poly[4-(1,2-dibromoethenyl)styrene]. The C, H, and Br percentages found by elemental analysis agreed well with those calculated as mentioned in the Experimental Section. Thus, quantitative transformation of poly(4-ethynylstyrene) into poly[4-(1,2-dibromoethenyl)styrene] is evident.

Interestingly, the shapes of the SEC peaks of the polymers before and after bromination were almost identical, indicating that the poly[4-(1,2-dibromoethenyl)styrene] retained a narrow molecular weight distribution of the parent polymer. All these results indicate that the bromination reaction proceeds cleanly under the conditions employed here. Accordingly, the bromination of poly(4-ethynylstyrene) provides a new route to obtain well-defined poly[4-(1,2-dibromoethenyl)styrene]s with regulated chain lengths.

Conclusions

The results described here demonstrate that the well-defined poly(ethynylstyrene)s are synthesized by the anionic living polymerization of ethynylstyrenes through the trimethylsilyl protection for terminal ethynyl functions, followed by complete deprotection. As a result, poly(4-ethynylstyrene), poly(3-ethynylstyrene), and poly(2-ethynylstyrene) were obtained by this method. Some novel block copolymers with these poly(ethynylstyrene) segments are also synthesized. In addition, the bromination of poly(4-ethynylstyrene) is found to proceed quantitatively to provide a well-defined poly[4-(1,2-dibromoethenyl)styrene] with a narrow molecular weight distribution.

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