# Effect of Isomeric Pyridine Moieties in Ethynylstyrene Derivatives on Their Anionic Polymerization

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Received 19 May 2011; accepted 1 September 2011; published online 26 September 2011 DOI: 10.1002/pola.24989

**ABSTRACT:** The anionic polymerization behaviors of ethynylstyrene derivatives containing isomeric pyridine moieties, 2-(2-(4vinylphenyl)ethynyl)pyridine (**A**), 3-(2-(4-vinylphenyl)ethynyl)pyridine (**B**), and 4-(2-(4-vinylphenyl)ethynyl)pyridine (**C**), were investigated in the identical conditions. The anionic polymerization of **A-C** was performed with (diphenylmethyl)potassium (Ph<sub>2</sub>CHK) in tetrahydrofuran (THF) at -78 °C. The polymerization of **A** proceeded quantitatively at -78 °C for 4 h, and the resulting poly(**A**) possessed predictable molecular weights ( $M_n = 3300-68,500$ ) and narrow molecular weight distributions (MWDs) ( $M_w/M_n = 1.04-$ 1.11). In contrast, the anionic polymerization of **B** was not performed at -78 °C for 4 h due to the occurrence of side reactions. The monomer **B** was quantitatively recovered after the reaction. In the polymerization of **C** performed at -78 °C for 6 h, observed  $M_n$ 

**INTRODUCTION** Since Szwarc first reported the living anionic polymerization of styrene, there have been numerous reports of the living anionic polymerization of styrene derivatives *para*-substituted with a variety of functional groups. The living polymers could be obtained by the anionic polymerization of styrene derivatives *para*-substituted with alkyl,<sup>2</sup> alkenyl,<sup>3-5</sup> and alkynyl<sup>6</sup> groups without the occurrence of side reactions. In contrast, the living anionic polymerization of styrene derivatives *para*-substituted with heterocyclic groups was problematic because the functional groups could be easily attacked by highly reactive anionic species such as anionic initiators and propagating chain-end carbanions.<sup>7-10</sup>

In our group, we have been studying anionic polymerization behaviors of methyl methacrylate (MMA) and styrene derivatives.<sup>9–15</sup> Especially, we reported that the living anionic polymerization of styrene derivatives *para*-substituted with pyridine,<sup>9</sup> triphenylamine,<sup>10</sup> and carbazole<sup>13</sup> moieties can be achieved by controlling polymerization conditions (temperature, reaction time, additive, and initiator) or introducing protecting group. In recent years, these polymers have values of the resulting poly(**C**) were in good agreement with calculated molecular weights based on monomer to initiator ratios, but the MWDs were somewhat broad ( $M_w/M_n = 1.23-1.31$ ). To estimate the reactivity of **A** and to characterize its living nature, the block copolymerization of **A** with 2-vinylpyridine (2VP) and methyl methacrylate (MMA) was performed. The well-defined block copolymers, poly(2VP)-*b*-poly(**A**) and poly(**A**)-*b*-poly(MMA), were successfully synthesized without any additives. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 5199–5209, 2011

**KEYWORDS**: block copolymers; ethynylstyrene derivatives; gel permeation chromatography (GPC); heteroatom-containing polymers; isomeric pyridine moieties; living anionic polymerization

attracted significant interest because of unique properties, which are hole-transporting properties of triphenylamine and carbazole moieties,  $^{16-22}$  and hydrophilic properties of pyridine moieties.  $^{23-26}$ 

In particular, polymers containing pyridine moieties have received continuous attention due to the hydrophilic properties, which are contributed by the nitrogen atom on the aromatic ring. To date, our group has successfully synthesized the well-defined homopolymer with pyridine moieties and block copolymers with 2-vinylpyridine (2VP) to study their morphological behaviors.<sup>9,23-26</sup> For example, the micellization behavior of the amphiphilic homopolymer poly(2-(4-vinylphenyl)pyridine) and the effect of solvent composition on the transformation of micelles to vesicles of rod-coil poly(*n*hexyl isocyanate)-*b*-poly(2VP) diblock copolymer were investigated.<sup>25,26</sup>

In addition, there have been considerable interests in the synthesis of polymers with ethynyl groups because these are highly useful materials that can be thermally crosslinked and can also provide interesting five-membered heterocycles by

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CHART 1 Summary of anionic polymerization of A-C with Ph<sub>2</sub>CHK in THF at -78 °C.

click reactions with azide groups.<sup>27–31</sup> Ishizone et al.<sup>6,32,33</sup> actually performed the anionic polymerization of 4-ethynyl-styrene derivatives *para*-substituted with *tert*-butyl, trimethylsilyl, and phenyl groups with *sec*-butyllithium and oligo ( $\alpha$ -methylstyryl)dipotassium in tetrahydrofuran (THF) at -78 °C. They reported that the polymerizations proceeded quantitatively for 0.5 h without any side reactions, and well-defined polymers with predictable molecular weights and narrow molecular weight distributions (MWDs) were obtained.

Furthermore, studies on the living anionic polymerization of positional isomers of para-substituted styrene derivatives, ortho- and meta-substituted styrene derivatives, have been performed to demonstrate the positional effects of the substituent on polymerization behavior. To investigate the positional effects of the substituent, Nakahama and coworkers performed the anionic polymerization of three positional isomers (ortho, meta, and para) of styrenes substituted with (trimethylsilyl)ethynyl,<sup>32,33</sup> fluoro,<sup>34</sup> 1,3-dioxolane,<sup>35</sup> N-cyclohexylimino,<sup>36,37</sup> and cyano<sup>38,39</sup> groups. In all cases, they observed that anionic polymerization behaviors have been determined by the position of the substituent. For instance, the styrene monomer para-substituted with a cyano group underwent living anionic polymerization, but the living anionic polymerizations of ortho- and meta-substituted isomers were not successful. It has been suggested that the positional effect of the substituent is a crucial factor for achieving the living anionic polymerization of substituted styrene isomers.

In this study, we have prepared functional ethynylstyrene derivatives containing isomeric pyridine moieties, 2-(2-(4-vinylphenyl)ethynyl)pyridine (**A**), 3-(2-(4-vinylphenyl)ethynyl)pyridine (**C**), and the anionic polymerization of **A**–**C** has been performed to obtain well-defined polymers because, as aforementioned, ethynylpyridine moieties possess attractive functionalities. Herein, we mainly described that isomeric pyridine moieties of **A**–**C** (Chart 1). Additionally, the block copolymerization of **A** with 2VP and MMA was performed to estimate the reactivity of **A** and the nucleophilicity of living poly(**A**).

# EXPERIMENTAL

## Materials

4-Bromostyrene (Aldrich, 98%), 2-ethynylpyridine (Aldrich, 98%), 3-ethynylpyridine (Aldrich, 98%), 4-ethynylpyridine hydrochloride (Aldrich, 97%), copper(I) iodide (Aldrich, 99.999%), triphenylphosphine (Aldrich, 99%), and bis(triphenylphosphine)palladium(II) chloride (Tokyo Chemical Industry) were used without further purification. Triethylamine (Aldrich,  $\geq$ 99.5%) was distilled from calcium hydride (CaH<sub>2</sub>) under vacuum. 2VP and MMA were passed through an alumina column, washed with an aqueous 5% sodium hydroxide (NaOH) solution, and then dried over anhydrous sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) for 24 h. These were distilled from CaH<sub>2</sub> under vacuum and then further distilled from CaH<sub>2</sub> on a vacuum line. The monomers were diluted with THF and sealed in ampoules with break-seals on a vacuum line. THF used for polymerization was refluxed over sodium for 5 h and then distilled from a sodium naphthalenide solution on a vacuum line.

#### Measurements

Monomers and polymers were identified by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (JEOL JNM-ECX400) at 25 °C using CDCl<sub>3</sub> as a solvent. Chemical shifts were calculated in reference to tetramethylsilane at 0 ppm. Elemental analyses were performed by the Busan Center of the Korea Basic Science Institute (Vario-EL III, Elementar Analysensysteme GmbH). Molecular weights of the polymers were measured using size exclusion chromatography (SEC, Waters M77251, M510) with four columns (HR 0.5, HR 1, HR 3, and HR 4, Waters Styragel columns run in series; the pore size of the columns was 50, 100, 1000, and 10,000 Å, respectively) with a refractive index detector at a flow rate of 1 mL/min using THF containing 2% triethylamine as the eluent at 40 °C and calibrated with styrene standards (American Polymer Standards Corp.). The Fourier transform infrared (FTIR) spectra were obtained from Perkins-Elmer Spectrum 2000 using KBr pellets. Thermal properties were investigated using thermogravimetric analysis (TGA, TA Instrument (TGA-Q50)) and differential scanning calorimetry (DSC, TA Instrument (DSC-Q20)) at a heating rate of 10 °C/min under nitrogen.



**SCHEME 1** Synthesis of 2-(2-(4-vinylphenyl)ethynyl)pyridine (**A**), 3-(2-(4-vinylphenyl)ethynyl)pyridine (**B**), and 4-(2-(4-vinylphenyl)ethynyl)pyridine (**C**).

#### Initiators

The synthesis of (diphenylmethyl)potassium (Ph<sub>2</sub>CHK) was performed by the reaction of potassium naphthalenide (K-Naph) and a 1.5 M excess of diphenylmethane in dry THF at room temperature for 3 days. The initiator solution was stored at -30 °C in ampoules equipped with break-seals. The initiator efficiency was measured by titration with octylalcohol in a sealed reactor under vacuum.

#### 2-(2-(4-Vinylphenyl)ethynyl)pyridine (A)

A solution of 4-bromostyrene (5.00 g, 27.3 mmol), 2-ethynylpyridine (3.94 g, 38.2 mmol), copper(I) iodide (0.210 g, 1.07 mmol), and triphenylphosphine (0.350 g, 1.35 mmol) in dry triethylamine (50 mL) was bubbled with nitrogen for 1 h at room temperature. Bis(triphenylphosphine)palladium(II) chloride (0.370 g, 0.530 mmol) was added to the solution, and the mixture was stirred at 80 °C for 24 h under nitrogen (Scheme 1). The crude mixture was cooled to room temperature. The reaction mixture was filtered and then concentrated under vacuum. The residue was dissolved in *n*-hexane and washed with 2 N HCl and water. The organic solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. After evaporation of the solvent, the residue was purified by silica column chromatography with diethyl ether and *n*-hexane (3:7) and subsequently recrystallized from *n*-hexane to give a white solid (1.68 g, 8.19 mmol, 30%). <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ ):  $\delta = 5.31-5.34$  (d, 1H,  $CH_2$  = trans, J = 11.0 Hz), 5.78–5.82 (d, 1H,  $CH_2 = \text{cis}$ , I = 17.6 Hz), 6.68–6.75 (dd, 1H, =CH trans, J = 11.0 Hz and 17.6 Hz), 7.25–7.68 (m, 7H, phenyl and pyridine), 8.62–8.63 (m, 1H, CH=N of pyridine). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 89.3$ , 115.2 (CH<sub>2</sub>=), 121.5, 122.7, 126.2, 127.1, 132.3, 136.2, 138.1, 143.5, 150.1. FTIR (KBr, cm<sup>-1</sup>): 3049, 2220 (C≡C), 1625, 1560, 1465, 1427, 1151, 1001, 988, 923, 840. Anal. Calcd for C<sub>15</sub>H<sub>11</sub>N: C, 87.77; H, 5.40; N, 6.82. Found: C, 88.20; H, 5.42; N, 6.78.

# 3-(2-(4-Vinylphenyl)ethynyl)pyridine (B)

The same procedure was followed, as described above for **A**, using 4-bromostyrene (2.00 g, 10.9 mmol), 3-ethynylpyridine (1.60 g, 15.3 mmol), copper(I) iodide (0.083 g, 0.430 mmol), triphenylphosphine (0.140 g, 0.540 mmol), dry triethylamine (20 mL), and bis(triphenylphosphine)palladium(II) chloride (0.150 g, 0.210 mmol). The mixture was stirred at 80 °C for

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24 h under nitrogen (Scheme 1). The residue was purified by silica column chromatography with diethyl ether and *n*-hexane (3:7) and subsequently recrystallized from *n*-hexane to give a white solid (1.62 g, 7.89 mmol, 73%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 5.31-5.34$  (d, 1H,  $CH_2=$ trans, J = 11.0 Hz), 5.78–5.83 (d, 1H,  $CH_2=$  cis, J = 17.6 Hz), 6.69–6.76 (dd, 1H, =*CH* trans, J = 11.0 Hz and 17.6 Hz), 7.26–7.30 (m, 1H, pyridine), 7.40–7.52 (m, 4H, phenyl), 7.80–7.82 (m, 1H, pyridine), 8.54–8.56 (m, 1H, *CH*—N of pyridine), 8.76–8.77 (m, 1H, *CH*=N of pyridine). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 86.6$ , 92.7, 115.2 ( $CH_2=$ ), 120.5, 121.8, 123.0, 126.3, 131.9, 136.1, 138.0, 138.4, 148.6, 152.3. FTIR (KBr, cm<sup>-1</sup>): 3053, 2219 (C≡C), 1626, 1559, 1476, 1409, 1114, 1022, 990, 910, 845. Anal. Calcd for C<sub>15</sub>H<sub>11</sub>N: C, 87.77; H, 5.40; N, 6.82. Found: C, 86.54; H, 5.09; N, 6.58.

#### 4-(2-(4-Vinylphenyl)ethynyl)pyridine (C)

The same procedure was followed, as described above for A, using 4-bromostyrene (5.00 g, 27.3 mmol), 4-ethynylpyridine hydrochloride (5.33 g, 38.2 mmol), copper(I) iodide (0.210 g, 1.07 mmol), triphenylphosphine (0.350 g, 1.35 mmol), dry triethylamine (50 mL), and bis(triphenylphosphine)palladium(II) chloride (0.370 g, 0.530 mmol). The mixture was stirred at 80 °C for 24 h under nitrogen (Scheme 1). The residue was purified by silica column chromatography with diethyl ether and *n*-hexane (3:7) and subsequently recrystallized from *n*-hexane to give a white solid (1.74 g, 8.46 mmol, 31%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 5.33-5.36$  (d, 1H,  $CH_2 = \text{trans}, I = 11.0 \text{ Hz}, 5.79-5.84 \text{ (d, 1H, } CH_2 = \text{cis}, I = 1.0 \text{ Hz}, 1.0 \text{ Hz},$ 17.6 Hz), 6.69-6.76 (dd, 1H, =CH trans, J = 11.0 Hz and 17.6 Hz), 7.37-7.43 (m, 4H, phenyl), 7.50-7.52 (d, 2H, pyridine), 8.59–8.61 (m, 2H, CH–N and CH=N of pyridine).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 87.2$ , 94.1, 115.4 (*C*H<sub>2</sub>=), 121.2, 125.5, 126.3, 131.4, 132.1, 136.0, 138.4, 149.8. FTIR (KBr, cm<sup>-1</sup>): 3045, 2223 (C≡C), 1624, 1591, 1508, 1411, 1111, 1015, 988, 921, 827. Anal. Calcd for C<sub>15</sub>H<sub>11</sub>N: C, 87.77; H, 5.40; N, 6.82. Found: C, 86.56; H, 5.47; N, 6.38.

#### **Purification of Monomers**

After silica column chromatography and repeated recrystallization of **A–C**, the monomers were freeze-dried from their benzene solutions under reduced pressure for 12 h and then dried over phosphorus(V) oxide ( $P_2O_5$ ) at room temperature for 24 h in a glass apparatus equipped with break-seals on a vacuum line. The monomers were diluted with dry THF and stored at -30 °C in glass ampoules under high vacuum.

# Anionic Polymerization of A

The anionic polymerization of **A** was performed with  $Ph_2CHK$  in THF at -78 °C under high vacuum ( $10^{-6}$  Torr) in all-glass reactors equipped with break-seals. The reactor was prewashed with the initiator solution before polymerization. The orange color of  $Ph_2CHK$  was immediately changed to deep blue after addition of **A** to initiator solution. The color was obviously maintained during polymerization. The reaction was terminated with methanol, and the reaction solution was poured into a large amount of *n*-hexane to precipitate polymer. The polymer was reprecipitated in THF/*n*-hexane and freeze-dried from the benzene solution under reduced





FIGURE 1 <sup>1</sup>H NMR spectra of (a) A and (b) poly(A) in CDCl<sub>3</sub>.

pressure for characterization. The characterization of resulting polymer was performed using <sup>1</sup>H and <sup>13</sup>C NMR and FTIR. Poly(**A**); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 1.26-2.17$  (3H, *CH*<sub>2</sub>—*CH*), 6.52–7.49 (7H, phenyl and pyridine), 8.54 (1H, *CH*=N of pyridine). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta =$ 

TABLE 1 Anionic Polymerization of A-C With Ph<sub>2</sub>CHK in THF

40.0-42.0 (*C*H<sub>2</sub>−*C*H), 88.3 (pyridine−*C*≡*C*), 89.5 (pyridine−*C*≡*C*), 119.8, 122.4, 127.3, 127.7, 127.9, 131.9, 136.0, 143.7, 149.9 (phenyl and pyridine). FTIR (KBr, cm<sup>-1</sup>): 3,027, 2,926, 2,221 (*C*≡*C*), 1,582, 1,562, 1,506, 1,428, 1,156, 1,018, 989, 833.

### Anionic Polymerization of B

The same polymerization procedure was followed, as described above for anionic polymerization of A, using  $Ph_2CHK$  in THF at -78 and 0 °C. The colors of the polymerization solutions were deep violet at -78 °C and deep red at 0 °C, respectively. These distinct colors were obviously maintained during polymerization. The polymer was reprecipitated in THF/n-hexane and freeze-dried from the benzene solution under reduced pressure for characterization. The resulting polymer was characterized using <sup>1</sup>H and <sup>13</sup>C NMR and FTIR. Poly(**B**); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 1.25-2.18$ (3H, CH<sub>2</sub>-CH), 6.31-7.82 (6H, phenyl and pyridine), 8.47 (1H, CH—N of pyridine), 8.69 (1H, CH=N of pyridine).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 40.0-42.0 (CH<sub>2</sub>-CH), 85.7 (pyridine—*C*≡*C*), 92.6 (pyridine—*C*≡*C*), 120.4, 123.0, 127.6, 127.9, 131.6, 131.7, 138.2, 148.4, 152.0 (phenyl and pyridine). FTIR (KBr, cm<sup>-1</sup>): 3028, 2925, 2219 (C≡C), 1583, 1561, 1508, 1408, 1188, 1022, 950, 832.

### Anionic Polymerization of C

The same polymerization procedure was followed, as described above for anionic polymerization of **A**, using

		Initiator (mmol)		Temp (°C)	Time (h)	$M    imes  10^{-3}$			
Run	Monomer (mmol)		[ <i>M</i> ]/[/]ª			Calcd <sup>b</sup>	Obsd <sup>c</sup>	<i>M/M.</i> °	Yield (%)
1	<b>A</b> . 0.764	0.0140	55	-78	0.5	6.4	6.8	1.07	57.3
2	<b>A</b> , 2.10	0.0764	27	-78	1	4.2	3.3	1.06	74.4
3	<b>A</b> , 1.99	0.0195	102	-78	2	17.5	19.2	1.05	83.5
4	<b>A</b> , 0.837	0.0551	15	-78	4	3.1	3.3	1.06	100
5	<b>A</b> , 0.753	0.0225	33	-78	4	6.9	7.2	1.07	100
6	<b>A</b> , 0.982	0.0198	50	-78	4	10.3	10.7	1.09	100
7	<b>A</b> , 2.19	0.0226	97	-78	4	19.9	20.3	1.04	100
8	<b>A</b> , 4.47	0.0141	317	-78	4	65.1	68.5	1.11	100
9	<b>B</b> , 0.500	0.0202	25	-78	4	0.5	17.6	1.90	9.8
10	<b>B</b> , 1.04	0.0174	60	-78	24	1.2	69.5	2.42	9.4
11	<b>B</b> , 0.966	0.0140	69	0	1	10.2	11.0	1.23 <sup>d</sup>	72.0
12	<b>B</b> , 0.626	0.0296	21	0	2	4.3	5.0	1.16 <sup>d</sup>	100
13	<b>B</b> , 1.60	0.0175	91	0	2	18.8	20.8	1.19 <sup>d</sup>	100
14	<b>C</b> , 0.940	0.0141	67	-78	4	10.6	11.1	1.26	77.7
15	<b>C</b> , 1.35	0.0355	38	-78	6	7.8	8.1	1.23	100
16	<b>C</b> , 0.643	0.0147	44	-78	6	9.0	9.8	1.31	100
17	<b>C</b> , 0.747	0.0215	35	0	2	3.3	3.5	_e	45.8

<sup>a</sup> Calculated from the feed ratio of the initiator and monomer.

 $^{\rm b}$   $\textit{M}_{\rm n}$  (calcd) = (molecular weight of monomer)  $\times$  [monomer]/[initiator]  $\times$  yield.

 $^{\rm c}\ \dot{M}_{\rm n}({\rm obsd})$  and  $M_{\rm w}/M_{\rm n}$  were obtained by size exclusion chromatography calibration with polystyrene standards in THF solution containing 2% triethylamine as the eluent at 40 °C.

<sup>d</sup>  $M_w/M_n$  of main peak.

 $^{\rm e}$  The  $\mathit{M}_{w}\!\mathit{/}\!\mathit{M}_{n}$  was bimodal, presumably due to the intermolecular side reaction.

Ph<sub>2</sub>CHK in THF at −78 and 0 °C. When **C** was added to the initiator solution, the color of Ph<sub>2</sub>CHK turned to deep blue at −78 °C and navy blue at 0 °C, respectively. These distinct colors were obviously maintained during polymerization. The polymer was reprecipitated in THF/*n*-hexane and freeze-dried from the benzene solution under reduced pressure for characterization. The resulting polymers were characterized by means of <sup>1</sup>H and <sup>13</sup>C NMR and FTIR. Poly(**C**); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 1.26-2.18$  (3H, *CH*<sub>2</sub>−*CH*), 6.42–7.52 (6H, phenyl and pyridine), 8.51 (2H, *CH*−N and *CH*=N of pyridine). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 40.0-42.0$  (*C*H<sub>2</sub>−*C*H), 86.6 (pyridine−*C*≡*C*), 93.7 (pyridine−*C*≡*C*), 119.8, 125.3, 127.4, 127.6, 131.2, 131.8, 149.8 (phenyl and pyridine). FTIR (KBr, cm<sup>-1</sup>): 3,028, 2,924, 2,220 (C≡*C*), 1,592, 1,542, 1,510, 1,408, 1,215, 1,018, 989, 820.

#### **Block Copolymerization**

The first-stage polymerization of 2VP was performed with  $Ph_2CHK$  in THF at -78 °C for 0.5 h under high vacuum condition (10<sup>-6</sup> Torr). After sampling for characterization of poly(2VP), A was added into the living poly(2VP) solution and the reaction continued at -78 °C for 4 h. Both poly(2VP) and block copolymer were quantitatively obtained after termination with methanol. In the block copolymerization of A with MMA, MMA was added to the living poly(A) solution and the reaction continued at -78 °C for 0.5 h after preparation of living poly(**A**) with  $Ph_2CHK$  in THF at -78 °C for 4 h. The resulting block copolymers were characterized by <sup>1</sup>H NMR and FTIR. Poly(2VP)-b-poly(A); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 1.27 - 1.83$  (CH<sub>2</sub>—CH of poly(2VP) and poly(A)), 2.21-2.40 (CH2-CH of poly(2VP)), 6.19-7.60 (phenyl and pyridine poly(2VP) and poly(A)), 8.16-8.36 (CH=N of poly(2VP)), 8.53 (CH=N of poly(A)). FTIR (KBr, cm<sup>-1</sup>): 3,005, 2,932, 2,221 (C=C), 1,592, 1,570, 1,508, 1,474, 1,435, 1,150, 994. Poly(A)-b-poly(MMA); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta =$ 0.70–2.12 (CH<sub>2</sub>—CH of poly(A) and CH<sub>2</sub>—C(CH<sub>3</sub>) of poly (MMA)), 3.60 (OCH<sub>3</sub> of poly(MMA)), 6.51-7.52 (phenyl and pyridine of poly(A)), 8.53 (CH=N of poly(A)). FTIR (KBr, cm<sup>-1</sup>): 2,995, 2,951, 2,222 (C≡C), 1,730 (C=O), 1,583, 1,561, 1,508, 1,464, 1,388, 1,242, 1,193, 1,150, 989, 839, 779, 753.

#### **RESULTS AND DISCUSSION**

#### Living Anionic Polymerization of A

First, the anionic polymerization of **A** was performed with  $Ph_2CHK$  in THF at -78 °C for 0.5-4 h. After addition of **A** to the solution of  $Ph_2CHK$ , the color of polymerization solution became deep blue (Fig. S3 in the Supporting Information). This color that indicates propagating carbanion of living poly(**A**) was maintained during polymerization. The yield increased from 57.3 to 100% with increasing polymerization time from 0.5 to 4 h. The <sup>1</sup>H NMR spectra shown in Figure 1 illustrate that the polymerization reaction proceeded exclusively because the vinyl peak of **A** vanished while the broad peak of the main polymer chain and the broad characteristic HC=N peak of the pyridine unit appeared at 1.26–2.17 and 8.54 ppm, respectively. The anionic polymerization results for **A** are summarized in Table 1.



**FIGURE 2** SEC curves of (a) poly(**A**) synthesized with Ph<sub>2</sub>CHK in THF at -78 °C for 4 h (Table 1, run 7):  $M_n(\text{obsd}) = 20,300$ ,  $M_w/M_n = 1.04$ , (b) polymeric product produced by the anionic polymerization of **B** with Ph<sub>2</sub>CHK in THF at -78 °C for 4 h (Table 1, run 9):  $M_n(\text{obsd}) = 17,600$ ,  $M_w/M_n = 1.90$ , and (c) poly(**C**) synthesized with Ph<sub>2</sub>CHK in THF at -78 °C for 6 h (Table 1, run 16):  $M_n(\text{obsd}) = 9800$ ,  $M_w/M_n = 1.31$ .

All SEC curves of the resulting poly(**A**) were unimodal and the polydispersity indices,  $M_w/M_n$ , were ~1.10. Furthermore, observed  $M_n$  values determined by SEC were in good agreement with calculated molecular weights based on monomer to initiator ratios. For example, the polymerization proceeded quantitatively with Ph<sub>2</sub>CHK for 4 h (Table 1, run 7). As illustrated in Figure 2(a), the SEC profile showed a unimodal and





SCHEME 2 Living anionic polymerization of A with Ph<sub>2</sub>CHK in THF at -78 °C.

symmetrical shape with a narrow MWD ( $M_w/M_n = 1.04$ ). The molecular weight ( $M_n = 20,300$ ) was in well accordance with the calculated molecular weight (19,900). The results shown in Table 1 and Figure 2(a) demonstrate that the anionic polymerization of **A** with Ph<sub>2</sub>CHK proceeded quantitatively without the occurrence of any side reactions, indicating that the living poly(**A**) is stable at -78 °C for 4 h (Scheme 2).

This conclusion supports that the anionic polymerization of **A** was successfully performed under the conditions used in our previous study on the anionic polymerization of 2-(4-vinylphenyl)pyridine.<sup>9</sup> However, the polymerization times required for 100% yield of the polymers were 4 h for **A** and 2.5 h for 2-(4-vinylphenyl)pyridine, respectively, suggesting that the polymerization rate of **A** appeared to be slower than that of 2-(4-vinylphenyl)pyridine under the same polymerization conditions. Therefore, it is considered from this observation that the different behavior of these polymerizations is ascribed to ethynyl group that may affect the reactivity of **A**.

Additionally, poly(**A**) was prepared using various molar ratios of **A** to Ph<sub>2</sub>CHK to confirm the living nature (Table 1, run 4–7). As shown in Figure 3, the good linear relationship between  $M_n$  value and the feed ratio of **A** to Ph<sub>2</sub>CHK indicates a living nature of poly(**A**).



**FIGURE 3** Plot of the feed ratio of **A** to  $Ph_2CHK$  versus  $M_n$  and  $M_w/M_n$ .

#### Anionic Polymerization of B

Table 1 shows the results of anionic polymerizations of **B**. First, the anionic polymerization of **B** was performed at -78 °C for 4 h. After termination, a polymeric product with a low yield was obtained, and most of the unreacted monomer was recovered. <sup>1</sup>H NMR and SEC measurements confirmed that a polymeric product with a much higher molecular weight than expected and a broad MWD had been produced [Fig. 2(b) and Fig. S2 in the Supporting Information]. Next, we performed the polymerization of **B** for a longer time (24 h), but the well-defined poly(**B**) was not successfully synthesized, as summarized in Table 1. The <sup>1</sup>H NMR and SEC analyses of the resulting polymeric product revealed identical results to those of the polymerization performed for 4 h.

To the best of our knowledge, we now suppose that these results are attributed to side reactions based on the results of our previous study on the anionic polymerization of 2-(4-vinylphenyl)pyridine performed with K-Naph or *sec*-BuLi at -78 °C.<sup>9</sup> In this article, it was demonstrated that a polymeric product having a broad MWD and a much higher  $M_n$  value than predicted was obtained in a very low yield, and 2-(4-vinylphenyl)pyridine was quantitatively recovered after the reaction. Accordingly, it is proposed from these findings that the plausible side reactions, which include direct nucleophilic attack of Ph<sub>2</sub>CHK on the pyridine moiety during initiation (Scheme 3, case 1) and nucleophilic attack of the propagating carbanion on the pyridine moiety between polymer chains during propagation (Scheme 3, case 2), occurred during the course of the polymerization of **B** at -78 °C.

In contrast, the polymerization of **B** proceeded quantitatively at a higher temperature (0 °C) for 2 h. The chemical structure of the resulting polymer and the occurrence of the anionic polymerization were confirmed by <sup>1</sup>H (Fig. S2 in the Supporting Information) and <sup>13</sup>C NMR and FTIR. Moreover, the observed  $M_n$  values determined by SEC agreed well with the calculated molecular weights, and the MWDs of the resulting poly(**B**) were ~1.20. However, a bimodal peak with a small trace at the high  $M_n$  region was observed in the SEC curve (Fig. 4). For 1 h polymerization time, the analyses of the polymerization were identical to those of the polymerization performed for 2 h, although the polymer yield was only

# case 1



SCHEME 3 Proposed anionic polymerization behavior of B with Ph<sub>2</sub>CHK in THF at -78 °C.

72.0%. These results indicate that side reactions may take place to some extent between polymer chains during polymerization of **B** at 0 °C.<sup>10,39</sup> The observation that the colors of polymerization solutions of **B** were deep violet at -78 °C and deep red at 0 °C, respectively, strongly supports the con-



FIGURE 4 SEC curves of poly(B) synthesized with  $\mathsf{Ph}_2\mathsf{CHK}$  in THF at 0 °C for 1 and 2 h.

clusion that polymerization behaviors of B at -78 and 0  $^\circ C$  are different (Fig. S3 in the Supporting Information).

#### Anionic Polymerization of C

We performed the anionic polymerization of **C** at -78 °C (Table 1, run 14–16). When **C** was added to the initiator solution, the color of Ph<sub>2</sub>CHK immediately changed to deep blue (Fig. S3 in the Supporting Information). This distinct color derived from propagating carbanion of living poly(**C**) was kept during the course of the polymerization. The yield increased from 77.7% to 100% as the polymerization time increased from 4 to 6 h. All the observed  $M_n$  values estimated by SEC were in good agreement with calculated molecular weights. As shown in Figure 2(c), the SEC curve of the resulting poly(**C**) was observed to be unimodal and symmetrical, although the MWD was somewhat broad ( $M_w/M_n = 1.31$ ).

It was reported that poly(4-vinylpyridine) above a certain molecular weight is not soluble in THF, and this gives rise to a heterogeneous polymerization medium, which results in synthesis of polymer with somewhat broad MWD.<sup>40,41</sup> However, in our study, poly(**C**) having more than  $M_n$  of 10,000 was soluble in THF. In addition, the reaction medium was deep blue observed in the anionic polymerization of **A** under the same conditions (Fig. S3 in the Supporting Information). From these results, we hypothesized that the relatively broad

TABLE 2 Block Copol	lymerization of <b>A</b> With	2-Vinvlovridine and Met	hyl Methacrylate Usi	ng Ph <sub>a</sub> CHK in THE at -	-78 °Ca
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				Block C	Viold		
	Initiator	Мог	Monomer			$M_{ m n} imes$ 10 <sup>-3</sup>	
Run	(mmol)	1st (mmol)	2nd (mmol)	Calcd <sup>b</sup>	Obsd <sup>c</sup>	$M_{\rm w}/M_{\rm n}^{\rm c}$	(%)
1	0.0139	<b>A</b> , 0.485	2VP, <sup>e</sup> 0.644	13.6 (7.2)	- <sup>f</sup> (6.8)	- <sup>f</sup> (1.07)	100
2	0.0144	2VP, 1.53	<b>A</b> , 0.218	15.3 (11.2)	14.0 (11.4)	1.10 (1.09)	100
3	0.0199	<b>A</b> , 0.739	MMA, <sup>g</sup> 0.483	10.2 (7.6)	10.8 (7.3)	1.13 (1.07)	100
4	0.0197	MMA, 1.95	<b>A</b> , 0.617	17.4 (9.9)	- <sup>h</sup> (10.7)	- <sup>h</sup> (1.18)	0

 $^{\rm a}$  Total polymerization times were 4.5 h, 4 h for  ${\rm \textbf{A}}$  and 0.5 h for 2VP and MMA.

<sup>b</sup>  $M_n$ (calcd) = (molecular weight of monomer) × [monomer]/[initiator].

 $^{\rm c}$   $M_{\rm n}({\rm obsd})$  and  $M_{\rm w}/M_{\rm n}$  were obtained by size exclusion chromatography calibration with polystyrene standards in THF solution containing 2% triethylamine as the eluent at 40 °C.

MWD might be caused by a slower rate of initiation as compared to the rate of propagation.<sup>33</sup> Thus, the polymerization of **C** was attempted at elevated temperature (0 °C) for 2 h. The yield of the polymer was found to be 45.8%, and the presence of a shoulder at the high  $M_n$  region of the SEC curve was confirmed (Fig. S4 in the Supporting Information). These indicate that side reactions probably take place intermolecularly between polymer chains during the polymerization of **C** at 0 °C.<sup>40</sup>

From the results of the anionic polymerizations of **A–C**, it was apparent that their polymerization behaviors were quite different depending on the position of the nitrogen atom on

<sup>d</sup> Yield of the second-stage polymerization. <sup>e</sup> 2-Vinylpyridine.

<sup>f</sup> The initiator efficiency was not quantitative, forming a mixture of homopolymer and block copolymer.

<sup>g</sup> Methyl metharylate.

<sup>h</sup> No second-stage polymerization proceeded.

the pyridine moiety. Living anionic polymerization of **A** was performed successfully, whereas side reactions took place between the polymer chains during the course of the polymerizations of **B**, and the poly(**C**) with a relatively broad MWD was obtained from the polymerization of **C**. It can be suggested that these results are likely due to the resonance effects and electron-withdrawing characters of isomeric pyridine moieties, which may have significant effects on the reactivities of **A**–C.<sup>33,39</sup>

#### Block Copolymerization of A with 2VP and MMA

From the synthetic point of view, well-defined block copolymers containing ethynylpyridine moieties can be synthesized



**FIGURE 5** SEC curves of (a) poly(**A**) at the first-stage polymerization and copolymerization product at the second-stage polymerization with 2VP (Table 2, run 1): poly(**A**),  $M_n$ (obsd) = 6800,  $M_w/M_n = 1.07$ , (b) poly(2VP) at the first-stage polymerization and copolymerization product at the second-stage polymerization with **A** (Table 2, run 2): poly(2VP),  $M_n$ (obsd) = 11,400,  $M_w/M_n = 1.09$ ; poly(2VP)-*b*-poly(**A**),  $M_n$ (obsd) = 14,000,  $M_w/M_n = 1.10$ , (c) poly(**A**) at the first-stage polymerization and copolymerization product at the second-stage polymerization with MMA (Table 2, run 3): poly(**A**),  $M_n$ (obsd) = 7300,  $M_w/M_n = 1.07$ ; poly(**A**)-*b*-poly(methyl methacrylate),  $M_n$ (obsd) = 10,800,  $M_w/M_n = 1.13$ , and (d) nucleophilicity order of living poly(**A**).

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SCHEME 4 Block copolymerization of 2VP with A with Ph<sub>2</sub>CHK in THF at -78 °C.

via the successful living anionic polymerization of  $\mathbf{A}$ . Furthermore, the relative reactivity of  $\mathbf{A}$  and the terminal carbanion of the resulting living polymer can be confirmed based on the results of block copolymerization. Thus, 2VP and MMA were chosen as comonomers for  $\mathbf{A}$ .

The results of block copolymerization are summarized in Table 2. First, the block copolymerization of A with 2VP was attempted by the sequential addition of **A** as the first monomer and 2VP as the second monomer. The polymer yield was quantitative, but the SEC curve was bimodal [Fig. 5(a)]. While the peak at the low  $M_n$  region matched that of poly(A), the peak at the high  $M_n$  region might correspond to a block copolymer with an  $M_n$  value much higher than expected. These results could be due to slow initiation with rapid consumption of 2VP by the newly formed polystyryl anion.<sup>6,10</sup> This means that the living poly(A) cannot completely polymerize 2VP, suggesting low nucleophilicity of the living poly(A) toward 2VP. In contrast, a well-defined block copolymer, poly(2VP)-b-poly(A), with a predictable molecular weight  $(M_{\rm n} = 14,000)$  and a narrow MWD  $(M_{\rm w}/M_{\rm n} = 1.10)$ was quantitatively obtained by the reverse addition of two monomers (Scheme 4). As shown in Figure 5(b), the SEC

TABLE 3 Solubilities of Poly(A-C) and Poly(2-vinylpyridine)

	Polymer			
Solvent	Poly ( <b>A</b> )	Poly ( <b>B</b> )	Poly ( <b>C</b> )	Poly (2-vinylpyridine)
<i>n</i> -Hexane	I	I	I	I
Cyclohexane	1	1	I	1
Diethyl ether	I.	1	I	I
Ethyl acetate	1	1	I	S
Chloroform	S	S	S	S
Acetone	1	1	I	S
1,4-dioxane	S	S	S	S
Tetrahydrofuran	S	S	S	S
N,N-dimethylformamide	S	S	S	S
Dimethyl sulfoxide	S	S	S	S
Ethanol	I.	I.	I	S
Methanol	1	1	I	S
Water	I	I	I	1

S: soluble, l: insoluble.



curve of block copolymer was symmetrical and unimodal and completely shifted to the higher  $M_n$  region after **A** was added. These observations indicate that living poly(2VP) is sufficiently nucleophilic to polymerize **A** under the conditions used here.

Next, the block copolymerization of A with MMA was performed in the absence of any additives. As listed in Table 2, the polymerization proceeded quantitatively, and poly(A)-bpoly(MMA) had predictable molecular weight and narrow MWD. Figure 5(c) shows that the SEC curve of the resulting block copolymer was unimodal and symmetrical and shifted from the starting poly(A) toward the higher molecular side. Therefore, it is suggested that living poly(A) is stable at -78°C for 4 h and can certainly polymerize MMA without any additives. Subsequently, the block copolymerization was performed by the sequential addition of MMA as the first monomer and A as the second monomer. However, <sup>1</sup>H NMR and SEC analyses of the resulting polymers confirmed that no polymerization proceeded at the second-stage. No block copolymer was obtained, and the second monomer, A, was quantitatively recovered after termination. Accordingly, it can be concluded from the results of block copolymerization that the nucleophilicity of living poly(A) is between that of 2VP and MMA, as shown in Figure 5(d).



**FIGURE 6** TGA thermogram of poly(A-C) under nitrogen with a heating rate of 10 °C/min.

TABLE 4 Thermal Properties of Poly(A-C)

Polymer	<i>M</i> <sub>n</sub> (obsd)	<i>T</i> ₅ <sup>a</sup> (°C)	τ <sub>g</sub> <sup>b</sup> (°C)
Poly( <b>A</b> )	20,300	494	166
Poly( <b>B</b> )	20,800	478	160
Poly( <b>C</b> )	9800	475	174

<sup>a</sup> 5% Weight loss temperature.

<sup>b</sup> Determined by the second scan.

#### **Solubilities and Thermal Properties**

The solubilities of poly(A-C) were tested using common organic solvents at room temperature, as shown in Table 3. These polymers were soluble in chloroform, 1,4-dioxane, tetrahydrofuran, *N*,*N*-dimethylformamide, and dimethylsulfoxide, but were insoluble in *n*-hexane, cyclohexane, diethyl ether, ethyl acetate, acetone, ethanol, methanol, and water. Interestingly, they were insoluble in ethanol and methanol, while poly(2VP) was soluble in both of these solvents. This discrepancy is likely due to the lower polarity of the ethynylpyridine moieties compared with the pyridine ring.<sup>42</sup>

The thermal stabilities of poly(**A**–**C**) were determined by TGA under nitrogen. The TGA thermograms and the values of the 5% weight loss temperatures ( $T_5$ s) of the polymers are shown in Figure 6 and Table 4. They exhibited high  $T_5$  values, corresponding to good thermal stability. The glass transition temperatures ( $T_g$ s) of the resulting poly(**A**–**C**) measured by DSC was summarized in Table 4. They were found to have  $T_g$  values comparable with that (163 °C) of poly(4-(phenylethynyl)styrene).<sup>6</sup>

### CONCLUSIONS

The anionic polymerization results of three ethynylstyrene derivatives containing isomeric pyridine moieties, 2-(2-(4vinylphenyl)ethynyl)pyridine (A), 3-(2-(4-vinylphenyl)ethynyl)pyridine (B), and 4-(2-(4-vinylphenyl)ethynyl)pyridine (C), illustrate that the polymerization behaviors of these monomers were strongly influenced by the position of the nitrogen atom on the pyridine moiety under the polymerization conditions used in this study. The poly(A) possessed predictable molecular weights and narrow MWDs. In contrast, living anionic polymerization of **B** and **C** was not performed successfully. In the polymerization of B, side reactions occurred between the polymer chains during the polymerization at both -78 and 0 °C, and the resulting poly(C) synthesized at -78 °C possessed somewhat broad MWDs because of slow initiation. It is believed that the different outcomes of these polymerization reactions are due to the resonance effects and electron-withdrawing characters of the isomeric pyridine moieties, which may have significant effects on the reactivities of A-C. Moreover, it was found that the nucleophilicity of living poly(A) is between that of 2VP and MMA. Further studies on the functionalities of ethynylpyridine moieties will be undertaken in the near future.

This work was supported by the Program for Integrated Molecular System (PIMS) and the World Class University (WCU) Program (Project No. R31-20008-000-10026-0). The authors thank the Korea Basic Science Institute (KBSI) for assistance with EA measurements.

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