Novel Amphiphilic Homopolymers Containing *meta*- and *para*-Pyridine Moieties with Living Characteristics and Their Self-Assembly

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ABSTRACT: Amphiphilic monomers containing the isomeric pyridine moieties 3-(4-vinylphenyl)pyridine (3VPPy) and 4-(4-vinylphenyl)pyridine (4VPPy) were synthesized using the Suzuki coupling reaction. A living anionic polymerization of 3VPPy and 4VPPy was successfully performed under various conditions to overcome the limitations of anionic polymerization and to compare their properties with those of poly(2-(4-vinylphenyl)pyridine) as reported previously. Several characteristics of the resulting isomeric P3VPPy and P4VPPy were studied, such as thermal stability, solubility, and the living nature. The block copolymerization of 4VPPy with 2-vinylpyridine and MMA was carried out without additive to estimate the nucleophilicity of P4VPPy and to confirm its living nature. Additionally, each amphiphilic homopolymer of P3VPPy and P4VPPy containing both a hydrophilic pyridine unit and a hydrophobic styrene unit was tested for self-assembly behavior in a mixed solvent (THF/water) and monitored with TEM and SEM. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 3458–3469

KEYWORDS: amphiphilic homopolymers; anionic polymerization; block copolymers; isomeric pyridine moiety; living polymerization; micelles; self-assembly; styrene derivatives

INTRODUCTION Since the discovery that certain vinyl monomers can be polymerized via a living process, there have been numerous attempts to establish a living anionic polymerization process for *para*-substituted styrene derivatives with a variety of functional groups[1–4] because it is one of the best methods for synthesizing various functionalized polymers with a controlled molecular weight (M_n) and narrow molecular weight distribution (MWD).[5] Recently, several polymers containing pyridine units have been of interest due to the good functionality of the nitrogen heteroatom in the aromatic ring. In particular, these polymers could be used as polymeric templates for metal nanoparticles, polymeric reagents, ligands of metalated complexes,[6] quaterization with alkyl halides or inorganic acids,[7] and so on.

Among pyridine-containing polymers, poly(2-vinylpyridine) (P2VP), poly(4-vinylpyridine) (P4VP), and their copolymers with styrene, butadiene, and methylmethacrylate have been studied more extensively than poly(3-vinylpyridine) (P3VP). Preparation of P3VP by anionic polymerization is impossible because of induction stabilization of the intermediate anion from the nitrogen in the pyridine ring, which decreases with distance from the carbanion site: 2-vinylpyridine (2VP) > 4-vinylpyridine (4VP) > 3-vinylpyridine (3VP). 3VP cannot stabilize the anion via resonance delocalization because the negative charge does not shift onto the electronegative nitrogen atom, in contrast to 2VP and 4VP.

In the case of anionic polymerization of 4VP, more specialized polymerization conditions are required compared to that of 2VP due to the low solubility in certain solvents[8] for preparation of P4VP with controlled high M_n and narrower MWD. Although it is difficult to synthesize the P4VP by anionic polymerization, this polymer has been widely studied because of its favorable properties attributed to its greater accessibility of nitrogen[8] than for *ortho*- and *meta*-substituted pyridine-containing polymers. For example, P4VP has been utilized for molecular imprinting polymers,[9] ion-exchange resins,[10] biosensor materials,[11] microfiltration membranes,[12] and production of thermoplastic elastomers due to easier quaterization than with P2VP.[7] However, controlled P3VP was synthesized by nitroxide-mediated radical polymerization (NMRP) in ethylene glycol.[13]

Additional Supporting Information may be found in the online version of this article.

*Yoon-Hyung Hur and Nam-Goo Kang contributed equally to this work.

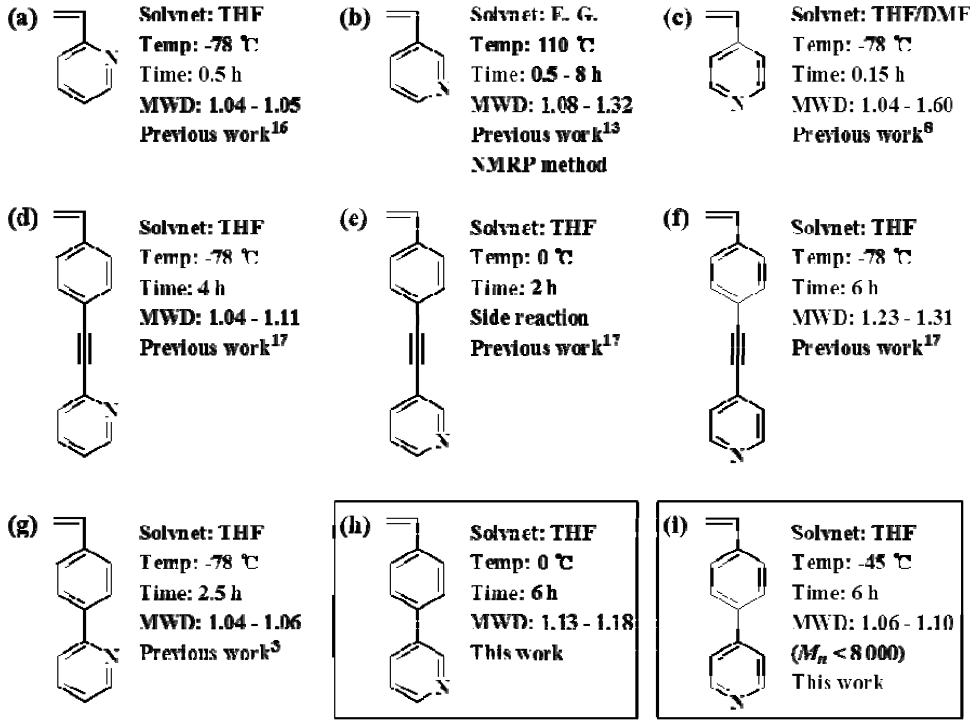


CHART 1 Summary of anionic polymerization of vinyl pyridine derivatives with Ph_2CHK except (b). The (b) was synthesized by nitroxide-mediated radical polymerization (NMRP) in ethylene glycol (EG).

It has been reported that controlling anionic polymerization of pyridine-containing monomers such as 2VP and 4VP is difficult.[14,15] However, our group synthesized the well-defined P2VP as well as various block copolymers based on 2VP by anionic polymerization to investigate their morphological behavior.[16–20]

We also performed successful living anionic polymerizations of *para*-substituted styrene derivatives with pyridine,[3] triphenylamine,[4] and carbazole units and block copolymerizations using special conditions for hole transporting with triphenylamine,[4] carbazole,[21,22] and using the amphiphilic properties of pyridine units.[3,19,20]

To investigate the effect of positional substituents on the polymeric behavior of styrene derivatives, Nakahama et al. carried out the anionic polymerizations of three positional isomers (*ortho*-, *meta*-, and *para*-) of styrene derivatives.[23,24] Furthermore, we studied polymeric behavior as a function of the position of the nitrogen atom in the pyridine ring of an ethynylstyrene derivative in Chart 1(d–f).[17] It was proven that the difference between the electron-withdrawing character and the π-resonance stabilization of the terminal propagating carbanion at each substituent position can affect the polymerization behavior. In addition, our group reported the successful living anionic polymerization of 2-(4-vinylphenyl)-pyridine (2VPPy) using diphenylmethyl potassium (Ph_2CHK) as an initiator in THF at -78 °C as shown in Chart 1(g).[3]

Self-assembly is a common phenomenon in natural and synthetic materials. In general, block copolymers self-assemble in various well-defined nanostructures and are used extensively in materials and biomedical sciences.[25,26] It is well known that block copolymer aggregates have superior stability to and greater loading capacity than small molecule surfactants[19,20] and that self-assembly in polymeric systems can be modified by external stimuli, such as solvent polarity, temperature, and pH. However, precise control of the ratio of block segments is difficult. Recently, a series of amphiphilic homopolymers has been developed, and the nature of their self-assembly as well as applications have been systematically studied.[27] In particular, Thayumanavan et al. studied a novel class of styrene graft polymers containing both hydrophilic and hydrophobic functional groups that form various colloidal aggregates in selective solvents.[28,29] Our group previously synthesized well-defined, coil–coil and coil–rod block copolymers based on PS, P2VP, and PIC blocks via living anionic polymerization. We performed proof-of-concept experiments that explored applications of self-organized, nanostructured materials and molecular assemblies of block copolymers. For instance, a self-assembled monolayer of block copolymers composed of poly(2-vinylpyridine)-*b*-poly(*n*-hexylisocyanate) (P2VP-*b*-PHIC),[30] microphase separation of P2VP-*b*-PHIC depending on block ratio,[16] micellization behavior of amphiphilic PS-*b*-P2VP and PHIC-*b*-P2VP-*b*-PHIC,[31,32] monolayers and multilayers of polymeric nanoparticles of PS-*b*-P2VP with TiO_2,[33] Au-coated PS-*b*-P2VP,[34] nanoporous thin film with Au nanoparticles,[35] and nanocomposites embedding two nanoparticles into the core of PS-*b*-P2VP micellar templates[36] were reported. Recently, we studied the formation of unique open mouth vesicles using an amphiphilic homopolymer, poly(2-(4-vinylphenyl)pyridine) (P2VPPy) with pyridine moieties, in a mixed solvent of tetrahydrofuran (THF) and water with a wide range of compositions (THF/water, 6/4 to 1/9 v/v).[19] Moreover, we reported a one-step process for the formation of stable and unimolecularly thick hollow micelles using an amphiphilic homopolymer of P2VPPy in THF/water (95/5 v/v) azeotropic solvent.[20] As mentioned above, the pyridine-containing homopolymer is of interest in supramolecular chemistry due to its nitrogen heteroatom for various applications.[6–12,18–20]

As described in Chart 1, the anionic polymerization of various styrene derivatives containing pyridine moieties has been carried out because of their potential possibility for nanotechnology, organic electronics, life science, and so forth.[6,7,9–12] However, the living nature of all polymers was not investigated. Herein, we performed the anionic polymerization of the amphiphilic monomers, 3-(4-vinylphenyl)pyridine (3VPPy) and 4-(4-vinylphenyl)pyridine (4VPPy), to investigate the living nature of each homopolymer and to study the effect of positional substituent (*meta*- and *para*-) of isomeric styrene derivatives by comparing with *ortho*-substituted P2VPPy. Additionally, we compared the living natures of living P3VPPy and P4VPPy with those of 2VP and 4VP and with those of pyridine-containing ethynylstyrene derivatives, ((vinylphenyl)ethynyl)pyridine (VPEthPy). Furthermore, the self-assemble behavior of each amphiphilic homopolymer was inspected in the mixed solvent (THF/water) by changing the composition.

EXPERIMENTAL

Materials

(4-Vinylphenyl)boronic acid (Aldrich), 3-bromopyridine (Aldrich, 99%), 4-bromopyridine hydrochloride (TCI, >98%), tetrahydrofuran (Aldrich, ACS reagent, >99%) and tetrakis (triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$, Aldrich) were used without further purification. Potassium carbonate solution (Aldrich, 2 M K_2CO_3 in H_2O, 99%) was prepared. 2VP and MMA were purified in an alumina column, washed with an aqueous 5% sodium hydroxide (NaOH) solution, and dried over anhydrous sodium sulfate (Na_2SO_4). The monomers were distilled from calcium hydride (CaH_2) first under vacuum and then again on a vacuum line. Potassium (K, Aldrich, 98%) and diphenylmethane (DPM, Aldrich, 99%) were used as received.

Measurements

^{1}H and ^{13}C NMR spectra (JEOL JNM-ECX400) were confirmed at 25 °C using $CDCl_3$ as a solvent. Chemical shifts were calculated in reference to tetramethylsilane (TMS) at 0 ppm. Elemental analyses were carried out by Vario-EL III, ElementarAnalysensysteme. Molecular weights of the polymers were estimated using size exclusion chromatography (SEC, Waters M 77251, M510) with four columns (HR 0.5, HR 1, HR 3, and HR 4, Waters Styragel columns run in series). The pore sizes of the columns were 50, 100, 1000, and 10,000 Å; the refractive index detector was set to a flow rate of 1 mL min^{-1} using THF with 2% triethylamine as the eluent at 40 °C and calibrated with styrene standards (American Polymer Standards). FTIR spectra were measured from 400 to 4000 cm^{-1} in a Perkins-Elmer Spectrum 2000 spectrometer using KBr pellets. Thermal properties were characterized with thermogravimetric analysis (TGA, TA Instrument TGA-Q50) and differential scanning calorimetry (DSC, TA Instrument DSC-Q20) with a heating rate of 10 °C min^{-1} under nitrogen. The microphased polymers were characterized with a field emission scanning electron microscope (FE-SEM, Hitachi S-4700) and an energy-filtering transmission electron microscope (EF-TEM, EM912 OMEGA [ZEISS, S-4700]).

Initiator

The initiator diphenylmethyl potassium (Ph_2CHK) was prepared by reaction of 1.5 molar excess of diphenylmethylene (2.8 g, 15.8 mmol) and potassium naphthalenide (Naph-K, 1.8 g, 10.5 mmol) in THF (100 mL) at room temperature for 3 days.[16] The efficiency of Ph_2CHK was determined by titration using octylalcohol (30–50%) in a sealed reactor under vacuum. All materials were diluted with THF (Fisher, GR grade) and sealed in ampules 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.

Synthesis of 3-(4-Vinylphenyl)pyridine

4-(Vinylphenyl)boronic acid (5.0 g, 33.8 mmol) was reacted with 3-bromopyridine (4.5 g, 28.2 mmol), using 2 M K_2CO_3 in H_2O (150 mL) and tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$, 1.0 g, 0.9 mmol) as catalysts in THF (200 mL). The mixture was stirred at 80 °C for 24 h under nitrogen atmosphere (see Supporting Information Scheme S1). After the reaction, the organic solution was evaporated under reduced pressure. The residue was extracted with ethyl acetate (200 mL) and a saturated solution of $NaHCO_3$ in deionized water (200 mL), and washed with deionized water three times. The organic solution was dried over anhydrous Na_2SO_4 and filtered. After evaporation of the solvent, the residue was purified by silica column chromatography using *n*-hexane and ethyl acetate (7:3) as the eluent and subsequently recrystallized from *n*-hexane to obtain a white solid (4.3 g, 83%).

^{1}H NMR (400 MHz, $CDCl_3$, δ) = 5.29–5.32 (d, 1H, $CH_2=$ trans, $J = 11.0$ Hz), 5.78–5.83 (d, 1H, $CH_2=$ cis, $J = 17.6$ Hz), 6.72–6.77 (m, 1H, $=CH$ trans, $J = 11.0$ Hz), 7.50–7.56 (m, 5H, phenyl and pyridine), 7.85-7.86 (d, 1H, pyridine), 8.57 (d, 1H, $CH{-}N$ of pyridine), 8.85 (d, 1H, $CH{=}N$ of pyridine). ^{13}C NMR (100 MHz, $CDCl_3$ δ) = 114.5, 137.4 ($CH_2{=}$), 123.6, 126.8, 126.9, 127.1, 127.2, 134.1, 136.2, 136.3, 137.2, 148.1, 148.4 (phenyl and pyridine). IR (KBr, cm^{-1}): 3026, 1629 ($C{=}C$), 1573, 1474, 1391, 1133, 990, 912, 848, 804, 706. Anal. Calcd. for $C_{13}H_{11}N$: C 86.15, H 6.12, N 7.73; Found: C 86.20, H 6.16, N 7.68.

Synthesis of 4-(4-Vinylphenyl)pyridine

As described above for 3VPPy, the same procedure was followed: 4-(vinylphenyl)boronic acid (5.0 g, 33.8 mmol) was reacted with 4-bromopyridine hydrochloride (4.5 g, 28.2

mmol) using 2 M K_2CO_3 in H_2O (150 mL) and tetrakis(triphenyl-phosphine)palladium(0) (1.0 g, 0.9 mmol) in THF (200 mL) (see Supporting Information Scheme S1). After the reaction, a white solid was obtained (4.2 g, 84%).

^{1}H NMR (400 MHz, $CDCl_3$ δ) = 5.32–5.35 (d, 1H, C*H₂*= trans, *J* = 11.0 Hz), 5.81–5.86 (d, 1H, C*H₂*= cis, *J* = 17.6 Hz), 6.73–6.78 (d, 1H, =C*H* trans, *J* = 11.0 Hz), 7.52–7.61 (m, 6H, phenyl and pyridine, 8.65–8.67 (m, 2H, C*H*=N of pyridine). ^{13}C NMR (100 MHz, $CDCl_3$, δ) = 115.2, 136.1 (*C*H₂=), 121.4, 126.9, 127.1, 137.3, 138.1, 148.4, 150.3 (phenyl and pyridine). IR (KBr, cm^{-1}): 3036, 1626 (C=C), 1594, 1489, 1400, 1129, 996, 924, 833, 817, 703. Anal. Calcd. for $C_{13}H_{11}N$: C 86.15, H 6.12, N 7.73; Found: C 86.13, H 6.18, N 7.78.

Purification of Monomers

The monomers, which were purified by silica column chromatography and recrystallization, were freeze-dried in a benzene solution under reduced pressure for 24 h and then dried without a drying agent at room temperature for 24 h in a glass apparatus equipped with break-seals under high vacuum (10^{-6} Torr). The monomers were then diluted with dry THF and stored at −30 °C in glass ampoules.

Anionic Polymerization of 3VPPy

The 3VPPy was polymerized anionically with Ph_2CHK in THF at 0 °C for 6 h under high vacuum (10^{-6} Torr) in all-glass reactors equipped with break-seals. The glass reactor was sealed from the vacuum line and was then washed with the initiator solution before polymerization. After addition of 3VPPy to the initiator solution, the orange color of Ph_2CHK in the reaction medium immediately changed to reddish brown and remained that color during polymerization. The polymerization was terminated with methanol, and the reaction solution was precipitated with a copious amount of *n*-hexane. The polymer was reprecipitated in THF/*n*-hexane and freeze-dried from a benzene solution under reduced pressure for characterization. The resulting polymer was characterized with ^{1}H and ^{13}C NMR and FTIR.

^{1}H NMR (400 MHz, $CDCl_3$, δ) = 1.26–2.17 (3H, C*H₂*—C*H*), 6.58–7.52 (7H, phenyl and pyridine), 8.54 (1H, C*H*=N of pyridine). ^{13}C NMR (100 MHz, $CDCl_3$, δ) = 40.0–42.0 (*C*H₂—*C*H), 123.5, 126.8, 126.9, 127.1, 127.2, 134.1, 136.2, 136.3, 137.2, 148.1, 148.4 (phenyl and pyridine). IR (KBr, cm^{-1}): 2920, 2842 (C*H*—C*H*), 1576, 1514, 1475, 1429, 1397, 840, 802, 743, 710.

Anionic Polymerization of 4VPPy

As described above for anionic polymerization of 3VPPy, the anionic polymerization of 4VPPy was carried out according to the same polymerization procedure with Ph_2CHK in THF at −78 °C for 15 h. The color of the polymerization solutions was deep violet at −78 °C, and this color was obviously maintained during polymerization. The polymer was purified following the same procedure in anionic polymerization of 3VPPy. The resulting polymer was characterized using ^{1}H and ^{13}C NMR and FTIR.

^{1}H NMR (400 MHz, $CDCl_3$, δ) = 1.26–2.22 (3H, C*H₂*—C*H*), 6.52–7.51 (6H, phenyl and pyridine), 8.50 (1H, C*H*—N of pyridine), 8.66 (1H, C*H*=N of pyridine). ^{13}C NMR (100 MHz, $CDCl_3$, δ) = 40.0–42.0 (*C*H₂—*C*H), 121.3, 126.8, 127.4, 137.1, 138.1, 148.1, 150.7 (phenyl and pyridine). IR (KBr, cm^{-1}): 2920, 2843 (C*H*—C*H*), 1597, 1516, 1487, 1404, 850, 820, 791, 733.

Block Copolymerization of 4VPPy

The first portion in the block copolymer, 2VP, was polymerized anionically with Ph_2CHK in THF at −78 °C for 0.5 h under high vacuum condition (10^{-6} Torr). 4VPPywas added to the living P2VP solution after a portion of living P2VP had been withdrawn by an attached receiver glass apparatus for characterization of the P2VP and the polymerization continued at −78 °C for 15 h. The polymerization of P2VP and the block copolymerization were completed after termination with methanol and then precipitated with a large amount of *n*-hexane. 4VPPy was block-copolymerized with 2VP in a different order to characterize the nucleophilicity of 4VPPy; block copolymerization with MMA was also performed with Ph_2CHK as mentioned above. The resulting block copolymers were characterized by ^{1}H and ^{13}C NMR. P2VP-*b*-P4VPPy.

^{1}H NMR (400 MHz, $CDCl_3$, δ) = 1.27–2.17 (C*H₂*–C*H* of P2VP and P4VPPy), 2.24–2.41 (C*H₂*—C*H* of P2VP), 6.21–7.51 (phenyl and pyridine P2VP and P4VPPy), 8.16–8.32 (C*H*=N of P2VP), 8.58 (C*H*=N of P4VPPy). ^{13}C NMR (100 MHz, $CDCl_3$, δ) = 40.0–42.0 (*C*H₂–*C*H), 120.7, 123.1, 126.7, 128.2, 135.3, 135.6, 148.7, 148.8, 150.3 (phenyl and pyridine).

Preparation of Samples for TEM and SEM

For TEM sample preparation, each homopolymer solution in mixed solvent (THF/water) was drop-casted on the carbon-coated copper grid and dried at room temperature for 48 h. The sample was stained with I_2 vapor for 8 h, and the excess I_2 was removed under vacuum at room temperature for 24 h. For SEM sample preparation, each homo polymer solution that dissolved in mixed solvents (THF/water) was drop-casted on the silicon wafer and dried at room temperature for 48 h.

RESULTS AND DISCUSSION

Living Anionic Polymerization of 3VPPy

The results of anionic polymerization of 3VPPy are summarized in Table 1. The color of the initiator usually changed after the addition of monomer in anionic polymerization. However, there was no change in color in the anionic polymerization of 3VPPy with Ph_2CHK at −78 and −45 °C. Consequently, neither initiation nor propagation occurred at these temperatures. After increasing the temperature to 0 °C, both initiation by Ph_2CHK and propagation occurred. The initiated solution color changed from the orange of Ph_2CHK to reddish brown after addition of 3VPPy, and the color remained the same before the termination. The P3VPPy anion was detected through the color change, and the constant solution color demonstrated that the polymerization was successful.

TABLE 1 Anionic Polymerization of 3VPPy with Ph_2CHK in Different Temperatures

					M_n x 10^{-3}			
Run	Monomer (mmol)	Initiator[a] (mmol)	Temperature (°C)	Time (h)	Calcd[b] (cal)[c]	Obsd[d]	M_w/M_n[d]	Yield (%)
1	2.56	0.0501	−78	1.5	9.3 (9.3)	–[e]	–[e]	–
2	1.90	0.0570	−45	1.5	6.0 (6.0)	–[e]	–[e]	–
3	1.78	0.0278	0	1.5	2.9 (11.6)	2.8	1.25	25
4	1.76	0.0367	0	4.5	6.9 (8.7)	7.0	1.20	80
5	1.55	0.0395	0	6	7.1 (7.1)	7.0	1.18	99
6	2.15	0.0342	0	6	11.4 (11.4)	11.3	1.14	99
7	2.11	0.0258	0	6	20.2 (20.2)	20.5	1.14	100
8	3.46	0.0226	0	6	25.7 (25.7)	25.8	1.13	100
9	2.86	0.0244	25	4	21.2 (21.2)	21.5	1.35	99

[a] (Diphenylmethyl)potassium.

[b] M_n(calcd) = (MW of monomer) × [monomer]/[initiator] × yield + MW of initiator residue.

[c] M_n(calcd) = (MW of monomer) × [monomer]/[initiator].

[d] M_n(obsd) and M_w/M_n were gained by size exclusion chromatography calibration by using polystyrene standards in THF solution containing 2% triethylamine as the eluent at 40 °C.

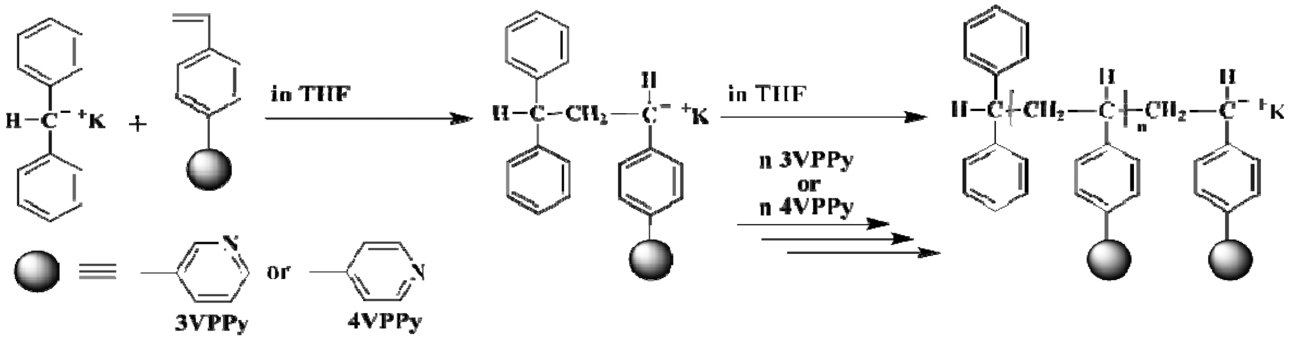
[e] No initiation proceeded.

As observed in Scheme 1, increasing the polymerization time from 1.5 to 6 h at 0 °C increased the yield from 25 to 100%. The resulting polymeric product was confirmed with ^{1}H NMR (Fig. 1); the vinyl peak ($CH_2{=}CH$) of 3VPPy disappeared, but the broad alkyl ($CH_2{-}CH$) and pyridine ($HC{=}N$) peaks were visible at 1.26–2.17 and 8.58–8.68 ppm, respectively.

The resulting polymers were unimodal and possessed somewhat broad MWDs; $M_w/M_n = 1.13$ [Table 1, run 8 and Fig. 2(a)], 1.14 (run 6 and 7), and 1.18 (run 5). To identify the living nature of P3VPPy, anionic polymerizations were carried out with different molar ratios of initiator and 3VPPy. The M_n ofP3VPPy, ranging from 2800 to 25,800 (Table 1, runs 3–8), were obtained and verified by ^{1}H NMR and SEC.

There was good agreement between the M_n obtained by SEC and the calculated M_n and a good linear relationship between the M_n of the polymer and the feed ratio of monomer to initiator as illustrated in Figure 3, which proved the living nature of P3VPPy. As mentioned earlier, 3VP could not be synthesized by anionic polymerization due to the inability of the negative charge to shift to the electronegative nitrogen atom. However, the introduction of a phenyl ring between the vinyl and pyridine groups could stabilize the anion, thereby facilitating the anionic polymerization of styrene derivatives containing *meta*-pyridine.

As explained above, P3VPPy was synthesized by anionic polymerization using optimal conditions with Ph_2CHK for 6 h at 0 °C without side reactions, whereas 2VPPy, an amphiphilic styrene derivative with an *ortho*-pyridine substituent, was polymerized anionically with Ph_2CHK initiator for 2.5 h at −78 °C.[3] The generated electron-withdrawing property and the electrophilicity due to strong stabilization by π-resonance stabilization of the terminal propagating carbanion made initiation and propagation of 3VPPy possible only at 0 °C in Ph_2CHK system because the 3VPPy does not have enough electrophilicity which determines rate of initiation at −78 °C. However, in our previous work, 3VPEthPy, an ethynylstyrene derivative with *meta*-pyridine, did not polymerize successfully at −78 °C, and the resulting product had a very low yield, uncontrolled molecular weight, and a broad MWD.[17] It was suggested that the behavior of anionic polymerization was affected by the polarity of the substituted position of the nitrogen atom in the pyridine ring and that



SCHEME 1 Anionic polymerization of 3VPPy or 4VPPy with Ph_2CHK in THF.

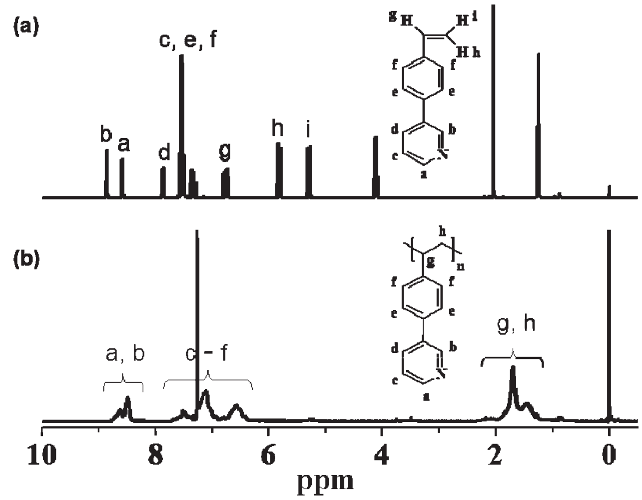


FIGURE 1 ^{1}H NMR of (a) 3VPPy and (b) P3VPPy.

various substituents in the styrene derivatives could induce different reactivities of the monomers.[17,37] In addition, anionic polymerization was performed at room temperature (Table 1, Run 9), and a slightly broader profile of the resulting polymer was observed in SEC as shown in Figure 2(b) because the propagation rate of 3VPPy was faster than the initiation rate.

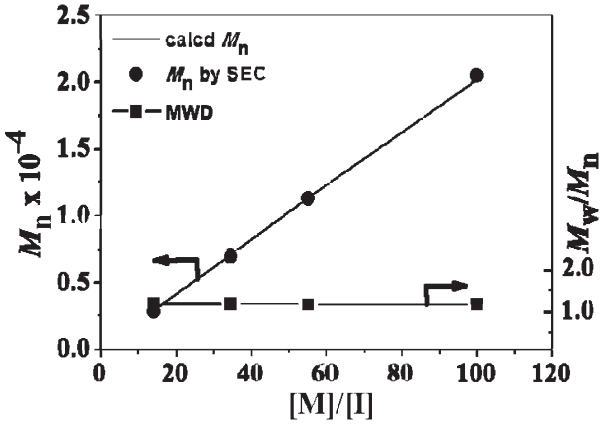


FIGURE 3 A graph shows the good relationship between M_n of the P3VPPy and the feed ratio of the monomer to the initiator.

Anionic Polymerization of 4VPPy

The results of the anionic polymerization of 4VPPy are summarized in Table 2. The polymerization of 4VPPy was performed, and the resulting polymer was characterized by ^{1}H NMR (see Supporting Information Fig. S1) and SEC measurements, as with 3VPPy. The color of the 4VPPy anion after initiation remained deep violet during polymerization, and polymers with narrow MWD were obtained following termination. As the polymerization time increased from 1.5 to 15

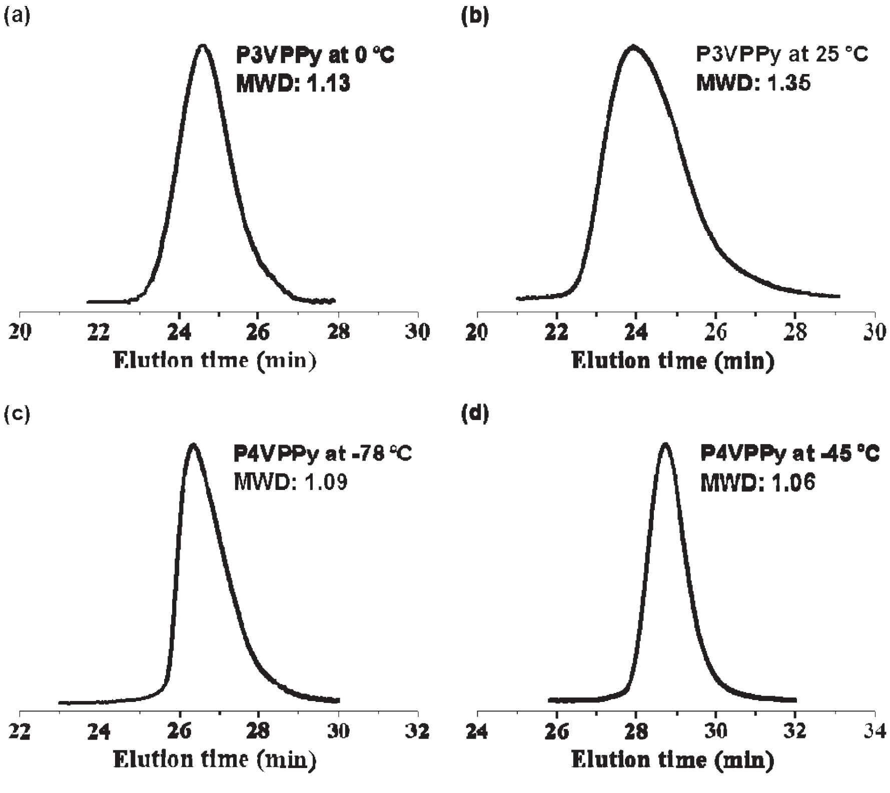


FIGURE 2 SEC curves of (a) P3VPPy synthesized with Ph_2CHK in THF at 0 °C for 6 h (Table 1, Run 8), (b) P3VPPy synthesized with Ph_2CHK in THF at 25 °C for 6 h (Table 1, Run 9), (c) P4VPPy synthesizedwithPh_2CHK in THF at −78 °C for 15 h (Table 2, Run 5), and (d) P4VPPy synthesizedwithPh_2CHK in THF at −45 °C for 6 h (Table 2, Run 11).

TABLE 2 Anionic Polymerization of 4VPPy with Ph_2CHK in Various Conditions

					M_n x 10^{-3}			
Run	Monomer (mmol)	Initiator[a] (mmol)	Temperature (°C)	Time (h)	Calcd[b] (cal)[c]	Obsd[d]	M_w/M_n[d]	Yield (%)
1	2.13	0.0176	−78	1.5	3.3 (21.9)	3.3	1.08	15
2	2.49	0.0486	−78	7.5	6.5 (9.3)	6.6	1.11	70
3	1.72	0.0989	−78	15	3.2 (3.2)	3.3	1.08	100
4	2.15	0.0762	−78	15	5.1 (5.1)	5.0	1.08	100
5	2.14	0.0546	−78	15	7.1 (7.1)	7.1	1.09	100
6	8.16	0.0580	−78	15	6.9 (25.5)	6.9	1.15	27
7[e]	2.56	0.0416	−78	15	6.9 (11.2)	7.0	1.09	62
8[f]	4.21	0.0389	−78	15	7.6 (19.6)	7.7	1.06	39
9[g]	4.28	0.0413	−78	15	7.1 (18.7)	7.1	1.08	38
10	2.41	0.0567	−45	4.5	6.4 (7.7)	6.4	1.09	82
11	2.02	0.0508	−45	6	7.2 (7.2)	7.1	1.06	100
12	4.59	0.0535	−45	6	7.0 (15.0)	6.8	1.06	45
13	2.79	0.0343	0	4	14.8 (14.8)	–[h]	–[h]	–

[a] (Diphenylmethyl)potassium.

[b] M_n(calcd) = (MW of monomer) × [monomer]/[initiator] × yield + MW of initiator residue.

[c] M_n(calcd) = (MW of monomer) × [monomer]/[initiator].

[d] M_n(obsd) and M_w/M_n were gained by size exclusion chromatography calibration by using polystyrene standards in THF solution containing 2% triethylamine as the eluent at 40 °C.

[e] DMF/THF (1/4) was used to polymerize.

[f] DMF/THF (1/3) was used to polymerize.

[g] DMF/THF (1/2) was used to polymerize.

[h] Crosslinked product proceeded.

h at −78 °C, 4VPPy was quantitatively polymerized when the M_n of the resulting polymer was below 8000, as shown in Table 2 and Figure 2(c). This result demonstrated that the solubility of living P4VPPy in THF dominated the propagation in anionic polymerization.

The anionic polymerization of *ortho*- and *meta*-substituted pyridines, 2VPPy and 3VPPy, was successfully carried out, and the resulting polymers possessed predictable molecular weights. Additionally, 4VPEthPy, an ethynylstyrene derivative with a *para*-pyridine substituent, was polymerized anionically for 6 h at −78 °C, and the resulting polymer possessed a predictable M_n and broad MWD (1.23–1.31).[17] In contrast, P4VPPy with 30–40 repeat units was precipitated in THF during polymerization; thus, P4VPPy with a high M_n over 8000 could not be synthesized. It was demonstrated that this low solubility at −78 °C caused the precipitation of the living P4VPPy, which resulted in polymers with limited molecular weight. A similar phenomenon was observed previously by Eisenberg et al., where P4VP possessing a certain molecular weight (DP of cal. 45) was insoluble in THF.[8]

Additionally, according to the study reported by Natta et al., the double bond and the nitrogen atom of the 2VP molecules are coordinated to the alkali metal (K^+) of the initiator (Ph_2CHK) when the extra monomer was added in reacted solution. Thus, the polymerization process was carried out without side reaction or precipitation. However, coordination of 4VP with the alkali metal (K^+) is difficult because the location of the nitrogen atom in the monomer is far from the vinyl double bond.[14,15] Furthermore, with an increasing degree of polymerization of 4VP, the dissociation constant of the ion pair ($4VP^-K^+$) approached that of polystyrene ($K_D1 \approx 10^{-7}$) due to the intermolecular solvation of the alkali cation (K^+) by the living poly(4VP). Cationic solvation affected the reactivity of 2VP and 4VP in a similar manner; solvent, initiator, and temperature influenced the precipitation of propagated 4VP in THF. Furthermore, it was anticipated that precipitation of 4VPPy was observed during the propagation of monomers in THF. Therefore, polymers with limited molecular weights were obtained.

To prevent precipitation of 4VPPy, *N,N*-dimethylmethanamide (DMF), which is one of the good solvents for 4VPPy, was used with THF in the polymerization at −78 °C. The mixed solvent of DMF/THF could be regarded to prevent the precipitation of the propagating anion. As described in Table 2 (Runs 7–9), however, low yield of the polymerization was obtained in various compositions of the mixed solvents. A much lower M_n than the expected M_n was observed by ^1H NMR and SEC.

Next, we attempted to polymerize 4VPPy at −45 °C; the results are summarized in Table 2. In general, solubility can be improved with a high temperature. Therefore, it is expected that faster propagation of P4VPPy during polymerization could be induced at −45 °C than at −78 °C, accompanied by a reduced polymerization time. A polymer with a predictable M_n and a narrow MWD was successfully synthesized in the range of M_n below 8000 with 30–40 repeat

TABLE 3 Block Copolymerization of 4VPPy with 2VP and MMA with Ph_2CHK in THF at -78 °C

				Block Copolymer (Homopolymer)			
		Monomer		M_n x 10^{-3}			
Run	Initiator[a] (mmol)	First (mmol)	Second (mmol)	Calcd[b]	Obsd[c]	M_w/M_n[c]	f_{VPPy} (%)
1	0.0435	4VPPy, 1.10	2VP,[d] 2.66	11.0 (4.6)	–[e] (4.6)	–[e] (1.09)	–
2	0.0401	2VP, 2.61	4VPPy, 0.911	10.9 (6.8)	10.5 (6.8)	1.15 (1.18)	0.24
3[f]	0.0342	2VP, 3.18	4VPPy, 0.975	15.3 (9.8)	15.4 (9.7)	1.15 (1.19)	0.26
4	0.0498	4VPPy, 1.04	MMA,[g] 3.29	10.7 (3.8)	–[e] (3.8)	–[e] (1.10)	–
5	0.0197	MMA, 1.95	4VPPy, 0.617	15.6 (9.9)	–[h] (10.7)	–[h] (1.32)	–

[a] (Diphenylmethyl)potassium.

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

[c] M_n(obsd) and M_w/M_n were gained by size exclusion chromatography calibration by using polystyrene standards in THF solution containing 2% triethylamine as the eluent at 40 °C.

[d] 2-Vinylpyridine.

[e] Poly(2-vinylpyridine) at the first-stage polymerization at -78 °C and copolymerization product at the second-stage polymerization with 4VPPy at -45 °C.

[f] Methyl methacrylate.

[g] The initiation efficiency was not quantitative, forming a mixture of homopolymer and block copolymer.

[h] No second-stage polymerization proceeded.

units of 4VPPy (Table 2, Run 11), and it was confirmed by ^{1}H NMR and SEC [Fig. 2(d)]. Nevertheless, the precipitation of the well-controlled polymer that was targeted to M_n over 8000 was also observed during anionic polymerization.

As summarized in Table 2, to obtain 100% quantitative yield by increasing the solubility of living P4VPPy in THF, the anionic polymerization of 4VPPy by increasing the temperature from -78 and -45 to 0 °C for 3 h was performed. After termination with methanol, a gel polymeric material with a high yield was obtained (Table 2, Run 13). The formation of this gel product indicated the side reaction of 4VPPy, which was similar to the results of 2VP,[14,15] 4VP,[8] and our previous study on the anionic polymerization of 2VPPy[3] and 3VPEthPy.[17] From the successful anionic polymerization of 3VPPy at 0 °C and that of 4VPPy at -78 and -45 °C resulting in M_n below 8000, it was proved that different polymerization behaviors depended on the position of the nitrogen atom in the pyridine moiety. These results revealed that the difference of the resonance and electron withdrawing by the position of the nitrogen atom in the pyridine ring significantly affected the reactivity and nucleophilicity of 3VPPy and 4VPPy.

Block Copolymerization of 4VPPy with 2VP and MMA

Well-defined block copolymers of 4VPPy containing hydrophilic and hydrophobic moieties were synthesized by the sequential anionic polymerization to investigate the relative reactivity and nucleophilicity of 4VPPy compared with 2VP and MMA as well as to study the amphiphilic self-assembly of hollow micelles and vesicles. As shown in Table 3, block copolymerization was carried out with 4VPPy as the first and 2VP as the second monomer; however, no block copolymers were synthesized, as confirmed by ^{1}H NMR and SEC. The SEC profile of P4VPPy-*b*-P2VP showed a bimodal curve in Figure 4(a). The profiles of the low M_n region in Figure 4(a) matched that of P4VPPy, but the peak of the high M_n area of P4VPPy-*b*-P2VP was higher than the calculated M_n due to faster consumption of 2VP in the propagation procedure than initiation of the monomer, which could not induce polymerization of 2VP effectively. This result supported the notion that the nucleophilicity of the P2VP anion was much higher than the P4VPPy anion.

In opposite sequential order, block copolymerization of 4VPPy with 2VP as the first monomer was carried out and a well-defined P2VP-*b*-P4VPPy was synthesized with a predictable molecular weight ($M_n = 10{,}500$) and a narrow MWD ($M_w/M_n = 1.18$). For the block copolymer, the symmetrical and unimodal curves were observed, and SEC profiles were shifted completely to the higher M_n region after addition of 4VPPy [Fig. 4(b)]. Furthermore, block copolymerization of 4VPPy with 2VP at -45 °C reduced the reaction time of 4VPPy from 15 to 6 h. As shown in Figure 4(c), a well-defined block copolymer with a predictable molecular weight ($M_n = 14{,}000$) and a narrow MWD ($M_w/M_n = 1.16$) was obtained quantitatively at -45 °C.

Next, the P4VPPy-*b*-PMMA was synthesized by anionic polymerization using Ph_2CHK as an initiator without additives (Table 3). The yield of block copolymer was quantitative, but the SEC curve was bimodal as illustrated in Figure 4(d). This result also indicated that slower initiation than consumption of MMA in the propagation reaction by the newly formed polystyryl anion was similar to P2VP-*b*-P4VPPy. Additionally, block copolymerization with MMA as the first monomer and 4VPPy as the second monomer was carried out to identify the relative nucleophilic character of the monomers. However, a block copolymer of PMMA-*b*-P4VPPy was not synthesized, confirmed by ^{1}H NMR and SEC. This result proved that the nucleophilicity of living P4VPPy might be between that of 2VP and MMA as described in Figure 4(e).

Solubilities and Thermal Properties

The solubility of P3VPPy and P4VPPy was tested using common organic solvents at room temperature (see Supporting

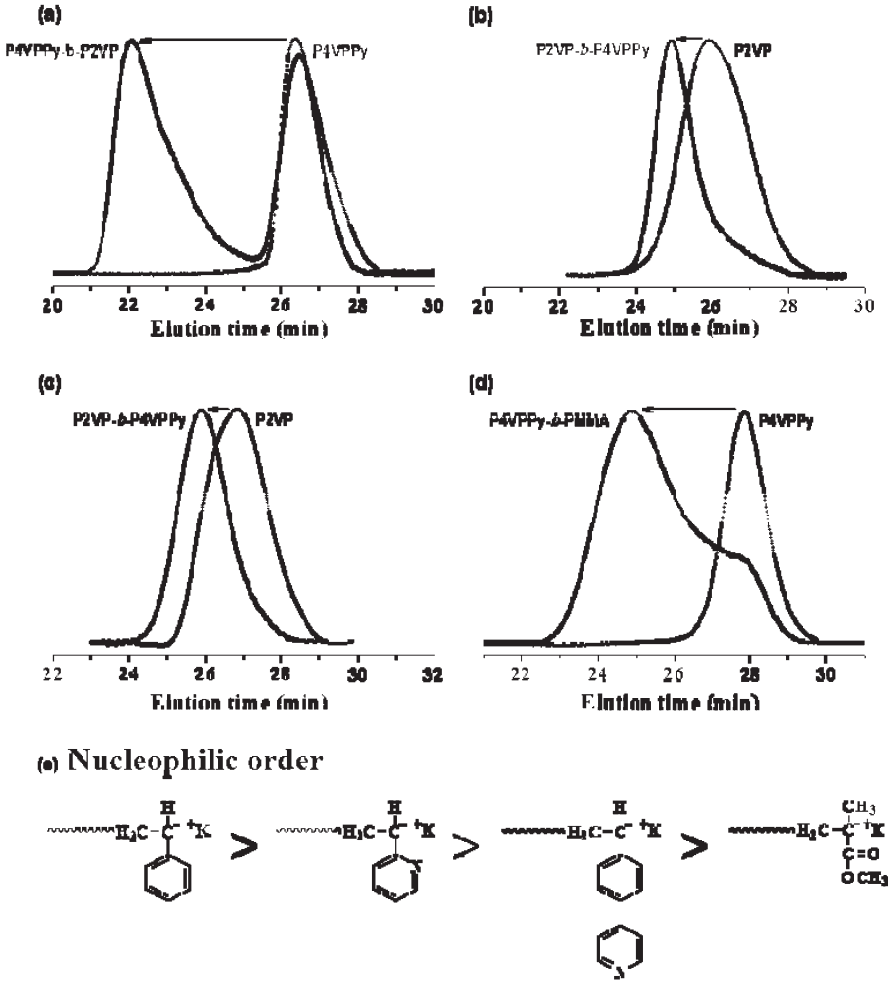


FIGURE 4 SEC curves of (a) P4VPPy at the first-stage polymerization and copolymerization product at the second-stage polymerization with 2VP (Table 3, Run 1), (b) P2VP at the first-stage polymerization and copolymerization product at the second-stage polymerization with 4VPPy (Table 3, Run 2), (c) P2VP at the first-stage polymerization at −78 °C and copolymerization product at the second-stage polymerization with 4VPPy at −45 °C (Table 3, Run 3), (d) P4VPPy at the first-stage polymerization and copolymerization product at the second-stage polymerization with MMA (Table 3, Run 4), and (e) Nucleophilic order of P4VPPy.

Information Table S1). Interestingly, the greatest difference between P3VPPy and P4VPPy occurred in THF. P3VPPy was soluble in THF, but P4VPPy was not. The solubility of P3VPPy was found to be similar to that of P2VPPy. The solubility behavior was likely caused by significant differences in polarity at the substituent position of the nitrogen atom in the pyridine ring.[17,38]

TGA and DSC of P3VPPy and P4VPPy were performed (see Supporting Information Fig. S2). P3VPPy possessed T_d and T_g of 365 and 154 °C, respectively, and those of P4VPPy were 376 and 188 °C, respectively. In contrast, the T_d and T_g of P2VPPy were 387 and 173 °C,[3] respectively, due to the effect of its substituent position on the nitrogen atom in the pyridine ring.

Self-Assembly Behavior of Homopolymers

P3VPPy and P4VPPy were dissolved in mixed solvents of THF/water in the ratio of 9/1 (*v*/*v*) for 6 h, and the resulting solutions were confirmed by dynamic light scattering, which is a noninvasive method for analyzing aggregates in solution. SEM and TEM were used to study the relation between the assemblies in solution and the dried sample on the silicon substrate. The structure and the information regarding these polymers are described in Figure 5(a,f), respectively. TEM and SEM micrographs of P3VPPy aggregates are shown in Figure 5(b,c), respectively. TEM and SEM micrographs of the morphologies of the P4VPPy aggregates when dried are shown in Figure 5(g,h), respectively. The size of P3VPPy (180 ± 20 nm) and P4VPPy (150 ± 12 nm) aggregates calculated from TEM and SEM micrograph match with the hydrodynamic size of the aggregates under the experimental limit conditions.[20]

The dried-state morphologies of P3VPPy aggregates at different ratios of THF/water, 6/4 and 4/6 v/v, are shown in Figure 5(d,e), respectively. Open-mouth vesicle type aggregates with diverse diameters were observed in a mixed

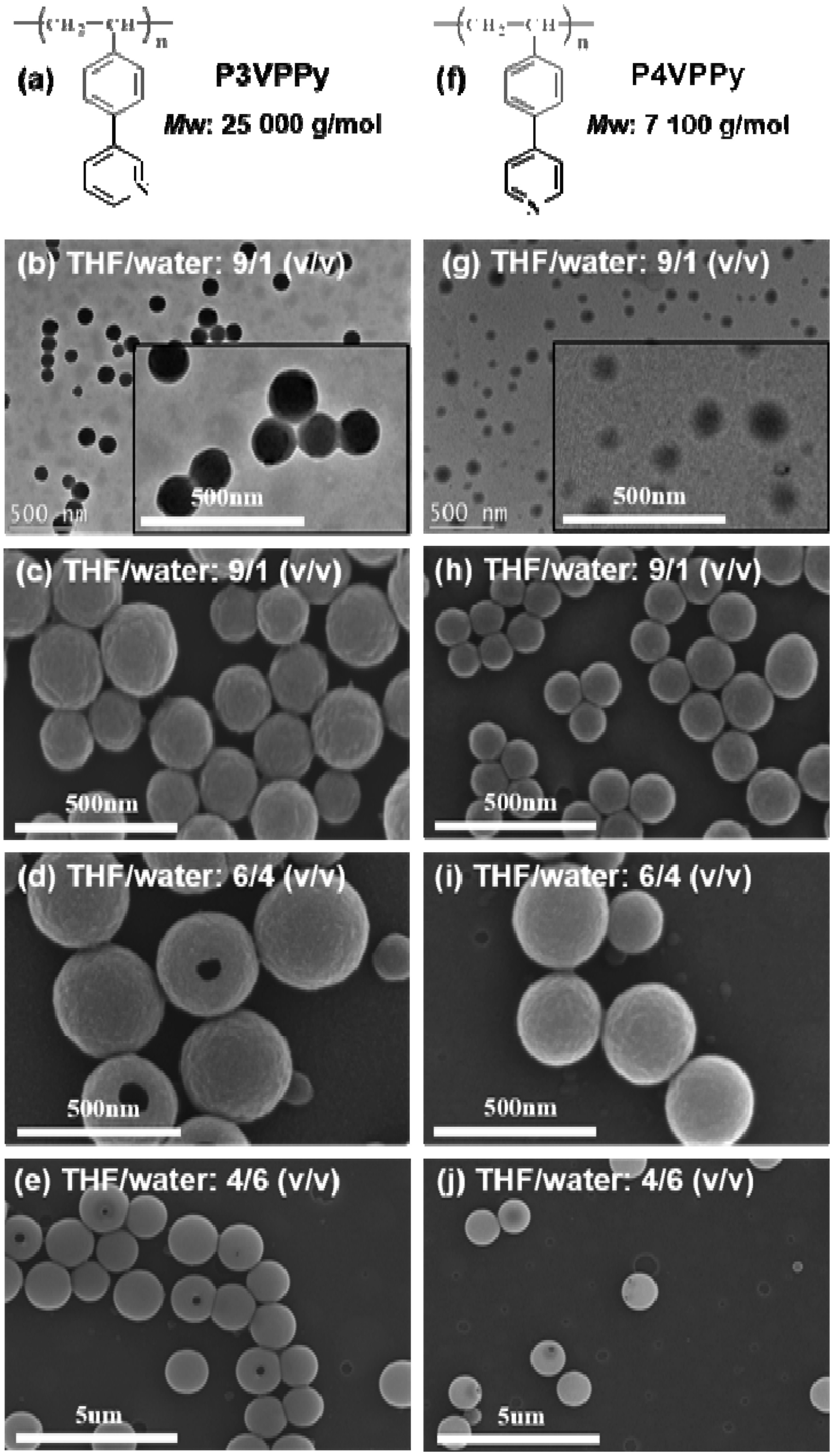
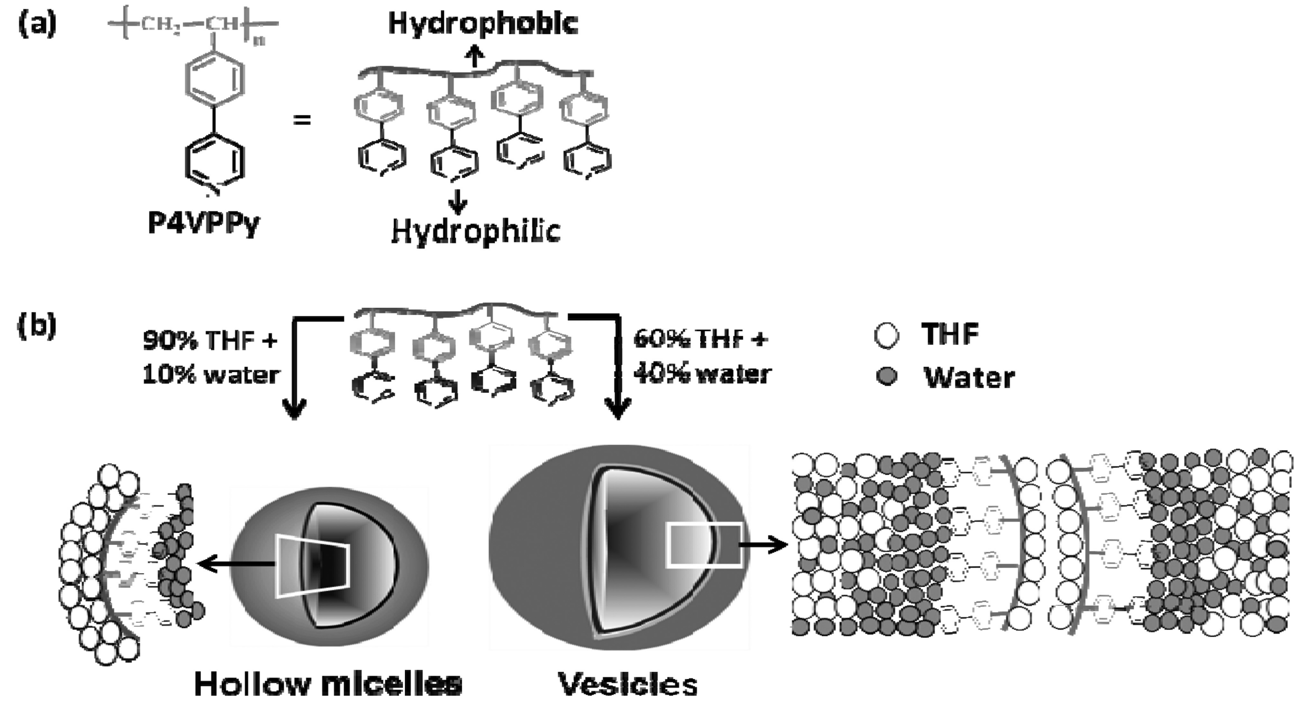


FIGURE 5 Structure of (a) P3VPPy and (f) P4VPPy, HRTEM micrograph of (b) P3VPPy and (g) P4VPPy, SEM micrograph of (c), (d), and (e) P3VPPy and (h), (i), and (j) P4VPPy. The concentration of polymers is 1 mg mL^{-1} in THF/water. Samples were stained with iodine vapor for TEM images.

solvent of THF/water (6/4 and 4/6 v/v, respectively) (see Supporting Information Fig. S4), whereas close-mouth spherical aggregates (250 ± 20 nm) of P4VPPy were observed in THF/water at a ratio of 6/4 v/v [Fig. 5(i)]. Increasing the water content in the THF/water mixed solvent from 6/4 to 4/6 v/v increased the size of the aggregates roughly fivefold



SCHEME 2 Mechanism for the formation of hollow micelles and vesicles from amphiphilic poly(4-(4-vinylphenyl)pyridine) in mixed solvent of THF and water.

for both the P3VPPy and P4VPPy homopolymers. However, further increases in water content in the THF/water mixed solvent beyond 4/6 v/v decreased the size of the aggregates observed (data not shown). Remarkably, no collapsed aggregate structures were observed during SEM and TEM analyses of the samples, which demonstrated the extended stability of the aggregate membrane due to the enhanced stiffness of the phenylpyridine group during packing of the membrane.

Herein, THF forms an azeotrope of up to 6.7% water in mass fraction, and the remaining water molecules are consider being free molecules. At 10% v/v water content, when a Lewis base class P3VPPy or P4VPPy homopolymer was added to the solvent, water molecules interact with the pyridine moiety of the polymer chain due to stronger affinity; the interacting pyridine group acts as a hydrophilic group, whereas the vinyl backbone (coil) of the polymer collectively acts as a hydrophobic (tail) group for each side chain pyridine group.[19,20] The THF solvent is more favorable to the hydrophobic vinyl backbone of the amphiphilic homopolymer P3VPPy/P4VPPy, which makes the backbone curve to form a spherical hollow micelle with a phenylpyridine interior (Scheme 2). As the content of water increased in the mixed solvent of THF/water from a ratio of 9/1 to 6/4 or 4/6 v/v, the polarity of the mixed solvent considerably increased, and to protect the hydrophobic vinyl backbone, P3VPPy/P4VPPy formed bilayer vesicles [Fig. 5(d,e,i,j)] [see Supporting Information Figs. S3(c,d,h,j) and S4]. An azeotropic mixture of THF/water and free water molecules is the most likely continuous phase, which interacts with the outer layer of a membrane that contains pyridine moieties and free THF molecules in its interior of vesicles membrane (Scheme 2). The results suggest that the free molecular rotation of sigma bond between vinyl carbon and phenylpyridine group of the P3VPPy/P4VPPy homopolymer is influenced by the hydrogen-bonding capacity of the pyridine groups with water molecules when oriented outside of vesicles membrane. This result indicated that the main backbone of the polymer which was made by the short relaxation time, glassy nature of these polymers, and the thin thickness of the membrane, was flexible.

CONCLUSIONS

The anionic polymerizations of 3VPPy and 4VPPy, two styrene derivatives containing pyridine moieties, were carried out successfully with Ph_2CHK initiator at 0 °C for 6 h and -78 °C for 15 h, respectively, and the resulting polymers possessed controllable M_n and MWDs because the introduction of a phenyl ring stabilized the anion more than a vinyl pyridine. In particular, the M_n of P4VPPy was controlled until 30–40 monomer repeat units had been propagated. It was verified that P3VPPy and P4VPPy have different anionic polymerization characteristics, compared with P2VPPy. The living P4VPPy polymer with 30–40 repeat units was precipitated in THF at -78 and -45 °C during a propagation procedure similar to the precipitation of living P4VP polymer in THF at -78 °C. This result proved that the different effect of electron withdrawing by inducing the substituted group affected the anionic behavior of the polymers. Furthermore, due to the amphiphilic characteristics of homopolymers, self-assemblies of P3VPPy and P4VPPy, especially hollow micelles and vesicles, were formed, depending on the composition of the mixed solvents of THF/water.

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REFERENCES AND NOTES

1 A. Hirao, S. Nakahama, *Prog. Polym. Sci.* **1990**, *15*, 299–335.

2 A. Hirao, S. Loykulnant, T. Ishizone, *Prog. Polym. Sci.* **2002**, *27*, 1399–1471.

3 N. G. Kang, M. Changez, J. S. Lee, *Macromolecules* **2007**, *40*, 8553–8559.

4 B. G. Kang, N. G. Kang, J. S. Lee, *Macromolecules* **2010**, *43*, 8400–8408.

5 S. Penczek, P. Kubisa, K. Matyjaszewski, *Adv. Polym. Sci.* **1980**, *37*, 1–2.

6 T. Hashimoto, M. Harada, N. Sakamoto, *Macromolecules* **1999**, *32*, 6867–6870.

7 Y. Frere, Ph. Granmain, *Macromolecules* **1992**, *25*, 3184–3189.

8 S. K. Varshney, X. F. Zhong, A. Eisenberg, *Macromolecules* **1993**, *26*, 701–706.

9 C. Baggiani, G. Giraudi, C. Giovannoli, C. Tozzi, L. Anfossi, *Anal. Chim. Acta.* **2004**, *504*, 43–52.

10 C. T. L. Luz, F. M. B. Coutinho, *Eur. Polym. J.* **2000**, *36*, 547–553.

11 J. N. Cha, Y. Zhang, H. S. P. Wong, S. Raoux, C. Rettner, L. Krupp, V. Deline, *Chem. Mater.* **2007**, *19*, 839–843.

12 L. Ying, G. Zhai, A. Y. Winata, E. T. Kang, K. G. Neoh, *J. Colloid Interface Sci.* **2003**, *65*, 396–403.

13 X. Z. Ding, A. Fischer, A. Brembill, P. Lochon, *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 3067–3073.

14 M. Tardi, P. Sigwalt, *Eur. Polym. J.* **1972**, *8*, 137–149.

15 M. Tardi, P. Sigwalt, *Eur. Polym. J.* **1972**, *8*, 151–162.

16 Y. D. Shin, S. H. Han, S. Samal, J. S. Lee, *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 607–615.

17 B. G. Kang, N. G. Kang, J. S. Lee, *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 5199–5209.

18 N. G. Kang, B. G. Kang, H. D. Koh, M. Changez, J. S. Lee, *React. Funct. Polym.* **2009**, *69*, 470–479.

19 M. Changez, N. G. Kang, C. H. Lee, J. S. Lee, *Small* **2010**, *6*, 63–68.

20 M. Changez, N. G. Kang, J. S. Lee, *Small* **2012**, *8*, 1173–1179.

21 N. G. Kang, B. J. Cho, B. G. Kang, S. H. Song, T. H. Lee, J. S. Lee, *Adv. Mater.* **2012**, *24*, 385–390.

22 S. G. Hahm, N. G. Kang, W. Kwon, K. Kim, Y. K. Ko, S. Ahn, B. G. Kang, T. Chang, J. S. Lee, M. Ree, *Adv. Mater.* **2012**, *24*, 1062–1066.

23 K. Sugiyama, T. Ishizone, A. Hirao, S. Nakahama, *Acta Polym.* **1995**, *46*, 424–431.

24 T. Ishizone, R. Kato, Y. Ishino, A. Hirao, S. Nakahama, *Macromolecules* **1991**, *24*, 1449–1454.

25 G. M. Whitesides, B. Grzybowski, *Science* **2002**, *295*, 2418–2421.

26 G. M. Whitesides, J. P. Mathias, C. P. Seto, *Science* **1991**, *254*, 1312–1319.

27 H. D. Koh, J. W. Park, M. S. Rahman, M. Changez, J. S. Lee, *Chem. Commun.* **2009**, *32*, 4824–4826.

28 E. N. Savariar, S. V. Aathimanikandan, S. Thayumanavan, *J. Am. Chem. Soc.* **2006**, *128*, 16224–16230.

29 B. S. Sandanaraj, R. Demont, S. Thayumanavan, *J. Am. Chem. Soc.* **2007**, *129*, 3506–3507.

30 J. H. Kim, M. S. Rahman, J. S. Lee, J. W. Park, *J. Am. Chem. Soc.* **2007**, *129*, 7756–7757.

31 M. S. Rahman, S. Samal, J. S. Lee, *Macromolecules* **2006**, *39*, 5009–5014.

32 M. S. Rahman, S. Samal, J. S. Lee, *Macromolecules* **2007**, *40*, 9279–9283.

33 Y. H. Cho, G. Cho, J. S. Lee, *Adv. Mater.* **2004**, *16*, 1814–1817.

34 W. J. Shin, F. Basarir, T. H. Yoon, J. S. Lee, *Langmuir* **2009**, *25*, 3344–3348.

35 H. D. Koh, N. G. Kang, J. S. Lee, *Langmuir* **2007**, *23*, 12817–12820.

36 H. D. Koh, J. P. Lee, J. S. Lee, *Macromol. Rapid Commun.* **2009**, *30*, 976–980.

37 T. Ishizone, N. Oka, A. Hirao, S. Nakahama, *Macromolecules* **1996**, *29*, 528–534.

38 T. Ishizone, G. Uehara, A. Hirao, S. Nakahama, K. Tsuda, *Macromolecules* **1998**, *31*, 3764–3774.