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Living Anionic Polymerization of the Amphiphilic Monomer 2-(4-Vinylphenyl)pyridine

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ABSTRACT: The amphiphilic monomer 2-(4-vinylphenyl)pyridine (VPPy) has been successfully polymerized using a complex of *sec*-butyllithium (*s*-BuLi) with lithium chloride (LiCl) and coordination of VPPy with LiCl at −45 °C for 72 h without side reactions such as cross-linking and branching. However, it takes 3 days to complete the polymerization with 100% yield, and the polydispersity index ($M_w/M_n = 1.15$) was relatively broad. In contrast, the anionic polymerization using diphenylmethyl potassium (DPM-K) as the weak initiator was more feasible. The yield of the polymer reached 100% within 150 min at −78 °C, which significantly reduced polymerization time with a narrow molecular weight distribution below 1.1. To investigate their living nature and reactivity, the block copolymerization of VPPy with styrene, isoprene, 2-vinylpyridine, and methyl methacrylate were carried out by sequential anionic polymerizations without additives such as LiCl and Et_2Zn. The resulting block copolymers of PVPPy-*b*-PMMA in tetrahydrofuran showed the microphase separation, which was confirmed by transmission electron microscopy.

Introduction

Ever since living anionic polymerization of styrene was discovered,[1] the various vinyl monomers such as styrene, 2-vinylpyridine, and their derivatives have been widely studied. The living anionic polymerization of styrene can be carried out easily, but the polymerization of styrene derivatives containing functional groups is not straightforward due to the side reactions by the strong reactivity of the carbanion.[2] For the anionic polymerization of para-substituted styrene derivatives, the electron-withdrawing functional groups such as -CONR_2 (R = methyl, ethyl, propyl, or ally),[3] $\text{-COCH}_2\text{C(CH}_3\text{)N}$ (oxazolinyl),[4] -CN,[5] -COOR (R = methyl, isopropyl, or *tert*-butyl),[6] and -COR (R = H or methyl)[7] have been used extensively. These electron-withdrawing functional groups reduced electron density in the phenyl moiety of styrene, which weakened the nucleophilicity of the living polymer and stabilized the carbanions.[2d,5c] In addition, the polymerization of the para-substituted styrene derivatives with the electron-donating functional groups such as -CH_3,[8] -NH_2,[9] $\text{-(CH}_2)_n\text{NR}_2$ (R = H, or CH_3),[10] -OH,[11] $\text{-(CH}_2)_n$-OR (R = H, methyl, or *tert*-butyl),[12] $\text{-(CH}_2)_n\text{SH}$,[13] and $\text{-(CH}_2)_n\text{-SCH}_3$ [14] was also difficult to control because the nucleophilicity of the living polymer strengthened by the high electron density in the phenyl moiety of styrene caused side reactions such as cross-linking or branching.

Polymers with pyridine as a functional group, such as poly(2-vinylpyridine) (P2VP) and poly(4-vinylpyridine) (P4VP), are interesting materials due to the presence of the lone pair electrons in the nitrogen atom. These have found numerous applications as polymeric templates for metal nanoparticles, nanocomposites, quaternizations, polyelectrolytes, polymeric reagents, and ligands of metalated complexes.[15] During the anionic polymerization of 2-vinylpyridine (2VP) or 4-vinylpyridine (4VP) initiated by organolitium or a strong nucleophile, side reactions forming either branched or cross-linked polymers via the nucleophilic attack of another carbanion on the pyridine have been reported previously.[16] Therefore, to prevent the side reactions, many groups have researched various approaches such as using low temperature, adding lithium chloride (LiCl),[17] dibutylmagnesium (Bu_2Mg),[18] or 1,1-diphenylethylene (DPE),[19] and initiating by diphenylmethyl potassium (DPM-K) as a weak reactive initiator.[20]

Methylmethacrylate (MMA) is another class of interesting monomer. However, during the living anionic polymerization of MMA using alkyllithiums such as *n*- and *sec*-butyllithium, the side reaction takes place by strong nucleophilic attack on the carbonyl group of the monomer, which results in polymers with a broad molecular weight distribution (MWD) and low yield.[21] To suppress the side reactions, the reactivity of the initiators should be equal to that of the propagating chain ends. Therefore, many research groups have reported various initiation strategies based on the coordination of the additives to ester enolate for the successful anionic polymerization of MMA. 1,1-Diphenylalkyl metal is the most useful initiator because the reactivity of 1,1-diphenylalkyl metal is approximately the same as that of the propagating chain ends.[22] Teyssié and co-workers synthesized PMMA with high conversion, controlled MW, and narrow MWD using (1,1-diphenylalkyl)metal such as (1,1-diphenylhexyl)lithium (DPH-Li) and diphenylmethyl potassium (DPM-K), etc.[23] In addition, they used DPM-Li or DPH-Li plus various kinds of ligands such as 12-crown-4, lithium *tert*-butoxide, and triethylaluminum, etc.[24] Nakahama and co-workers found the novel initiation system for anionic polymerization of MMA and its derivatives using DPM-K/Et_2Zn as a Lewis acid, which produced well-defined polymers with narrow MWD.[25] Müller and co-workers reported successful anionic polymerization of MMA in the presence of aluminum alkyl in toluene at −78 °C.[26] In particular, Müller and Baskaran presented the review of controlling living anionic polymerization of alkyl (meth)acrylate.[21a,27]

The block copolymers containing hydrophilic and hydrophobic moieties usually have been studied for amphiphilic as-

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Table 1. Anionic Polymerization of VPPy in Presence of LiCl in THF

entry	initiator (mmol)	LiCl (mmol)	VPPy/LiCl (mmol)	temp (°C) I	temp (°C) P	time (h)	$M_n \times 10^{-3}$ calcd[a]	$M_n \times 10^{-3}$ obsd[b]	M_w/M_n [b]	yield of polymer (%)
				Naph-K						
1	0.137	0	2.62/0	−78	−78	1	1.5	32.6	1.61	22.0
				s-BuLi						
2	0.072	0	2.60/0	−78	−78	1	0.8	22.4	1.37	13.0
3	0.028	0.076	2.55/0	−78	−45	6	4.29	4.16	1.22	26.0
4	0.035	0.103	2.42/0	−78	−45	12	7.95	8.02	1.46	63.6
5	0.040	0.076	2.84/0	−78	−45	24	12.7	15.4	1.54	100
6	0.039	0	2.96/2.97	−78	−45	12	7.7	5.7	2.84	55.6
7	0.039	0	2.92/2.93	−78	−45	72	13.7	29.8	2.13	100
8	0.039	0.085	2.60/0.69	−78	−45	72	12.0	16.8	1.42	100
9	0.044	0.083	3.04/1.96	−78	−45	72	12.6	11.3	1.47	100
10	0.040	0.080	2.39/2.16	−78	−45	72	10.7	9.9	1.22	100
11	0.085	0.124	2.71/3.48	−78	−45	24	5.8	6.7	1.22	63.1
12	0.034	0.136	2.98/3.85	−78	−45	48	15.8	19.5	1.19	79.6
13	0.031	0.091	2.96/4.14	−78	−45	72	17.3	17.6	1.15	100

[a] M_n(calcd) = (MW of VPPy) × [VPPy]/[initiator] × yield of polymers (%). [b] M_n(obsd) and M_w/M_n were obtained by SEC calibration using polystyrene standard in THF containing 2% $(C_2H_5)_3N$ as the eluents at 40 °C.

semblies such as hollow micelle and vesicle, etc. Recently, some groups have introduced new classes of polymer superstructures in both a polar and nonpolar solvent of styrene-based homopolymers having a hydrophilic carboxylic acid moiety and a hydrophobic benzyl moiety within the same monomer.[28] In this prospective, the unique micellization behavior of the homopolymer, poly(2-(4-vinylphenyl)pyridine) (PVPPy) is predicted in view of the fact that it contains hydrophilic (pyridyl) and hydrophobic (phenyl) moieties in the same monomer.

In this study, amphiphilic monomer, 2-(4-vinylphenyl)-pyridine (VPPy) was synthesized by a Suzuki coupling reaction and was polymerized anionically. For the preparation of their well-defined homopolymers and block copolymers, we have applied two different approaches: (i) the conventional procedure of using the complex of *s*-BuLi with LiCl to reduce the reactivity of carbanion and to protect the reactive α-carbon of the pyridine moiety, and (ii) a simple method of using DPM-K as a weak initiator for prevention of side reactions. The block copolymerization of VPPy with various monomers, the nucleophilicity of living PVPPy, electrophilicity of VPPy, and its living nature were also investigated.

Experimental Section

Materials. (4-Vinylphenyl)boronic acid (Aldrich), 2-bromopyridine (Aldrich, 99%), and tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$, Aldrich) were used as received. K_2CO_3 solution (Aldrich, 2M in H_2O, 99%) in distilled water was prepared. LiCl (Aldrich, 99.99%) was dried at 150 °C for 24 h under reduced pressure. *s*-BuLi (Aldrich, 1.4 M in cyclohexane) was used as received; naphthalenide potassium (Naph-K) was prepared and stored at −30 °C in ampules equipped with break-seals. Styrene (St, Aldrich, 99%), isoprene (IP, Aldrich, 99%), 2-vinylpyridine (2VP, Aldrich, 97%), and methyl methacrylate (MMA, Aldrich, 99%) were passed through an alumina column, washed with aqueous NaOH solution to remove inhibitors, then rinsed with distilled water, dried for 24 h over anhydrous CaH_2, and distilled under reduced pressure. Tetrahydrofuran (THF, Fisher, GR grade) was distilled under N_2 after refluxing with sodium for 5 h. Potassium (K, Aldrich, 98%) and diphenylmethane (DPM, Aldrich, 99%) were used as received. DPM-K was prepared by the reaction of DPM and Naph-K in THF at room temperature for 2 days.[20,29] The efficiency of DPM-K was determined by titration using octyl alcohol (30−50%) and used for polymerization.

Synthesis of 2-(4-Vinylphenyl)pyridine. VPPy was synthesized and characterized according to our previously reported procedure.[30] VPPy was freeze-dried under the reduced pressure of 1 mmHg for 24 h and then dried without any drying agent at 10^{-6} mmHg for 24 h.

Polymerization of VPPy with *s*-BuLi or Naph-K. The anionic polymerization of VPPy in THF was carried out under high-vacuum conditions (10^{-6} mmHg) for 1 h in a glass apparatus equipped with break-seals in the usual manner. VPPy and initiator were prepared and divided in THF under reduced-vacuum condition.[31] *s*-BuLi in heptane or Naph-K in THF was transferred into the reaction flask, and then the solution was stabilized at −78 °C. VPPy in THF was added to the initiator solution, polymerized for 1 h at −78 °C, and terminated with methanol. After termination, the polymers were precipitated in a large amount of methanol, dried, dissolved in benzene, and freeze-dried. The polymers were characterized by NMR and SEC.

Polymerization of VPPy Using the Complex of *s*-BuLi and LiCl. LiCl in THF was added to the solution of *s*-BuLi in heptane at various mole ratios (Table 1, entries 3−5) at −78 °C, turning red immediately. Sequentially, VPPy in THF was added to the solution for initiation for 30 min and followed by propagation at −45 °C for 6, 12, and 24 h, respectively. The color of the reaction media changed from red to deep violet. The polymerization was terminated with methanol, precipitated in a large amount of methanol, dried, dissolved in benzene, and filtered in order to remove LiCl salt. The filtered polymer solution was freeze-dried with benzene, and the polymers were characterized by NMR and size exclusion chromatography (SEC).

Polymerization of VPPy Coordinated with LiCl. VPPy coordinated with LiCl in THF was initiated by *s*-BuLi in heptane solution at −78 °C for 30 min, and it was polymerized for 12 h, and 3 days at −45 °C, respectively (Table 1, entries 6 and 7). The solution turned from deep violet to dark green. After polymerization, purification was carried out as described above.

Polymerization of VPPy Coordinated with LiCl Using the Complex of *s*-BuLi and LiCl. LiCl in THF was added to *s*-BuLi in heptane solution, which turned red instantly because of formation of a complex of *s*-BuLi and LiCl. The coordinated VPPy with different amounts of LiCl (Table 1, entries 8−11) was initiated into the complex solution of *s*-BuLi and LiCl at −78 °C for 30 min and propagated at −45 °C for 24, 48, and 72 h, respectively. The reaction media maintained a dark green color. After polymerization, purification was carried out as described above.

Polymerization of VPPy Using DPM-K. DPM-K in THF was transferred into the reaction flask and stabilized at −78 °C. VPPy in THF was polymerized into DPM-K in THF solution at −78 °C for 30, 90, 120, and 150 min, respectively. After this, it turned deep violet instantly. After polymerization, purification was carried out as described above. The characterization of polymers was performed using ^{1}H NMR, SEC, FT-IR, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). PVPPy (MW, 18 900 g/mol; MWD, 1.06; Table 2, entry 7) T_g: 161.3 °C. T_d: 370 °C. ^{1}H NMR spectra ($CDCl_3$, 300 MHz; ppm): δ 6.4−7.8 (phenyl and pyridine of PVPPy), 8.6 (-N=C*H*-C=), 1.2−2.0

Table 2. Living Anionic Polymerization of VPPy Using DPM-K in THF

entry	DPM-K (mmol)	VPPy (mmol)	temp (°C)	time (min)	$M_n \times 10^{-3}$ calcd[a]	$M_n \times 10^{-3}$ obsd[b]	M_w/M_n[b]	yield of polymers (%)
1	0.0167	2.94	−78	30	15.0	15.8	1.04	47.2
2	0.0171	2.97	−78	90	22.1	20.4	1.04	70.3
3	0.0410	3.58	−78	120	14.6	15.6	1.10	92.0
4	0.0174	3.08	−78	150	32.0	32.2	1.04	100
5	0.0200	3.31	−78	150	29.9	30.2	1.05	100
6	0.0416	2.69	−78	150	11.7	11.9	1.06	100
7	0.0323	3.59	−78	150	20.1	18.9	1.06	100
8	0.0269	4.25	−78	150	28.7	29.2	1.04	100
9	0.0246	5.41	−78	150	37.8	39.7	1.06	100
10	0.0160	5.59	−78	150	63.4	64.5	1.04	100

[a] M_n(calcd) = (MW of VPPy) × [VPPy]/[DPM-K] × yield. [b] M_n(obsd) and M_w/M_n were obtained by SEC calibration using polystyrene standard in THF containing 2% $(C_2H_5)_3N$ as the eluents at 40 °C. Efficiencies of DPM-K were measured by titration using octyl alcohol.

Table 3. Block Copolymerization of VPPy at −78 °C

DPM-K[a] (mmol)	first monomer (mmol)	second monomer (mmol)	time (min)	block copolymer (homopolymer) $M_n \times 10^{-3}$ calcd[b]	block copolymer (homopolymer) $M_n \times 10^{-3}$ obsd[c]	M_w/M_n[c]	yield of block copolymer (%)	f_{VPPy}[d]
	VPPy	St						
0.0220	3.10	7.29	180	57.3(22.9)	23.9	1.04	0	
	VPPy	IP						
0.0223	2.98	7.04	360	45.8(25.5)	26.0	1.06	0	
	VPPy	2VP						
0.0392	3.53	5.16	180	40.2(16.3)	41.7(16.4)	1.08(1.06)	100	0.41
0.0460	9.49	1.52	180	40.6(37.0)	40.0(37.2)	1.07(1.07)	99	0.86
	2VP	VPPy						
0.0282	2.80	2.61	180	27.3(10.5)	28.7(13.8)	1.04(1.03)	99	0.48
0.0893	13.6	2.92	180	22.1(16.1)	22.7(18.5)	1.04(1.05)	100	0.18
	VPPy	MMA						
0.0201	1.85	5.55	180	44.4(16.7)	45.6(16.2)	1.04(1.09)	99	0.25
0.0244	3.04	3.29	180	36.1(22.6)	36.0(22.9)	1.10(1.08)	98	0.48
0.0310	6.99	2.16	180	47.8(40.8)	47.7(41.0)	1.09(1.07)	99	0.76

[a] Efficiencies of DPM-K were measured by titration using octyl alcohol. [b] M_n(calcd) = (MW of first monomer) × [first monomer]/[DPM-K] + (MW of second monomer) × [second monomer]/[DPM-K]. [c] M_n(obsd) and M_w/M_n were measured by SEC calibration using polystyrene standard in THF containing 2% $(C_2H_5)_3N$ as the eluent at 40 °C. [d] Block copolymer composition was determined by means of ^{1}H NMR spectroscopy.

(-C*H₂*−C*H*-). ^{13}C NMR ($CDCl_3$, 75 MHz; ppm): δ 47−38 (-*C*H₂−*C*H-), 148, 135.4−137.5, 124.9−129.8 (phenyl of PVPPy), 157.8, 149.4−151.5, 145.1−146.9, 119.1−122.9 (pyridine of PVPPy). FT-IR (KBr, cm^{-1}): 3150 and 3000 (aromatic =C−H), 2925, 2850 (aliphatic -C−H), 1588, 1472, 1439, 1410 (aromatic amine -C=N, phenyl -C=C).

Block Copolymerization of VPPy with 2VP, MMA, St, and IP, Respectively. VPPy in THF was polymerized in DPM-K in THF solution at −78 °C for 150 min in an all-glass apparatus under reduced vacuum (10^{-6} mmHg). The living PVPPy solution was deep violet. A portion of living PVPPy was withdrawn to an attached receiver for the characterization of the homopolymer. Sequentially, either 2VP or MMA was added as the second monomer into the living PVPPy solution, and the copolymerization was carried out at −78 °C for 30 min. In the case of 2VP, the solution remained deep violet, whereas, for MMA, the deep violet solution turned pale yellow. After the polymerization, the purification was carried out as described above. The polymers were then characterized by ^{1}H NMR, SEC, and FT-IR. Block copolymerizations of VPPy with either styrene or isoprene were carried out by following the above procedure, but the block copolymerizations were not successful. Poly(2-(4-vinylphenyl)pyridine-*b*-2-vinylpyridine) (PVPPy-*b*-P2VP; f_{VPPy} = 0.48; MW, 28 700 g/mol; MWD, 1.04; Table 3). T_g: 98.5 (P2VP) and 191.4 °C (PVPPy). ^{1}H NMR spectra ($CDCL_3$, 300 MHz; ppm): δ 6.2−7.9 (phenyl and pyridine), 8.5 (-N=C*H*−C= of PVPPy), 8.1−8.4 (-N=C*H*−C= of poly-(2VP)), 1.2−2.0 (-C*H₂*−C*H*- of PVPPy and -C*H₂*−C*H*- of P2VP)), 2.1−2.4 (-C*H₂*−C*H*- of P2VP). FT-IR (KBr, cm^{-1}): 3150, 3000, 2925, 2850 (aromatic =C−H and aliphatic -C−H of PVPPy and P2VP), 1575, 1472, 1434 (aromatic amine −C=N, phenyl −C=C of PVPPy and P2VP). Poly(2-(4-vinylphenyl)pyridine-*b*-methylmethacrylate) (PVPPy-*b*-PMMA; f_{VPPy} = 0.76; MW, 47 700 g/mol; MWD, 1.09; Table 3). T_g: 119.1 (PMMA) and 177.6 °C (PVPPy). ^{1}H NMR spectra ($CDCL_3$, 300 MHz; ppm): δ 6.4−7.8 (phenyl and pyridine of PVPPy), 8.5 (-N=C*H*−C= of PVPPy), 3.6 (-OC*H₃* of PMMA), 0.7−2.3 (-C*H₂*−C*H*- of PVPPy and -C*H₂*−C(C*H₃*)- of PMMA).

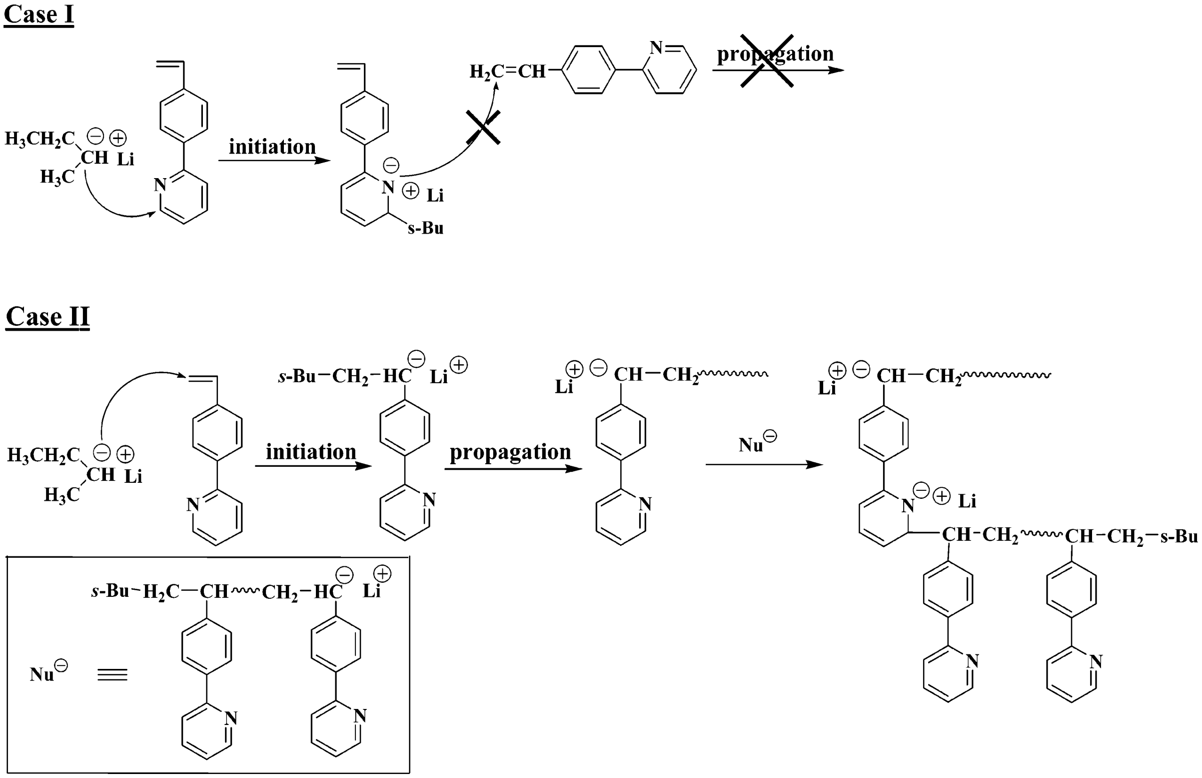
Preparation of Samples for Microphase Separation. The block copolymer solutions in THF (3 mg/mL) were drop cast on the carbon-coated copper grid and annealed at 190 °C under reduced pressure (10^{-1} mmHg) for 24 h. The annealed sample was stained with I_2 vapor for 8 h, and the excess I_2 was removed under vacuum at 25 °C for 24 h.

Characterization. Molecular weights of the polymers were estimated using SEC (Waters M 77251, M 510) 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, 10^3, and 10^4 Å, respectively, with a refractive index detector at a flow rate of 1 mL/min using THF containing 2% $(C_2H_5)_3N$ as elution solvent at 40 °C and calibrated with styrene standards (American Polymer Standards Corp.). The ^{1}H and ^{13}C NMR spectra (JEOL JNMLA300WB) were measured using $CDCl_3$ as the solvent. Chemical shifts were referred to tetramethylsilane (TMS) at 0 ppm. FT-IR spectra were run in Perkin-Elmer System 2000 using KBr pellets. Thermal properties were characterized using thermogravimetric analysis (TGA, TA-2050) and differential scanning calorimetry (DSC, TA2010) at 10 °C/min. Microphase preparation of block copolymers was confirmed using an energy-filtering transmission electron microscope (EF-TEM, EM912 OMEGA [ZEISS, S-4700]).

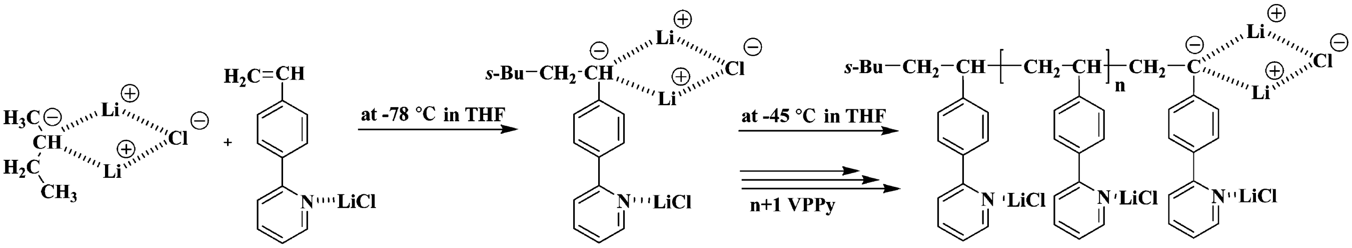
Results and Discussion

Effect of Initiators on Anionic Polymerization. The results of PVPPy polymerized using Naph-K in THF or *s*-BuLi in

Scheme 1. Possible Side Reactions in Polymerization of VPPy[16b,c]



Scheme 2. Anionic Polymerization of VPPy Coordinated with LiCl Using the Complex of *s*-BuLi and LiCl



heptane at −78 or −45 °C are shown in Table 1. The reaction solution changed from purple to brown with abrupt precipitation during the polymerization, and the yield of polymer was very low because of side reactions such as branching or cross-linking.[16] The possible side reactions in polymerization of VPPy are shown in Scheme 1. These are based on the reports of Tardi's and Sigwalt's groups, which suggested several possible side reactions, mainly during anionic polymerization of 2-vinylpyridine.[16b,c] The nucleophilicity of *s*-BuLi is strong enough both to initiate the vinyl group and to make an amine anion (N^-) of pyridine moiety during initiation. In case I, this side reaction takes place only during the initiation step because the nucleophilicity of the amine anion (N^-) is too weak to initiate the vinyl group. In addition, another side reaction also occurs during the propagation step as in case II. Therefore, anionic polymerization of VPPy was not controlled in this condition. (Table 1, entries 1 and 2).

Effect of LiCl on Anionic Polymerization of VPPy. LiCl as an additive was introduced into the polymerization in order to prevent the side reactions as shown in Scheme 1. The results of the polymerization under the three conditions using LiCl, (i) a complex of *s*-BuLi with LiCl, (ii) a coordination of VPPy with LiCl, and (iii) combination of i and ii, are summarized in Table 1.

In condition i, the solution of living VPPy initiated by the complex of *s*-BuLi with LiCl turned dark green without the precipitation during the polymerization. However, the MWD of PVPPy became broad as the polymerization time was increased from 6 to 24 h (Table 1, entries 3−5). The side reactions were reduced by the complex of *s*-BuLi with LiCl during initiation, but the carbanions attacked the α-carbon of the pyridine moiety (−N═CH-) which was not completely protected. This caused the side reaction to take place again.

In condition ii, coordination of VPPy with LiCl protected the α-carbon of the pyridine moiety. It was expected that the nucleophilicity of living VPPy would be reduced because LiCl withdraws electrons from the pyridine moiety. Therefore, it would not be strong enough to attack the α-carbon of the pyridine moiety. In contrast to this expectation, the precipitation was instantly observed during the polymerization (Table 1, entries 6 and 7). It showed that the reactivity of its nucleophilicity was still high enough to attack the α-carbon of the pyridine moiety even though the nitrogen of pyridine moiety was coordinated with LiCl. As a result, the further stabilization of nucleophilicity using a complex with LiCl is required as well as coordination of the nitrogen of pyridine with LiCl for living polymerization of VPPy.

In condition iii, the results are summarized in Table 1, entries 8−13. The polymerization of VPPy was successfully carried out with 100% yield by the combination involving the complex of the *s*-BuLi and coordination of VPPy with LiCl (Scheme 2).

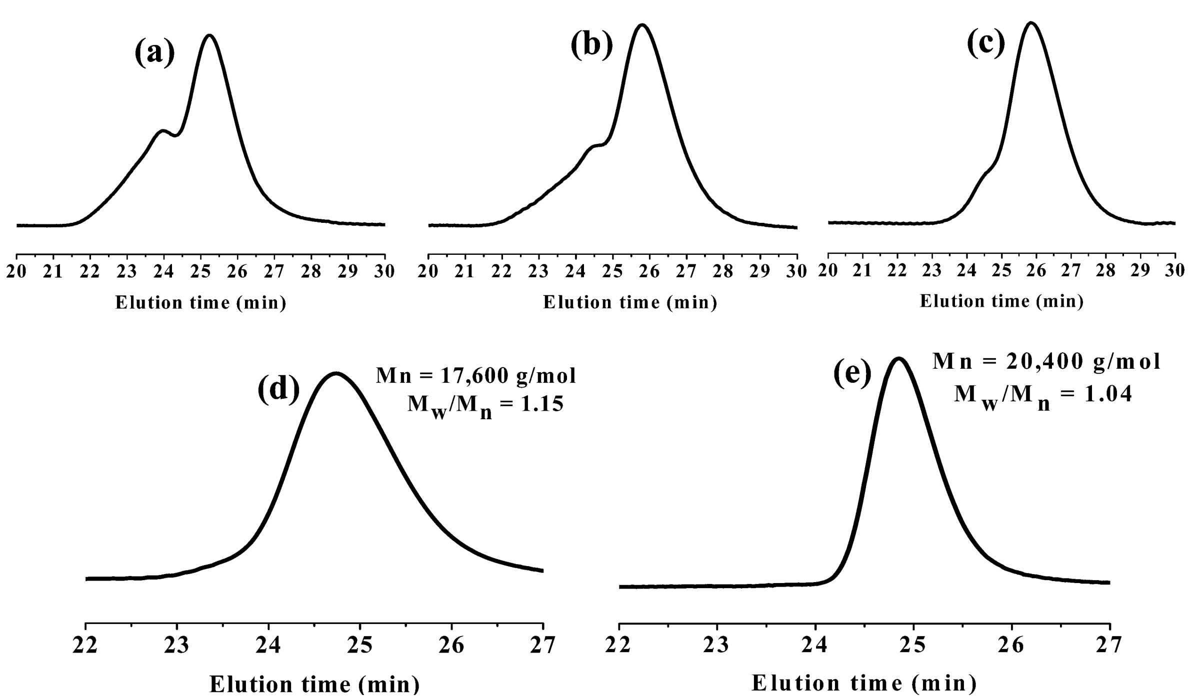
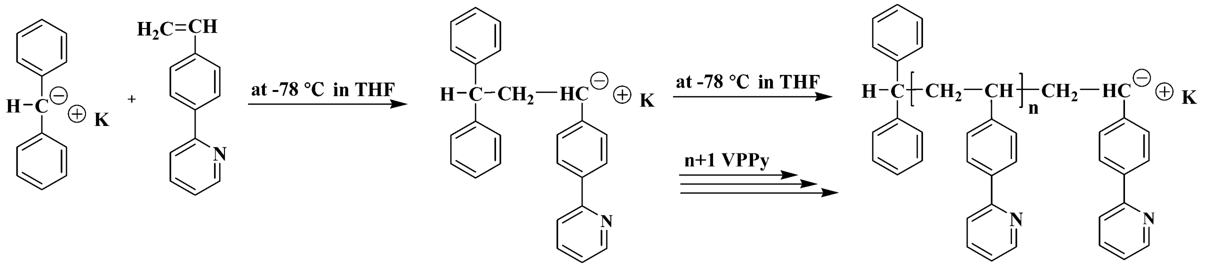


Figure 1. SEC profiles of poly(VPPy): (a) VPPy:LiCl = 1:0.26 (Table 1, entry 8), (b) VPPy:LiCl = 1:0.64 (Table 1, entry 9), (c) VPPy:LiCl = 1:0.9 (Table 1, entry 10), (d) VPPy:LiCl = 1:1.4 (Table 1, entry 13), and (e) VPPy initiated by DPM-K (Table 2, entry 2).

Scheme 3. Living Anionic Polymerization of VPPy Initiated by DPM-K



MW and MWD were gradually controlled by increasing LiCl in the ratio of VPPy to LiCl (Table 1, entries 8−10 and 13 and Figure 1a−d).

As mentioned above, the complex of *s*-BuLi with LiCl reduced the reactivity of the carbanion and coordination of VPPy with LiCl protected the α-carbon of the pyridine moiety as well. This reduced the reactivity of the carbanion because electrons withdrawn from the pyridine moiety to LiCl, which considerably controlled the anionic polymerization without side reactions. The monomodal SEC profile with narrow MWD also ensured that the polymerizations were successfully carried out.

The use of the complex of *s*-BuLi and coordination of VPPy with LiCl has some drawbacks. First, it takes 72 h to synthesize the polymers with controlled molecular weight and 100% yield even though it was polymerized in −45 °C because the propagation rate was reduced due to the coordination of initiator with LiCl. It also requires a complicated procedure to prepare LiCl in THF and to change reaction temperature.

Effect of DPM-K as an Initiator on the Polymerization of VPPy. DPM-K as an initiator with weak reactivity was introduced in order to circumvent the drawbacks of the three polymerization methods using addition of LiCl as mentioned above. The polymerization of VPPy with DPM-K was successfully carried out in various reaction times at −78 °C (Scheme 3), and the results are summarized in Table 2. The yield was increased from 47.2 to 100% as the polymerization time was increased from 30 to 150 min. The calculated molecular weight (M_n) was in the good agreement with the observed (M_n).

In comparison with the results of anionic polymerization using the coordination of VPPy with LiCl and the complex of *s*-BuLi with LiCl (Table 1), the introduction of DPM-K significantly reduced the polymerization time from 72 h to 150 min and showed very narrow molecular weight distribution because the polarizability of carbanion plus K^+ is higher than that of carbanion plus Li^+ with LiCl during propagation; the rate of the polymerization in the presence of DPM-K was higher (Table 2 and Figure 1e). At the same time, it diminished the chance for side reaction due to weak reactivity by steric hindrance and resonance of DPM-K during initiation, which prevents the attack on the α-carbon of the pyridine.[20]

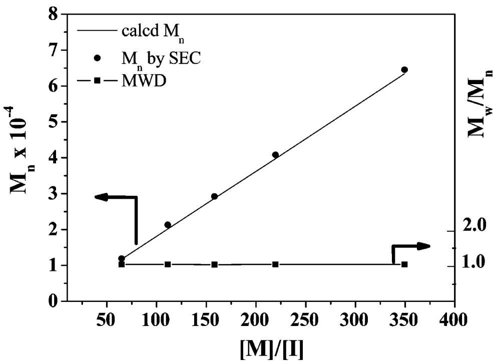


Figure 2. Molecular weight and molecular weight distribution vs the feed ratio of VPPy to DPM-K.

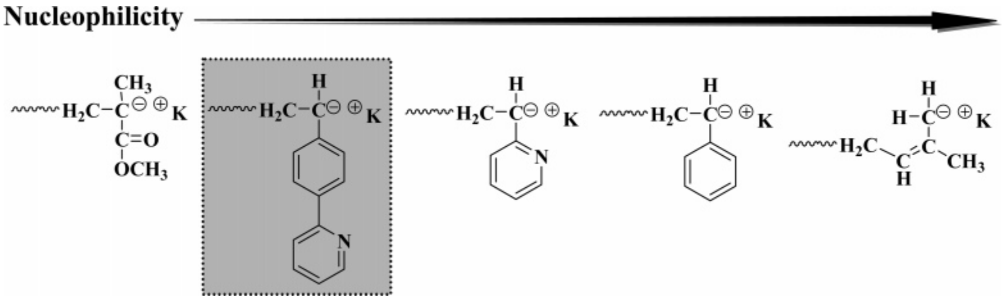


Figure 3. Nucleophilicity order of 2-(4-vinylphenyl)pyridine.

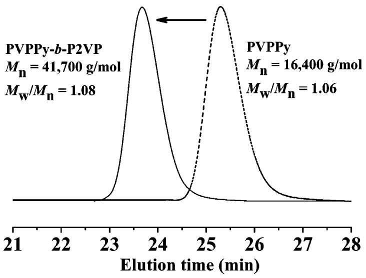


Figure 4. SEC profile of PVPPy homopolymer and PVPPy-*b*-P2VP block copolymer.

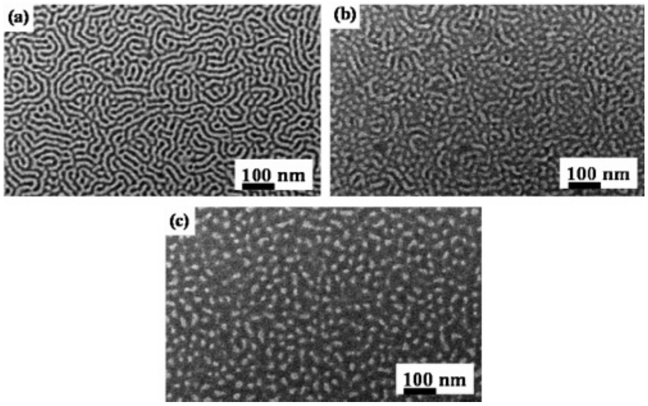


Figure 5. TEM images of PVPPy-*b*-PMMA block copolymers at 3 mg/mL concentration in THF, annealed at 190 °C under reduced pressure (10^{-1} mmHg) for 24 h: (a) $f_{\mathrm{VPPy}} = 0.25$, (b) $f_{\mathrm{VPPy}} = 0.48$, and (c) $f_{\mathrm{VPPy}} = 0.76$. The dark regions stained with I_2 vapor are PVPPy.

To prove the living nature, poly(2-(4-vinylphenyl)pyridine) was synthesized using various molar ratios of VPPy to DPM-K in the MW range of 11 900−64 500 g/mol (Table 2, entries 6−10). The good linear relationship between M_n and the feed ratio of VPPy to DPM-K as observed in Figure 2 verifies that the PVPPy has a living nature.

Block Copolymerization of VPPy with Various Monomers. To investigate the reactivity of living PVPPy, the block copolymerizaitons of VPPy were carried out with styrene (St), isoprene (IP), 2VP, and MMA using DPM-K. The results of block copolymerizations of VPPy are summarized in Table 3.

The block copolymerization of VPPy as the first monomer was carried out with the styrene first and isoprene second, but the block copolymers were not synthesized as confirmed by SEC and ^{1}H NMR. This means that the nucleophilicity of the living PVPPy is not strong enough to initiate styrene and isoprene. The two sequential block copolymerizations of either VPPy as the first monomer and 2VP as the second, or the opposite sequential order, in the absence of additives, were successfully carried out without side reactions. It was confirmed that the nucleophilicity of living PVPPy is similar to that of living 2VP.

The block copolymerization of VPPy with MMA was successfully carried out using DPM-K in the absence of any additives. As shown, MW and narrow MWD were controlled due to the pyridine moiety of styrene derivative (Table 3). However, the block copolymerization of 2VP with MMA in the absence of additives caused side reactions.[21] Fractionation was also required to obtain pure block copolymers of 2VP with MMA, and it was difficult to control MW and the block ratio without using some additives such as LiCl. From the block copolymerizations of VPPy with the various vinyl monomers, it was confirmed that the nucleophilicity of living PVPPy was between that of 2VP and that of MMA. Therefore, the increasing order of the nucleophilicity of living polymer is shown in Figure 3.

The electrophilicity of VPPy was compared again to that of St from β-carbon chemical shift values of VPPy and St. The β-carbon chemical shift of VPPy (114.25 ppm) from ^{13}C NMR is higher than that of styrene (113.7 ppm),[32] which means pyridine moieties in the para-position of VPPy played the role of a withdrawing group in reducing π-electron densities on the vinyl bonds. Therefore, the electrophilicity of VPPy is stronger than that of St (that is, electrophilicity of VPPy > that of St).

The observed MW of each block copolymer was in the good agreement with calculated MW, and the MWD was narrow, as shown in Table 3. The clear shift of the SEC profile from PVPPy to PVPPy-*b*-P2VP as shown in Figure 4 verified that block copolymers were successfully synthesized by sequential living anionic polymerization.

Study of Microphase Separation. The resulting block copolymers, PVPPy-*b*-PMMA ($f_{\mathrm{VPPy}} = 0.25$, $f_{\mathrm{VPPy}} = 0.48$, and $f_{\mathrm{VPPy}} = 0.76$), were utilized to study their phase separation behaviors by TEM, as shown in Figure 5. The phase separation of block copolymers depends on physical and chemical characteristics of the polymers such as molecular weight, block composition, and the kind of solvent for film casting, etc.[33] The dark regions are PVPPy segments of PVPPy-*b*-PMMA, and the gray regions are PMMA segments. As the volume fraction of VPPy in the block copolymer, PVPPy-*b*-PMMA, the dark region of the PVPPy domain was extended. The gray spherical domain of PMMA was observed from the block copolymer with $f_{\mathrm{VPPy}} = 0.76$ (Figure 5c). The change of morphology dependent upon the block ratio confirmed the synthesis of block copolymers by sequential anionic polymerization and the living property of poly(2-(4-vinylphenyl)pyridine).

Conclusions

The living anionic polymerization of 2-(4-vinylphenyl)pyridine (VPPy) was successfully optimized by using two different initiation systems: (i) using both the complex of *s*-BuLi with LiCl and the coordination of VPPy with LiCl and (ii) using DPM-K as an initiator. The living anionic polymerization of VPPy with the DPM-K initiator was more effective, as it significantly reduced the polymerization time to 150 min. Moreover, the calculated molecular weight (MW) was in good agreement with the observed MW. The living nature of poly-(2-(4-vinylphenyl)pyridine) (PVPPy) was observed through synthesis of the block copolymers by sequential anionic polymerization. It was clearly observed that the nucleophilicity of living PVPPy is between that of 2VP and MMA even though it is a styrene derivative containing pyridine as a withdrawing group. The block copolymerization of VPPy with either 2VP or MMA was successful in the absence of additives. The PVPPy homopolymer contained hydrophilic and hydrophobic moieties in its monomer unit, a fact which will be useful for studying the solution properties.

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