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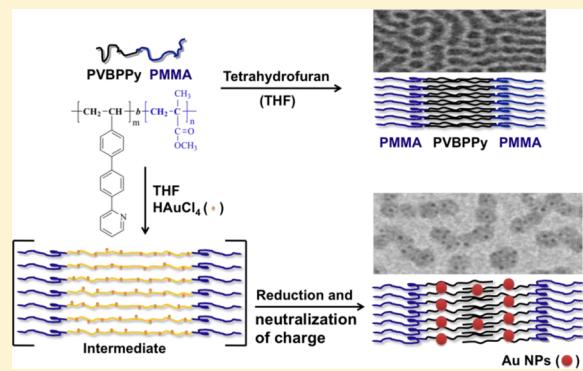
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Supporting Information

ABSTRACT: The pyridine-containing monomer 2-(4'-vinylbiphenyl-4-yl)pyridine (VBPPy), synthesized by the Suzuki coupling reaction, was successfully polymerized using diphenylmethylpotassium (DPM-K) as an initiator within 360 min at -78°C , resulting in 100% yield and polydispersity <1.3, as with the living anionic polymerization of 2-vinylpyridine (2VP) and 2-(4-vinylphenyl)pyridine (VPPy). By the block copolymerization of VBPPy with 2VP, VPPy, and methyl methacrylate (MMA), it was proven that the nucleophilicity of living poly(2-(4'-vinylbiphenyl-4-yl)pyridine) is between that of living poly(2-(4-vinylphenyl)pyridine) and that of living poly(methyl methacrylate). Among the block copolymers, PVBPPy-*b*-PMMA was used to make nanocomposites in which gold (Au) nanoparticles (NPs) were present only in the PVBPPy zone of the phase-separated PVBPPy-*b*-PMMA ($f_{\text{VBPPy}} = 0.23$) film.



INTRODUCTION

The living anionic polymerization of various styrene derivatives containing functional groups such as $-\text{CON}(\text{CH}_3)_2$, $-\text{CN}$, $-\text{COOCH}_3$, $-\text{COH}$, $-\text{CH}_3$, $-\text{NH}_2$, $-\text{OH}$, and $-\text{SH}$ has been successfully carried out by various methods of weakening the nucleophilicity of the living polymer, stabilizing the carbanions, and protecting the functional groups.^{1,2} The synthesis and application of well-controlled polystyrene and functionalized polystyrene derivatives have been widely reported in the academic and industrial fields.³ On the other hand, the synthesis of controlled pyridine-containing polymers by anionic polymerization has not been widely studied even though they are very important materials because of the various functionalization by the lone pair electrons in the pyridine ring and their pH sensitivity.^{4–6} In the anionic polymerization of 2-vinylpyridine (2VP), the nucleophilic attack of another carbanion on the pyridine can occur by strong nucleophiles, such as organolithium.^{7–9} To control the anionic polymerization without the side reactions, the reaction was performed using bulky and less reactive initiators such as (3-methyl-1,1-diphenylphenyl)lithium (DPE/s-BuLi) and diphenylmethylpotassium (DPM-K) in THF at low temperatures (-78°C) or an organolithium/LiCl complex.^{10–14}

Lee and co-workers reported the living anionic polymerization of the amphiphilic monomers 2-(4-vinylphenyl)pyridine (VPPy), 3-(4-vinylphenyl)pyridine (3VPPy), and 4-(4-vinylphenyl)pyridine (4VPPy) containing a phenyl moiety as a spacer between the vinyl and pyridine moieties. The structure and solubility of poly(2-(4-vinylphenyl)pyridine) (PVPPy), P3VPPy, and P4VPPy were close to those of poly(*p*-substituted styrene derivatives)

because the pyridine group is located at the para-position of styrene, and PVPPy is precipitated into methanol. However, considering the nucleophilicity of living PVPPy, the polymer was closer to vinylpyridine derivatives. This living anionic polymerization of VPPy, 3VPPy, and 4VPPy succeeded using two different initiation conditions: (i) a complex of *sec*-butyllithium (*s*-BuLi) with lithium chloride (LiCl) and coordination of VPPy with LiCl and (ii) DPM-K as a weak initiator. The living nature and reactivity of this living polymer were between those of living P2VP and MMA by confirmed block copolymerization.^{15,16}

In particular, block copolymers containing P2VP segments such as polystyrene-*b*-poly(2-vinylpyridine) (PSt-*b*-P2VP), polyisoprene-*b*-poly(2-vinylpyridine), poly(2-vinylpyridine)-*b*-poly(methyl methacrylate), poly(2-vinylpyridine)-*b*-poly(ethylene oxide), and poly(2-vinylpyridine)-*b*-poly(2-(4-vinylphenyl)pyridine) (P2VP-*b*-PVPPy) have been synthesized by anionic polymerization and have been widely used in nanomaterial, electrochemical, electrical, and optical applications.^{17–20} Among these block copolymers, P2VP-*b*-PVPPy formed hollow micelles with flower morphologies in a mixed solvent of methanol and water due to tangential packing of blocks of both P2VP and PVPPy at the interface. The chemical composition of the hollow flower micelles facilitates the formation of highly porous and stable bimetallic dendritic nanoparticles of Pt–Au through a solution-based process at room temperature, and these bimetallic

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dendritic nanoparticles have many applications such as in optical instruments, selective oxidation and dehydrogenation, catalysis, electrocatalysis, and sensors.²¹

The self-assembly process is a common phenomenon in nature and synthetic materials science. Generally, block copolymers with hydrophilic and hydrophobic moieties form amphiphilic assemblies such as microphase-separated nanostructures, hollow micelles, and vesicles in selective solvent. Recently, polymer superstructures with a miktoarm graft copolymer containing carboxylic acid as a hydrophilic moiety and benzyl as a hydrophobic moiety in both a polar and a nonpolar solvent have been reported.^{22–25} More recently, stimuli-sensitive vesicles, which act as a reservoir for both hydrophobic and hydrophilic molecules individually, were successfully formed through a one-step process with the controlled amphiphilic homopolymer PVPPy.^{26,27} In this prospective, the unique micellization behaviors of the homopolymer PVPPy are also predicted in view of the fact that it contains hydrophilic (pyridyl) and hydrophobic (biphenyl) moieties in the same monomer like the micellization behaviors of PVPPy.

Comparing P2VP with PVPPy as an amphiphilic homopolymer, PVPPy has the chemical structure of both polystyrene and P2VP. It is known that homopolymers with hydrophilic and hydrophobic moieties can also form vesicles and micelles similar to amphiphilic block copolymers. Additionally, the block copolymer of P2VP-*b*-PVPPy allowed the formation of flower micelles and bimetallic dendritic nanoparticles of Pt–Au by the different reactivity of the pyridine in the P2VP and the PVPPy blocks. Accordingly, to generate the different reactivity from P2VP and PVPPy, a new pyridine-containing monomer of 2-(4'-vinylbiphenyl-4-yl)pyridine (VBPPy) was designed by introducing biphenyl between the vinyl and pyridine moieties based on the structure of 2-vinylpyridine and the addition of biphenyl between vinyl and pyridine units could make more rigidity and hydrophobicity than P2VP and PVPPy. The VBPPy was synthesized by the Suzuki coupling reaction, and the possibility of anionic polymerization of 2-(4'-vinylbiphenyl-4-yl)pyridine (VBPPy) was evaluated using various reaction conditions for optimal results. The reactivity of living poly(2-(4'-vinylbiphenyl-4-yl)pyridine) (PVBPPy) containing biphenyl units was compared with that of P2VP and PVPPy by the block copolymerization of VBPPy with various monomers. Moreover, a phase-separated PVBPPy-*b*-PMMA ($f_{\text{VBPPy}} = 0.23$) diblock film was used as a template to form a nanocomposite in which gold (Au) nanoparticles (NPs) were present only in PVBPPy.

EXPERIMENTAL SECTION

Materials. 4-Vinylphenylboronic acid (Aldrich), 4-bromophenylboronic acid, 2-bromopyridine (Aldrich, 99%), and tetrakis(triphenylphosphine)palladium(0) ($\text{Pd}(\text{PPh}_3)_4$, Aldrich) were used as received. A 2 M solution of K_2CO_3 (Aldrich, 99%) in distilled water was prepared. As-received *s*-BuLi (Aldrich, 1.4 M in cyclohexane) and naphthalene potassium (Naph-K) prepared with naphthalene and potassium metal were stored at -30°C in ampules equipped with break-seals. 2-Vinylpyridine (2VP, Aldrich, 97%) and methyl methacrylate (MMA, Aldrich, 99%) were passed through an alumina column, 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. DPM-K was prepared according to a previously reported procedure.^{28,29} The efficiency of DPM-K was determined by titration with octyl alcohol.

2-(4-Bromophenyl)pyridine (BrPPy). 2-Bromopyridine (20.0 g, 126.7 mmol), 2 M potassium carbonate (K_2CO_3 , 14.0 g) in H_2O (50.0 mL), and tetrakis(triphenylphosphine)palladium(0) ($\text{Pd}(\text{PPh}_3)_4$,

Table 1. Synthesis of the Homopolymer VBPPy via Anionic Polymerization Using Various Initiators in THF at -78°C

initiator (mmol)	VBPPy (mmol)	additive (mmol)	time (min)	homopolymer			yield (%)
				calcd ^a	obsd ^b	M_w/M_n^b	
<i>s</i> -BuLi							
0.055	2.08		360	9.8	30.1	1.72	15.9
		α -MeSt					
0.099	2.14	0.34	360	6.7	5.9	1.21	97.2
		DPE					
0.090	2.14	0.17	390	6.1	8.3	1.17	10.0
0.036 ^c	3.32	0.18	390	23.8	5.7	1.23	24.0
DPM-K							
0.092	3.10		180	8.0	10.2	1.06	48.0
0.041	2.92		300	16.5	18.2	1.26	90.7
0.068	2.02		330	7.6	8.2	1.29	97.5
0.117 ^c	2.77		360	6.1	6.5	1.21	100
0.065 ^c	2.56		360	10.1	10.5	1.26	100
0.056	2.50		360	11.5	12.2	1.25	100
0.070 ^c	5.32		360	19.6	20.2	1.24	100
0.036 ^c	4.52		360	32.3	32.6	1.27	100
0.031 ^c	4.95		360	41.1	42.1	1.24	100
0.042 ^c	8.86		360	54.3	55.2	1.24	100

^a $M_n(\text{calcd}) = (\text{MW of VBPPy}) \times [\text{VBPPy}]/[\text{initiator}] \times \text{yield of polymers } (\%)$. ^b $M_n(\text{obsd})$ and M_w/M_n were obtained by SEC calibration using a polystyrene standard in tetrahydrofuran (THF) containing 2% triethylamine ($\text{C}_2\text{H}_5)_3\text{N}$ as an eluent at 40°C . ^c α -MeSt: α -methylstyrene; DPE: 1,1-diphenylethylene. ^cThe concentration of the solution of VBPPy in THF is 0.15 mol/mL.

3.0 mol %) in THF were reacted at 80°C for 2 h under a nitrogen atmosphere, and then 4-bromophenylboronic acid (10.0 g, 42.7 mmol) was slowly added dropwise over 30 min. After the reaction was complete, the solvent was evaporated under reduced pressure. The excess unreacted 2-bromopyridine was distilled at 110°C at 1.0 mmHg and 2-(4-bromophenyl)pyridine at 180°C at 1.0 mmHg as a white crystal. The yield was 72%. ¹H NMR spectra (CDCl_3 , 400 MHz), δ (ppm): 8.69 (d, 1H, $-\text{N}=\text{CH}-\text{C}=$ of pyridyl), 7.95 (d, 2H, $\text{Cl}-\text{C}=\text{CH}-\text{CH}=$ of phenyl), 7.74 (m, 2H, $=\text{N}-\text{C}=\text{CH}-\text{CH}=$ of phenyl), 7.45 (d, 2H, $-\text{CH}=\text{CCl}-\text{CH}=$ of phenyl), 7.24 (t, 1H, $-\text{N}=\text{CH}-\text{CH}=$ of pyridyl).

Synthesis of VBPPy. 4-Vinylphenylboronic acid (10.0 g, 67.6 mmol), 2-(4-bromophenyl)pyridine (13.9 g, 87.9 mmol), 2 M potassium carbonate (K_2CO_3 , 14.0 g) in H_2O (50 mL), and tetrakis(triphenylphosphine)palladium(0) ($\text{Pd}(\text{PPh}_3)_4$, 3.0 mol %) in THF were reacted at 80°C for 24 h under a nitrogen atmosphere. After the reaction was complete, the mixture was evaporated and extracted with ether/ H_2O . The concentrated mixtures were purified by column chromatography with hexane/ethyl acetate = 7/3 to obtain a yellowish-white solid and then recrystallized from acetone. The yield was 78.0%. Melting point (mp) = 142.5°C . Elemental analysis: calcd C (88.68%), H (5.88%), N (5.44%). Found: C (89.14%), H (5.49%), N (5.37%). ¹H NMR spectra (CDCl_3 , 400 MHz), δ (ppm): 8.64 (d, 1H, $-\text{N}=\text{CH}-\text{C}=$ of pyridyl), 8.09 (d, 2H, $=\text{N}-\text{C}-\text{C}=\text{CH}-$ of phenyl), 7.89 (m, 2H, $=\text{N}-\text{C}-\text{C}=\text{CH}-\text{CH}=$ of phenyl), 7.73 (d, 2H, $\text{CH}_2=\text{CH}-\text{C}=\text{CH}-\text{CH}=$ of phenyl), 7.62 (d, 2H, $=\text{N}-\text{C}=\text{CH}-\text{CH}=$ of pyridyl), 7.52 (d, 2H, $\text{CH}_2=\text{CH}-\text{C}=\text{CH}-$ of phenyl), 7.25 (t, 1H, $-\text{N}=\text{CH}-\text{CH}=$ of pyridyl), 6.76 (q, 1H, $\text{CH}_2=\text{CH}-$ of vinyl), 5.83 (d, 1H, $\text{CH}_2=\text{CH}-$ of vinyl), 5.30 (d, 1H, $\text{CH}_2=\text{CH}-$ of vinyl). ¹³C NMR (CDCl_3 , 75 MHz), δ (ppm): 114.1, 136.8 (vinyl-), 136.4, 126.7, 127.2, 139.9 (vinyl-phenyl), 136.9, 127.3, 127.2, 138.3 (-phenyl-pyridine), 157.0, 120.4, 141.2, 122.1, 149.7 (pyridine). FT-IR (KBr, cm^{-1}): 3150 and 3050 (vinyl C–H, aromatic $=\text{C}-\text{H}$), 1627 (vinyl C=C), 1588, 1472, 1439 (aromatic amine C=N, aromatic C=C).

Chart 1. Structure of (a) 2-Vinylpyridine (Liquid), (b) 2-(4-Vinylphenyl)pyridine (Viscous Liquid), and (c) 2-(4'-Vinylbiphenyl-4-yl)pyridine (Solid)

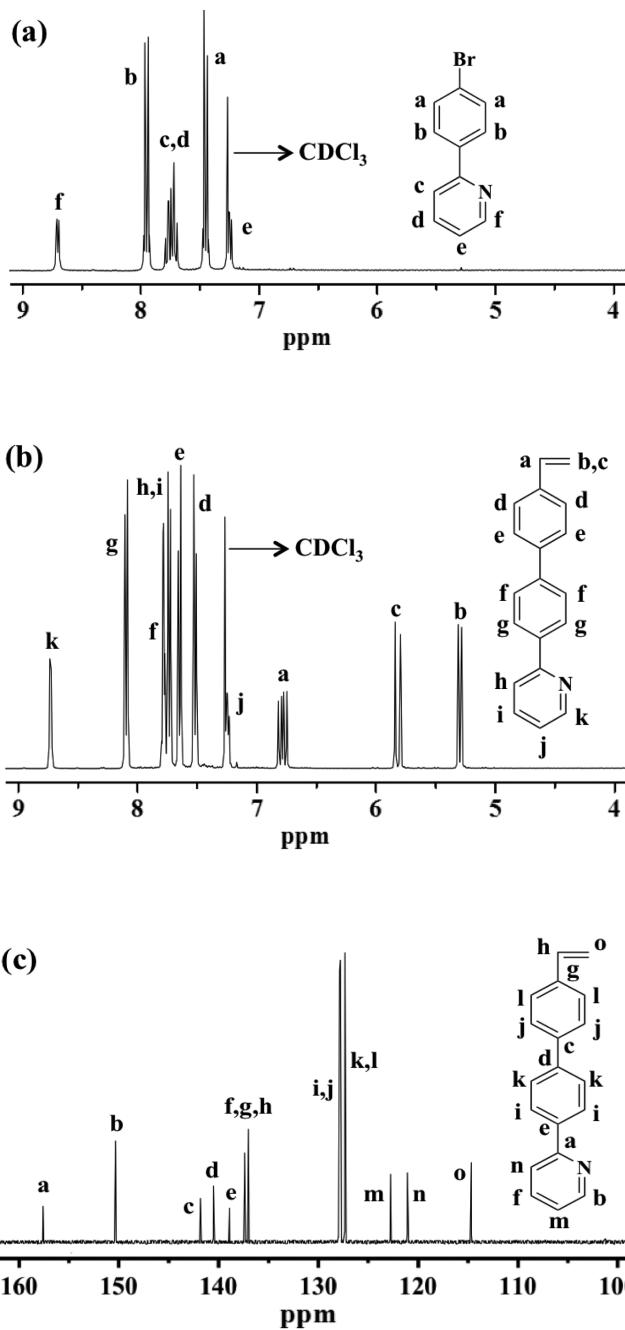
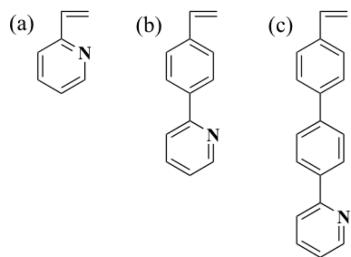
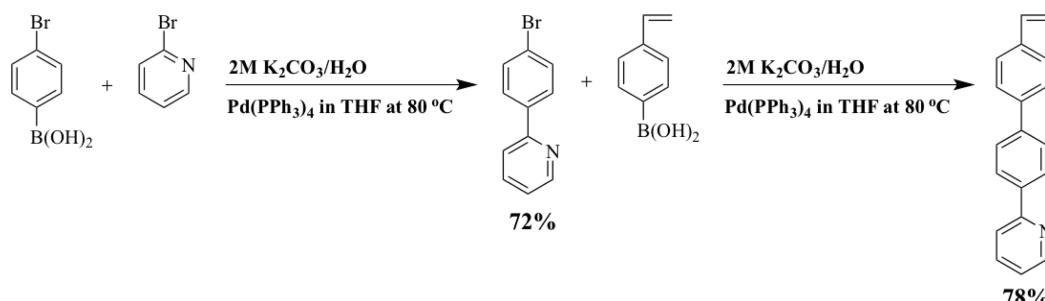
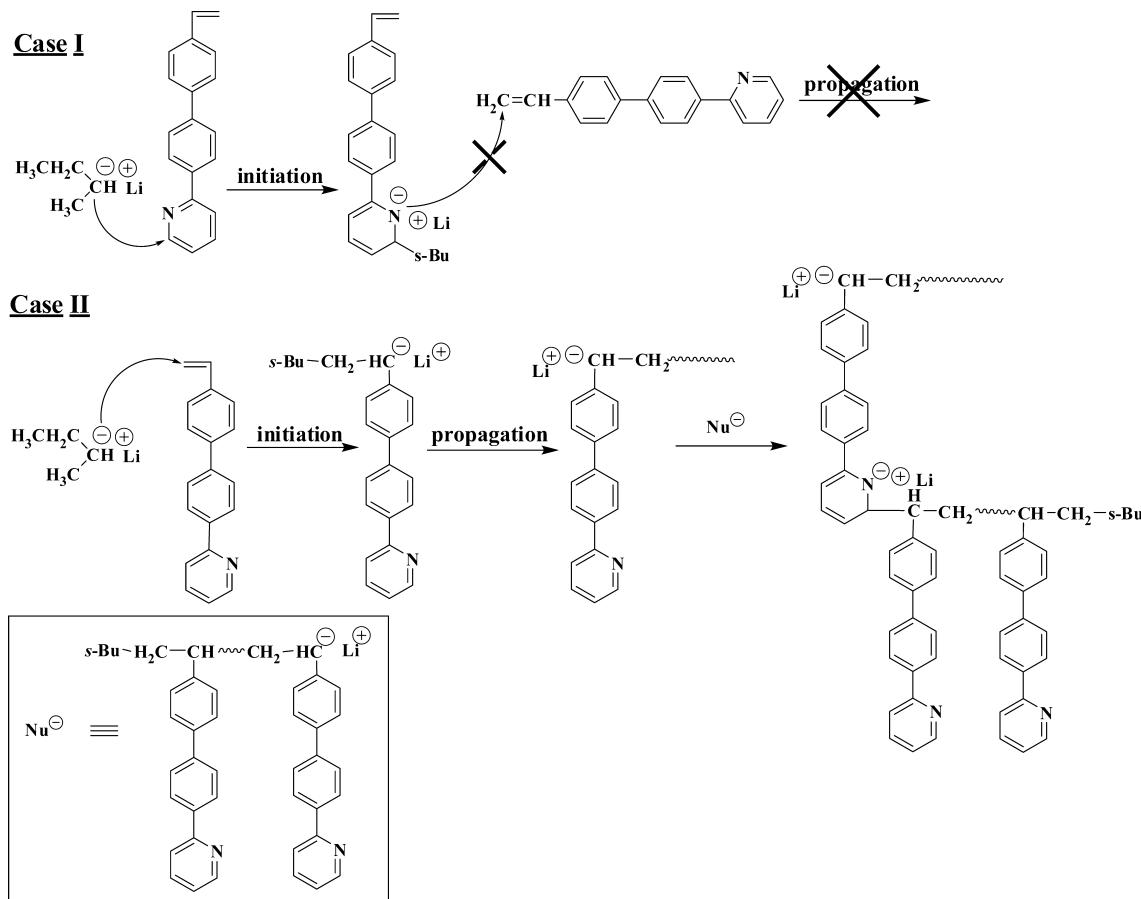
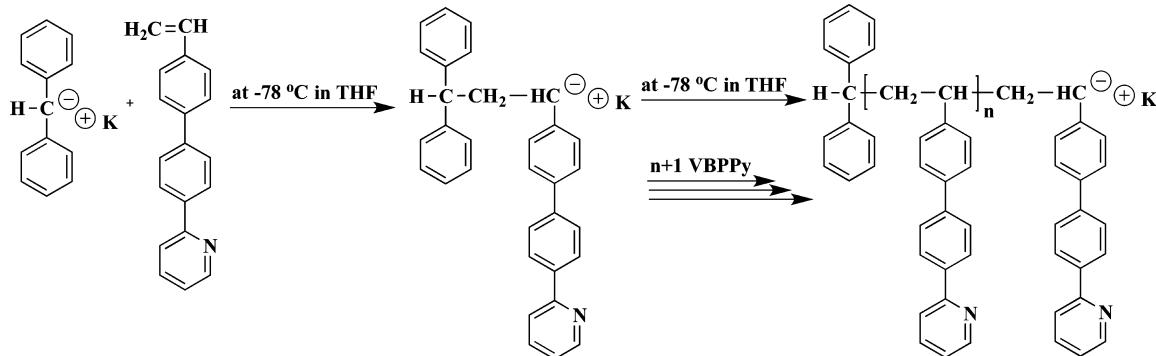


Figure 1. (a) ^1H NMR spectra of 2-(4-bromophenyl)pyridine (BrPPy), (b) ^1H NMR, and (c) ^{13}C NMR spectra of 2-(4'-vinylbiphenyl-4-yl)pyridine (VBPPy).

Scheme 1. Synthesis of 2-(4'-Vinylbiphenyl-4-yl)pyridine via Suzuki Coupling Reaction



Scheme 2. Possible Side Reactions in the Polymerization of VBPPy

Scheme 3. Living Anionic Polymerization of VBPPy Initiated by DPM-K in THF at -78°C 

Block Copolymerization of 2VP with VBPPy. Polymerization of 2VP using DPM-K as an initiator was performed in THF at -78°C for 30 min in an all-glass apparatus under reduced pressure (10^{-6} mmHg). A portion of the living poly(2-vinylpyridine) (P2VP) solution was withdrawn to an attached receiver for characterization of the homopolymer. Sequentially, VBPPy as a second monomer was added into the living P2VP solution, and the copolymerization was carried out at -78°C for 360 min (see Figure S6 in Supporting Information). After the polymerization, purification was carried out as described above. The polymers were then characterized using ^1H NMR and SEC. P2VP-*b*-PVBPPy ($f_{\text{VBPPy}} = 0.23$; MW: 19 500 g/mol; PDI: 1.25; Table 1). ^1H NMR spectra (CDCl_3 , 300 MHz), δ (ppm): 6.3–8.2 (phenyl and pyridine), 8.5–8.6 ($-\text{N}=\text{CH}-\text{C}=$ of PVBPPy), 8.0–8.3 ($-\text{N}=\text{CH}-\text{C}=$ of P2VP), 1.3–2.0 ($-\text{CH}_2-\text{CH}-$ of PVBPPy and $-\text{CH}_2-\text{CH}-$ of P2VP)), 2.1–2.9 ($-\text{CH}_2-\text{CH}-$ of P2VP) (see Figure S7 in Supporting Information).

Block Copolymerization of VPPy with VBPPy. Block copolymerization of VBPPy with VPPy was carried out following the above procedure for the block copolymerization of VBPPy with 2VP. After the polymerization, purification was carried out as described above. The polymers were then characterized using ^1H NMR and SEC. PVPPy-*b*-PVBPY ($f_{\text{VBPPy}} = 0.41$; MW: 17 400 g/mol; PDI: 1.25, Table 1). T_g : 179.6 $^{\circ}\text{C}$. T_d : 363 $^{\circ}\text{C}$. ^1H NMR spectra (CDCl_3 , 300 MHz), δ (ppm): 6.2–8.4 (phenyl and pyridine of PVPPY and PVBPPY), 8.4–8.7 ($-\text{N}=\text{CH}-\text{C}=$ of pyridine), 1.1–2.4 ($-\text{CH}_2-\text{CH}-$ of PVPPY and PVBPPY).

Block Copolymerization of VBPPy with VPPy. Using DPM-K as an initiator, VBPPy was polymerized in THF at -78°C for 360 min in an all-glass apparatus under reduced vacuum (10^{-6} mmHg). A portion of the living poly(2-(4'-vinylbiphenyl-4-yl)pyridine) (PVBPY) solution was withdrawn to an attached receiver for characterization of the homopolymer. Sequentially, VPPy as the second monomer was

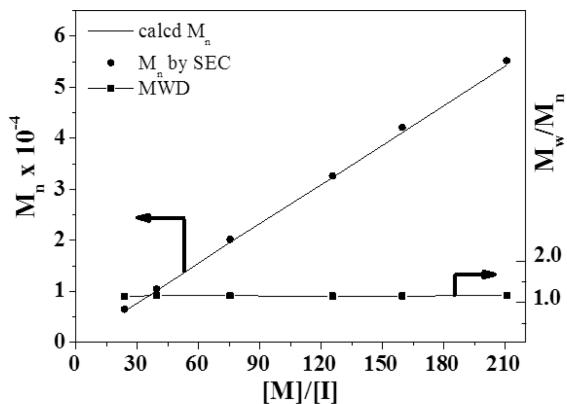


Figure 2. Molecular weight and molecular weight distribution vs the feed ratio of VBPPy to DPM-K.

added into the living PVBPPy solution, and the copolymerization was carried out at -78°C . The living polymeric solution remained deep violet. After the polymerization, purification was carried out as described above. The polymers were then characterized using ^1H NMR and SEC. PVBPPy-*b*-PVPPy ($f_{\text{VBPPy}} = 0.45$; MW: 51 000 g/mol; PDI: 1.26; Table 1). ^1H NMR spectra (CDCl_3 , 300 MHz), δ (ppm): 6.2–8.3 (phenyl and pyridine of PVPPy and PVBPPy), 8.5–8.7 ($-\text{N}=\text{CH}-\text{C}=$ of pyridine), 1.2–2.5 ($-\text{CH}_2-\text{CH}-$ of PVPPy and PVBPPy).

Block Copolymerization of VBPPy with MMA. Using DPM-K as an initiator, VBPPy was polymerized in THF at -78°C for 360 min in an all-glass apparatus under reduced vacuum (10^{-6} mmHg). A portion of the living poly(2-(4'-vinylbiphenyl-4-yl)pyridine) (PVBPPy) solution was withdrawn to an attached receiver for characterization of the homopolymer. Sequentially, MMA as the second monomer was added into the living PVBPPy solution, and the copolymerization was carried out at -78°C (see Figure S8 in Supporting Information). After the polymerization, purification was carried out as described above. The polymers were then characterized by ^1H NMR, SEC, DSC, and TGA. PVBPPy-*b*-PMMA ($f_{\text{VBPPy}} = 0.23$; MW: 48 100 g/mol; PDI: 1.21; Table 1) T_g : 122.5 °C (PMMA) and 195.1 °C (PVBPPy). T_d : 331.8 °C (PVBPPy). ^1H NMR spectra (CDCl_3 , 300 MHz), δ (ppm): 6.5–8.0 (phenyl and pyridine of PVBPPy), 8.6–8.7 ($-\text{N}=\text{CH}-\text{C}=$ of PVBPPy), 3.6 ($-\text{OCH}_3$ of PMMA), 0.6–2.1

($-\text{CH}_2-\text{CH}-$ of PVBPPy and $-\text{CH}_2-\text{C}(\text{CH}_3)-$ of PMMA) (see Figure S9 in Supporting Information).

Preparation of the Nanocomposite. The block copolymer solutions in THF (3 mg/mL) were drop-casted on a carbon-coated copper grid and annealed at 130°C under reduced pressure (10^{-1} mmHg) for 24 h. The annealed sample was stained with iodine (I_2) vapor for 8 h, and the excess I_2 was removed under vacuum at 25°C for 24 h. For gold (Au) nanoparticle (NPs) synthesis, pyridine units of PVBPPy were coordinated with AuCl_3 for 12 h and then reduced with hydrazine. The Au NPs were characterized by UV-vis and TEM.

Characterization. The molecular weights (MWs) of the polymers were estimated using size exclusion chromatography (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 sizes of the columns were 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% triethylamine (TEA, $(\text{C}_2\text{H}_5)_3\text{N}$) at 40°C as the elution solvent and calibrated with styrene standards (American Polymer Standards Corp.). The ^1H 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 using a PerkinElmer System 2000 with KBr pellets. Thermal properties were characterized with thermogravimetric analysis (TGA, TA-2050) and differential scanning calorimetry (DSC, TA2010) under nitrogen with a heat rate of 10 °C/min. Microphase separation of block copolymers was confirmed using an energy-filtering transmission electron microscope (EF-TEM, EM912 OMEGA [ZEISS, S-4700]).

RESULTS AND DISCUSSION

Synthesis of 2-(4'-Vinylbiphenyl-4-yl)pyridine (VBPPy). The pyridine-containing monomer of 2-(4'-vinylbiphenyl-4-yl)pyridine was designed by introducing biphenyl between the vinyl and pyridine moieties based on the structure of 2-vinylpyridine compared with 2-vinylphenylpyridine with one phenyl unit between vinyl and pyridine as shown in Chart 1.

For the synthesis of VBPPy, the synthetic route based on a previously reported procedure^{15,30} were performed as shown in Scheme 1.

Table 2. Block Copolymerization of VBPPy with Various Monomers via Anionic Polymerization

initiator (mmol)	1st monomer (mmol)	2nd monomer (mmol)	time (min)	homopolymer or block copolymer			yield (%)	f_{PVBPY}^c
				$M_n \times 10^{-3}$	M_w/M_n^b			
				calcd ^a	obsd ^b			
s-BuLi ^d	St	VBPPy						
0.059	4.69	2.60	390	19.5(8.2)	116.9(7.0)	1.19(1.04)	100	0.36
DPM-K	2VP							
0.068	7.77	2.37	390	21.7(12.4)	19.5(12.3)	1.25(1.06)	98	0.23
0.073	5.42	2.10	390	14.8(7.8)	15.7(8.2)	1.22(1.07)	97	0.28
0.053 ^e	4.29	2.01	390	18.2(8.5)	18.9(8.7)	1.24(1.07)	98	0.32
	VPPy	VBPPy						
0.082	3.63	2.52	540	16.1(8.0)	17.4(8.2)	1.25(1.06)	98	0.41
	VBPPy	VPPy						
0.022	1.57	1.96	540	34.5(18.4)	51.0(20.2)	1.26(1.25)	98	0.45
	VBPPy	MMA						
0.022	1.62	5.31	420	43.0(18.9)	48.1(21.6)	1.12(1.27)	99	0.23
0.040 ^e	1.93	11.07	420	40.1(12.4)	40.9(13.1)	1.17(1.26)	98	0.15

^a $M_n(\text{calcd}) = (\text{MW of 1st monomer}) \times [\text{1st monomer}]/[\text{initiator}] + (\text{MW of 2nd monomer}) \times [\text{2nd monomer}]/[\text{initiator}]$. ^b $M_n(\text{obsd})$ and M_w/M_n were measured by SEC calibration using a polystyrene standard in THF containing 2% $(\text{C}_2\text{H}_5)_3\text{N}$ as the eluent at 40°C . ^cBlock copolymer composition was determined by means of ^1H NMR spectroscopy. ^dDPE (0.188 mmol) in THF was added before introducing VBPPy monomer to living polystyrene. ^eThe concentration of the solution of VBPPy in THF is 0.15 mol/mL.

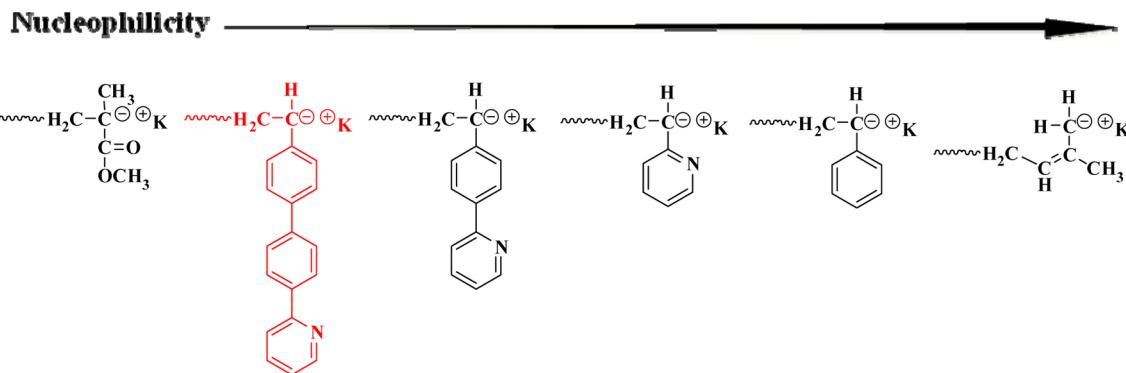


Figure 3. Nucleophilicity order of 2-(4'-vinylbiphenyl-4-yl)pyridine.

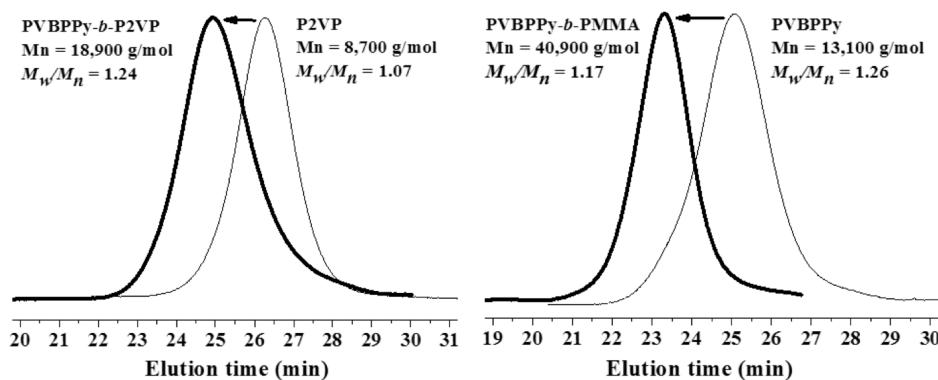


Figure 4. SEC profile from P2VP homopolymer to P2VP-*b*-PVBPPy block copolymer and from PVBPPy homopolymer to PVBPPy-*b*-PMMA block copolymer.

At first, 2-(4-bromophenyl)pyridine (BrPPy) was synthesized via Suzuki coupling reaction with 2-bromopyridine, 2 M potassium carbonate (K_2CO_3) in H_2O , tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$), and 4-bromophenylboronic acid in THF were reacted at $80\ ^\circ C$ for 2 h under a nitrogen atmosphere. To prevent the generation of byproducts such as dimer, trimer, etc., by coupling reaction of 4-bromophenylboronic acid by themselves and to obtain high conversion of BrPPy, the excess of 2-bromopyridine was added, and the solution of 4-bromophenylboronic acid in THF was introduced into the mixture solution dropwise for over 30 min. Next, the resulting product of BrVPPy with white crystal and 72% was added to the mixture solution of 4-vinylphenylboronic acid, 2 M K_2CO_3 in H_2O , and $Pd(PPh_3)_4$ in THF were reacted at $80\ ^\circ C$ for 24 h under a nitrogen atmosphere. The yellowish-white solid of VBPPy was obtained with 78.0% yield. The alternative method to synthesis of VBPPy is shown in Scheme S1 of the Supporting Information. The resulting VBPPy was dried under the drying agent P_2O_5 at 10^{-6} mmHg for anionic polymerization. The successful synthesis of BrVPPy and VBPPy was confirmed by measurement of 1H NMR spectra of 2-(4-bromophenyl)pyridine (BrPPy) and 1H and ^{13}C NMR spectra of 2-(4'-vinylbiphenyl-4-yl)pyridine (VBPPy) as shown in Figure 1.

Effect of Initiators on Anionic Polymerization. To optimize living anionic polymerization of VBPPy, various initiator systems were applied such as *s*-BuLi, *s*-BuLi/ α -MeSt, *s*-BuLi/DPE, and DPM-K. The details of the polymerizations using the various initiator systems are summarized in Table 1.

During the polymerization of VBPPy using *s*-BuLi, the polymeric solution changed from violet to brown and abrupt precipitation was observed. Because of side reactions such as

branching or cross-linking,^{3a} the yield was very low at 15.9%. To control the polymerization of VBPPy by reducing the nucleophilicity, polymerizations using *s*-BuLi/ α -MeSt and *s*-BuLi/DPE were performed. Although the yields were increased (97.2 and 100%, respectively) compared with the 15.9% yield of *s*-BuLi, the polymerizations were not controlled because a hump was observed in the SEC curves (see Figure S4 in Supporting Information). The potential side reactions during the polymerization of VBPPy using *s*-BuLi, *s*-BuLi/ α -MeSt, and *s*-BuLi/DPE are shown in Scheme 2 derived from previous reports by Tardi's Sigwalt's, and Lee's group.^{7,12} The highly nucleophilic *s*-BuLi initiates vinyl group and makes an amine anion (N^-) of the pyridine moiety.

The weak nucleophile DPM-K initiated VBPPy without side reactions and the anionic polymerization was successfully carried out at $-78\ ^\circ C$, as shown in Table 1 and Scheme 3. When comparing the anionic polymerization of VBPPy using *s*-BuLi-based initiation systems such as *s*-BuLi, *s*-BuLi/ α -MeSt, and *s*-BuLi/DPE, the introduction of DPM-K showed a narrow molecular weight distribution because of the higher polarizability of the carbanion with K^+ than that of the carbanion with Li^+ during propagation. It was proved that counteraction of K^+ and Li^+ had a significant effect on controlling anionic polymerization of VBPPy as well as greater steric hindrance and resonance of DPM-K, as reported previously.^{3,15} The yield was improved from 48 to 100% as the polymerization time was increased from 180 to 360 min, and the calculated molecular weight (M_n) was in the good agreement with the observed (M_n) in Table 1. In general, the anionic polymerization of 2-vinylpyridine (2VP) using DPM-K as an initiator took 30 min in THF at $-78\ ^\circ C$, and that of 2-(4-vinylphenyl)pyridine

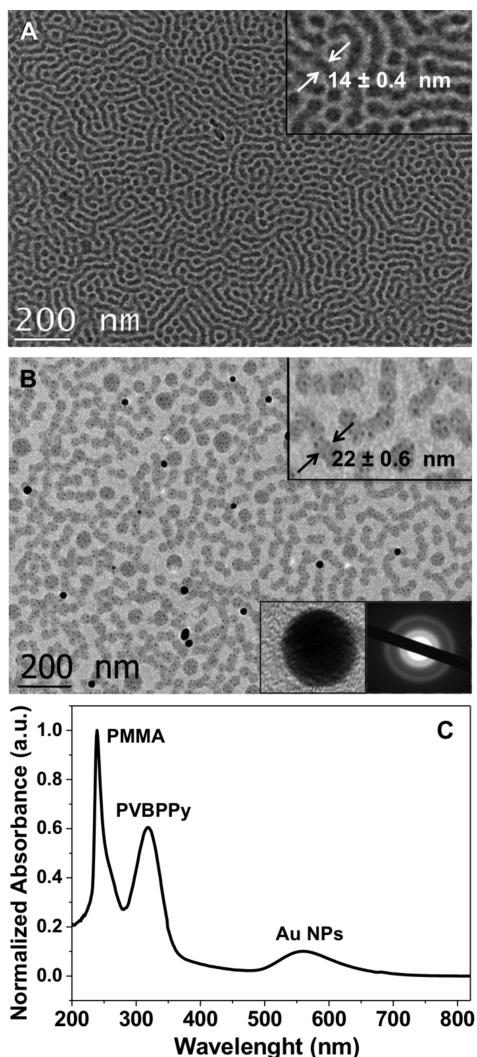


Figure 5. (A) TEM images of (A) PVBPPy-*b*-PMMA block copolymers at a 3 mg/mL concentration in THF after annealing it at 130 °C for 24 h ($f_{\text{VBPY}} = 0.23$). The dark regions stained with I₂ vapor are PVBPPy. (B) Au NPs synthesized using a PVBPPy-*b*-PMMA phase-separated solution as a template (inset micrographs are enlarge images of the marked area of (B), a single Au nanoparticle, and a selected area diffraction pattern of the film TEM micrograph without staining. (C) UV-vis spectrum of the PVBPPy-*b*-PMMA block copolymer solution in THF with synthesized Au NPs.

(VPPy) took 150 min in THF at -78 °C. On the other hand, it took 360 min to synthesize VBPPy by anionic polymerization using DPM-K in THF at -78 °C. As the number of phenyl group spacers between the vinyl and pyridine moiety increased from zero in 2VP to one in VPPy and two in VBPPy, the nucleophilicity was decreased because the strength of the withdrawing group increased by the electron-withdrawing effect in this order: pyridine < phenylpyridine < biphenylpyridine increased.

In order to prove that PVBPPy has a living nature even though the PDI of PVBPPy (<1.3) is broader than that of P2VP (<1.1) and PVPPy (<1.1), 2-(4'-vinylbiphenyl-4-yl)pyridine was synthesized using various molar ratios of the VBPPy to DPM-K in the molecular weight (MW) range of 6500–55 200 g/mol as shown in Table 1 (see Figure S10 in Supporting Information). The good linear relationship between M_n and the feed ratio of VBPPy to DPM-K as observed in Figure 2 verifies that the PVBPPy has a living nature.

Block Copolymerization of VBPPy with Various Monomers. Based on the nucleophilicity in the order of living P2VP > living PVPPy > living PMMA, the block copolymerization of VBPPy was carried out with 2-vinylpyridine (2VP), 2-(4-vinylphenyl)pyridine (VPPy), and methyl methacrylate (MMA) using DPM-K to study the reactivity of living PVBPPy. The detailed results of the block copolymerization of VBPPy are summarized in Table 2. The block copolymerization of 2VP as the first monomer and VBPPy as the second was performed, and controlled molecular weight (MW) and polydispersity (PDI) were observed from the SEC, which demonstrated that the nucleophilicity of living P2VP is higher than that of living PVBPPy. The two sequential block copolymerizations using either VBPPy as the first monomer and 2VP as the second or the opposite sequential order were successfully carried out. The block copolymerization of VPPy as the first monomer with VBPPy as the second was controlled. However, the block copolymerization of VBPPy as the first with VPPy as the second appeared bimodal from the SEC results, proving that the nucleophilicity of living PVPPy is stronger than that of living PVBPPy. The block copolymerization of VBPPy with MMA was also carried out using DPM-K and resulted in controlled MW and narrow PDI. From the block copolymerizations of VPPy with the various vinyl monomers, it was verified that the nucleophilicity of living PVBPPy was between that of living PVPPy and that of living MMA. Therefore, the increasing order of nucleophilicity of the living polymers is shown in Figure 3.

The observed MW of each block copolymer was in good agreement with the calculated MW, and the PDI was narrow, as shown in Table 2. Figure 4 showed the clear shift of the SEC profile from P2VP to P2VP-*b*-PVBPPy and from PVBPPy to PVBPPy-*b*-PMMA. This result of SEC verified that the block copolymers were successfully synthesized by sequential living anionic polymerization. However, the PDI reduced from PVBPPy (1.26) to PVBPPy-*b*-PMMA (1.17) and broadened from P2VP (1.07) to PVBPPy-*b*-P2VP (1.24). It is possible that the trace impurities in VBPPy monomer might react with DPM-K immediately during introducing VBPPy to the DPM-K in THF in the synthesis of PVBPPy-*b*-PMMA. Therefore, the PVBPPy living end can attack MMA without termination reaction or side reaction to form the block copolymer. On the other hand, in the case of the block copolymers of P2VP-*b*-PVBPPy, although the P2VP synthesized via anionic polymerization using DPM-K showed the controlled molecular weight and narrow PDI = 1.07, the anionic polymerization of VBPPy for the second block showed broader PDI = 1.24 due to the impurities in VBPPy monomer.

In Situ Formation of Nanocomposite Films. Functional materials having the combined properties of soft materials and inorganic nanoparticles are a technologically important class of polymer nanocomposites. The use of phase-separated diblock copolymers as scaffolds enables the self-organization of the nanoparticles (NPs) into long-range order. The self-assembled nanoparticle order and confinement are governed by the block copolymer domain symmetry because of their interactions that are thermodynamically most favorable.^{31–37}

The block copolymer poly(2-(4'-vinylbiphenyl-4-yl)pyridine-*b*-methyl methacrylate) (PVBPPy-*b*-PMMA) ($f_{\text{VBPY}} = 0.23$, $M_n = 48\,100$ g/mol) was utilized to study the phase separation behaviors in THF and scaffolds for formation of long-range Au nanoparticle pattern formation. Figure 5A shows a TEM micrograph of the phase-separated sample; dark regions represent PVBPPy segments of PVBPPy-*b*-PMMA selectively

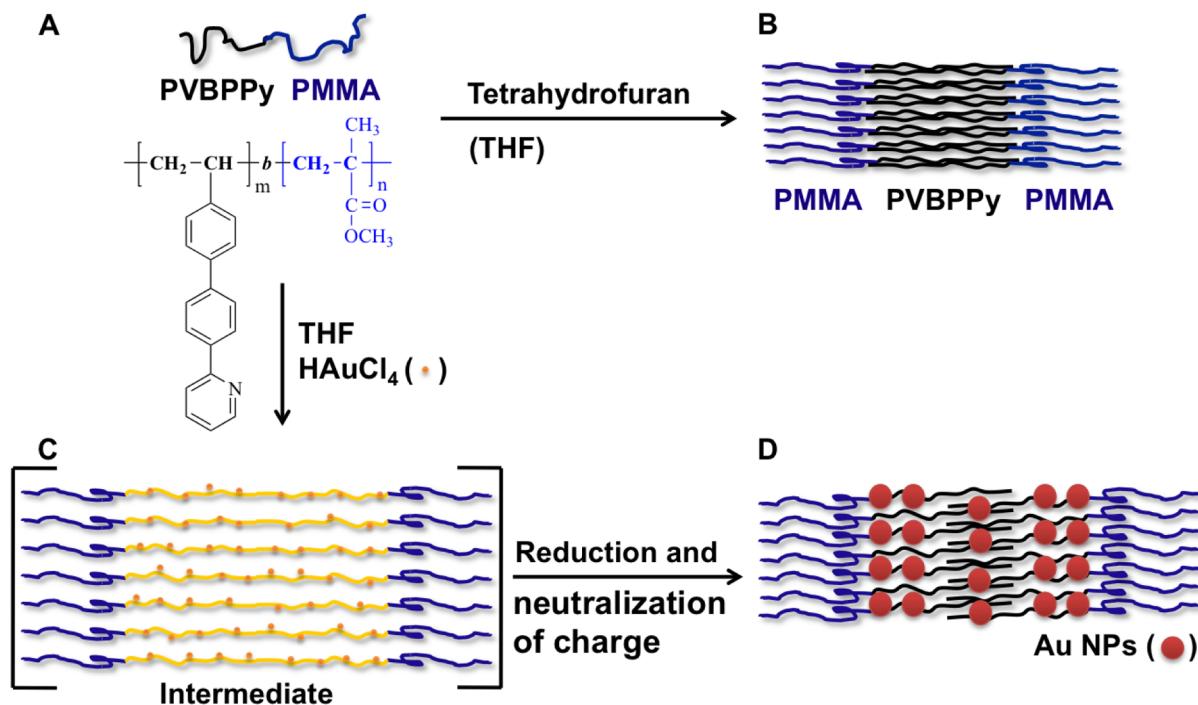


Figure 6. Scheme for in situ nanocomposite lamellar film formation from PVBPPy-*b*-PMMA block copolymers: (A) the structure of the block copolymer of PVBPPy-*b*-PMMA, (B) lamellar film of PVBPPy-*b*-PMMA, (C) charge introduction due to quaternization of nitrogen and expansion of the PVBPPy coil due to Coulombic repulsion (intermediate), and (D) segregation of more Au NPs near the PMMA/PVBPPy interface in THF.

coated with iodine vapor. Au NPs were synthesized using a phase-separated solution of PVBPPy-*b*-PMMA as a template. The lone pair electron in the pyridine moiety of the PVBPPy was used to coordinate with the Au precursor (HAuCl₄, 0.4 equiv per molar of pyridine derivative unit, 24 h, with constant rotation), followed by reduction with N₂H₄ H₂O. As the solution turned deep purple, it was stirred for a further 2 h and centrifuged for 10 min (300 rpm) to remove precipitates. Figure 5B shows the TEM micrograph of the nanocomposite containing Au NPs confined to selected areas of the film. The inset images represent an enlargement of the marked area in Figure 5B, a single Au nanoparticle, and the selected area diffraction pattern of the film, respectively. The size of the synthesized Au NPs is in the range of 6 nm; however, a few large particles can also be observed in Figure 5B, which correlates with the small broad plasma band of Au NPs in the solution state (Figure 5C).

The PVBPPy-*b*-PMMA has approximately 84 repeating units of VBPPy. Considering the 0.2 nm length of one unit of VBPPy, the fully extended length of the PVBPPy coil is approximately equal to 16 nm.^{26,27} THF is a common solvent for both blocks of PVBPPy-*b*-PMMA. For TEM analysis, PVBPPy blocks were selectively stained with iodine vapor. The dark areas in Figure 5A represent PVBPPy segments, and the gray areas represent PMMA segments in the PVBPPy-*b*-PMMA lamellar film. The average size of the dark areas in Figure 5A is 14 ± 0.4 nm, which indicates that two chains of the PVBPPy were very tightly packed in the lamellar film (Figure 6). However, after the coordination of HAuCl₄ with the pyridine nitrogen of the PVBPPy, charge was introduced, and due to Coulombic repulsion (the domain size increased to 22 ± 0.6 nm, inset Figure 5B), the PVBPPy chains were rearranged, which led to the formation of interdigitated (flip-flop) packing of the PVBPPy chains in the nanocomposite, as shown in Figure 4D. The distribution of inorganic nanoparticles in block copolymer

films depends on several factors, such as chemical interaction of the inorganic nanoparticles with the block copolymer segments, the nucleation and growth of nanoparticles, thermodynamic factors, geometry, symmetry, etc. Careful analysis of Figure 5B indicates that the synthesized Au NPs were located close to the PVBPPy/PMMA interface (Figure 5B). The distribution of the particles in the block was mainly governed by the interaction of the nanoparticles with the block copolymer segments. However, competition between penalties in conformational entropy, which must accommodate particles in the vicinity, and gains in translational entropy of the particles for free dispersion also play roles in nanoparticle distribution. In the in situ synthesis of nanoparticles, a reaction-diffusion controlled nucleation and growth process, which is first initiated by the formation of small clusters that act as further nucleation sites and deplete reactants from the surrounding polymer matrix, also plays an important part in the location of the nanoparticles in the block copolymer segments. In the present case, the lone pair electron of nitrogen had a strong affinity for the Au precursor, allowing it to diffuse well in the PVBPPy segments. However, the interdigitated arrangement of the PVBPPy chains at the center of the PVBPPy zone of the film most likely provided penalties in conformational entropy for starting the first nucleation reaction at the center; therefore, the nucleation process started near the PVBPPy/PMMA interface, which depleted the reactants in the direction of the center of the PVBPPy zone of the film. As a result, more nanoparticles were located near the interface, as shown in Figure 6.

CONCLUSIONS

The anionic polymerization of VBPPy was optimized using DPM-K as an initiator in THF at -78 °C for 360 min with 100% yield. The anionic polymerization of VBPPy using the DPM-K initiator takes a longer time (360 min) than those of

2VP (30 min) and VPPy (150 min). The calculated molecular weight (MW) was in good agreement with the observed MW, and the molecular weight distribution (PDI < 1.3) of PVBPPy was slightly broader than those of P2VP and P2VPPy (PDI < 1.1). The nucleophilicity of living PVBPPy was observed to be between those of living PVPPy and PMMA because of the highly rigid side chain of biphenylpyridine containing pyridine as a withdrawing group. The block copolymer of PVBPPy-*b*-PMMA was successfully synthesized via anionic polymerization in THF in the absence of additives, and the microphase separation of the PVBPPy-*b*-PMMA film was measured by TEM. In addition, gold (Au) nanoparticles (NPs) were present in the PVBPPy domain of the phase-separated PVBPPy-*b*-PMMA. Therefore, PVBPPy-*b*-PMMA can be used as a template and reservoir for the formation of nanocomposites.

ASSOCIATED CONTENT

Supporting Information

Experimental details, Scheme S1, and Figures S1–S10. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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