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Living Anionic Polymerization of Styrene Derivatives Containing Triphenylamine Moieties through Introduction of Protecting Group

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ABSTRACT: We carried out the anionic polymerization of styrene derivatives containing the triphenylamine moieties, 4,4′-vinylphenyltriphenylamine (**A**) and 4,4′-vinylphenyl-*N,N*-bis(4-*tert*-butylphenyl)-benzenamine (**B**), with a variety of initiators in tetrahydrofuran (THF) at −78 °C. The anionic polymerization of **A** was performed with *sec*-butyllithium, *sec*-butyllithium with additives, and (diphenylmethyl)potassium in THF at −78 °C. In all cases, an intermolecular side reaction took place between the polymer chains during polymerization. In contrast, the anionic polymerization of **B** was carried out successfully with *sec*-butyllithium and potassium naphthalenide in THF at −78 °C for 0.5 h without any observed intermolecular side reaction. Well-defined poly(**B**)s with predictable molecular weights and narrow molecular weight distributions (M_w/M_n = 1.05−1.11) were obtained. The sequential block copolymerization of **B** with styrene and 2-vinylpyridine was attempted subsequently, and the well-defined block copolymers, polystyrene-*b*-poly(**B**) and poly(**B**)-*b*-poly(2-vinylpyridine), were synthesized quantitatively. The solubilities as well as the thermal and optical properties of the resulting poly(**B**) were investigated.

Introduction

Polymers containing triphenylamine and its derivatives have received significant attention in numerous applications of organic electronic devices, such as organic light-emitting diodes (OLEDs) and photovoltaic cells, because they are materials that have an excellent ability to transport and inject hole.[1−5] In recent years, side-chain polymers with triphenylamine moieties and polymeric hole-transporting materials, in which the triphenylamine moieties are incorporated in the main chain, have attracted much interest because they are highly thermally stable and are suitable for low-cost fabrication processes such as spin-coating and inkjet printing for large areas and flexible displays.[6−13]

To date, a variety of polymerization methods have been used to prepare side-chain polymers containing triphenylamine moieties. The methods include anionic,[14−19] free or living radical,[9,20−26] and ring-opening methathesis polymerization.[27−29] Among these polymerization methods, anionic polymerization is the best methodology to synthesize polymers with predictable molecular weights and narrow molecular weight distributions (MWDs). Additionally, the well-controlled block copolymers with precise molecular architectures such as star-shaped, graft, comblike, and cyclic-shaped polymers can be prepared through this polymerization method.[30−35] Many polymeric hole-transporting materials, in which triphenylamine moieties are introduced in the side chain, have been studied widely by anionic polymerization.

Se et al. carried out a living anionic polymerization of *N,N*-dimethyl-4-vinylphenylamine using cumylpotassium as an initiator in tetrahydrofuran (THF) at −78 °C under high-vacuum conditions (10^{-6} Torr).[14] They reported that the well-defined poly(*N,N*-dimethyl-4-vinylphenylamine) with high molecular weights (<260 K) and narrow MWDs, which were less than 1.10, has been obtained. Feast et al. and Tew et al. have tried to perform the anionic polymerization of 4-vinyltriphenylamine under different anionic conditions.[16,17] However, it was confirmed from polymerization results that the polymerization was not controlled because the undesirable side reaction occurred in both polymerization systems.

During the past 2 years, there have been two advanced reports on the living anionic polymerization of 4-vinyltriphenylamine. The anionic polymerization of 4-vinyltriphenylamine was attempted by Natori et al. in toluene at 25 °C under dry argon using the initiator system of *tert*-butyllithium/*N,N,N′,N′*-tetramethylethylenediamine (TMEDA) (Chart 1a).[18] In the presence of TMEDA, the proton removal resulting from the reaction of toluene and *tert*-butyllithium produced tolyllithium, which was the real initiator in the polymerization. They could prepare high molecular weight polymers (~56 K), but the MWDs were relatively broad (M_w/M_n = 1.10−1.27), and it took 24 h to complete the polymerization with 100% yield. Very recently, Higashihara et al. achieved living anionic polymerization of 4-vinyltriphenylamine with *sec*-butyllithium in *tert*-butylbenzene at 25 °C for 24 h or with *sec*-butyllithium and lithium naphthalenide in THF at −78 °C for 12 h without any additives (Chart 1b).[19] The resulting poly(4-vinyltriphenylamine) with predictable high molecular weights (~30K) and narrow MWDs (M_w/M_n = 1.04−1.10) was synthesized quantitatively.

In our group, we have been studying the living anionic polymerization and block copolymerization of isocyanate, methacrylate, and styrene derivatives with various functional groups and established their anionic polymerization behaviors.[36,37] In particular, we have reported that methacrylate and styrene derivatives containing carbazole moieties, which show good hole-transporting properties, successfully undergo living anionic polymerization by controlling polymerization conditions such as time, initiator, and temperature.[37]

In this study, we have synthesized functional styrene derivatives containing triphenylamine moieties, 4,4′-vinylphenyltriphenylamine (**A**) and 4,4′-vinylphenyl-*N,N*-bis(4-*tert*-butylphenyl)-benzenamine (**B**), because triphenylamine derivatives show good

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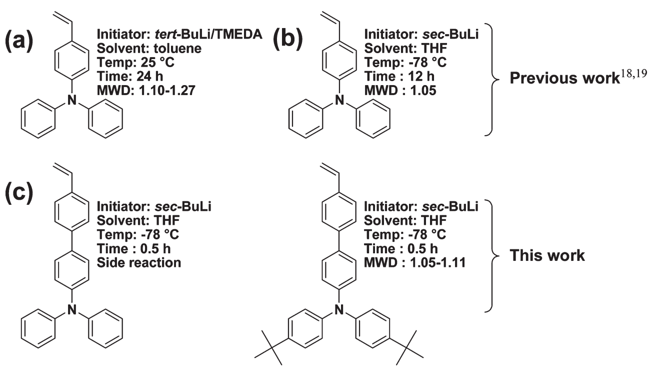
Chart 1. Summary of Anionic Polymerization of (a, b) 4-Vinyltriphenylamine and (c) 4,4′-Vinylphenyltriphenylamine and 4,4′-Vinylphenyl-*N*,*N*-bis(4-*tert*-butylphenyl)benzenamine



hole-transporting properties, and it has been reported that hole-transporting materials with high glass transition temperatures (T_gs) improve the thermal and long-term stability necessary for high efficiency of organic EL devices.[38] Therefore, it is expected that poly(**A**) and poly(**B**), which possess structurally bulky and rigid moieties, may show higher T_gs and better hole-transporting properties than those of poly(4-vinyltriphenylamine). Particularly, their anionic polymerization behaviors, strongly influenced by the introduction of a protecting *tert*-butyl group to the triphenylamine moiety, are mainly described in this paper (Chart 1c). Furthermore, the block copolymerization of **B** with styrene and 2-vinylpyridine was carried out to investigate the nucleophilicity of living poly(**B**) and its living nature.

Experimental Section

Materials. 4-Bromotriphenylamine (97%), 1-bromo-4-iodobenzene (98%), 1,2-dichlorobenzene (99%), copper powder (99%), 4-vinylphenylboronic acid, and tetrakis(triphenylphosphine)palladium(0) (99%) were purchased from Aldrich Chemical Co. and used without further purification. Bis(4-*tert*-butylphenyl)amine (>90%) was supplied from Tokyo Chemical Industry Co. Ltd. and was purified by repeated recrystallization from ethanol. Styrene (St), 2-vinylpyridine (2VP), and α-methylstyrene (α-MeSt) were passed through an alumina column, washed with an aqueous 5% sodium hydroxide (NaOH) solution, and then dried over anhydrous sodium sulfate (Na_2SO_4) for 24 h. These were distilled from calcium hydride (CaH_2) under vacuum and then further distilled from CaH_2 on a vacuum line. Lithium chloride (LiCl) was dried for 24 h at 150 °C under vacuum. All of the monomers and additives were diluted with tetrahydrofuran (THF) and divided in ampules with break-seals on a vacuum line. THF used in the polymerization reactions was refluxed over sodium for 5 h and then distilled on a vacuum line from a sodium naphthalenide solution.

Measurements. ^1H and ^{13}C NMR spectra were recorded at 25 °C using $CDCl_3$ as a solvent (JEOL JNM-ECX400). Chemical shifts were referred to tetramethylsilane (TMS) at 0 ppm. FT-IR spectroscopy was carried out from 4000 to 400 cm^{-1} using KBr pellets (Perkins-Elmer Spectrum 2000). Elemental analyses were performed by the Seoul Branch Analytical Laboratory of the Korea Basic Science Institute (Flash EA 1112series, CE Instruments). Mass values were detected by a gas chromatograph mass spectrometer (GCMS, Shimadzu, GCMS-QP2010). The polymers were characterized by size exclusion chromatography (SEC, Waters M 77251, M510). Molecular weights of the polymers were measured by SEC 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 is 50, 100, 10^3, and 10^4 Å, respectively) with a refractive index detector at a flow rate of 1.0 mL/min using THF containing 2% triethylamine as the eluent at 40 °C and calibrated with polystyrene standards (American Polymer Standards Corp.). Thermal properties were characterized using thermogravimetric analysis (TGA, TA2050) and differential scanning calorimetry (DSC, TA2010) at a heating rate of 10 °C/min under nitrogen. UV−vis absorption and photoluminescence (PL) spectra were obtained using an Agilent 8453 UV−vis spectrophotometer and a Hitachi F-7000 fluorescence spectophotometer, respectively.

Initiators. (Diphenylmethyl)potassium (Ph_2CHK) was synthesized by the reaction of potassium naphthalenide (K-Naph) and a 1.5 M excess of diphenylmethane in dry THF at 25 °C for 3 days. Commercially available *sec*-butyllithium (*sec*-BuLi, 1.0 M in cyclohexane, Kanto Chemical Co., Inc.) was used without purification and was diluted with dry *n*-heptane. The diluted Ph_2CHK and *sec*-BuLi solutions were stored at −30 °C in ampules equipped with break-seals prior to anionic polymerization. The efficiency of initiators was determined by titration with octyl alcohol in a sealed reactor under vacuum.

4,4′-Vinylphenyltriphenylamine (A). 4-Bromotriphenylamine (8.40 g, 26.0 mmol), 4-vinylphenylboronic acid (5.00 g, 33.8 mmol), and tetrakis(triphenylphosphine)palladium(0) (1.10 g) were stirred in 100 mL of THF. After adding 30 mL of aqueous 2 M K_2CO_3, the reaction mixture was reacted at 80 °C for 24 h (Scheme 1). The crude mixture was cooled to ambient temperature. The solvent was removed by evaporation under reduced pressure, and the reaction mixture was poured into water and extracted with methylene chloride three times. The combined organic solution was dried over anhydrous Na_2SO_4 and filtered. After evaporation of the solvent, the residue was purified by silica column chromatography with *n*-hexane and methylene chloride (9.5:0.5) to give a white solid (7.20 g, 20.7 mmol, 80%, mp = 119 °C). ^1H NMR (400 MHz, $CDCl_3$): δ = 5.24−5.27 (d, 1H, $CH_2=$ trans, J = 11.0 Hz), 5.75−5.80 (d, 1H, $CH_2=$ cis, J = 17.6 Hz), 6.71−6.78 (dd, 1H, $=CH$ trans, J = 11.0 and 17.6 Hz), 7.03−7.55 (m, 18H, aromatic). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 113.6 ($CH_2=$), 123.0, 123.8, 124.4, 126.6, 126.7, 127.6, 129.3, 134.5, 136.1, 136.4 ($=CH$), 140.0, 147.2, 147.6. FT-IR (KBr, cm^{-1}): 3038, 1592, 1526, 1488, 1333, 1279, 990, 908, 826, 748. Anal. Calcd for $C_{26}H_{21}N$: C, 89.88; H, 6.09; N, 4.03. Found: C, 90.03; H, 5.89; N, 4.08. MS (EI): m/z 347.05 (M^+).

***N*,*N*-Bis(4-*tert*-butylphenyl)-4-bromobenzenamine.** To a stirred solution of bis(4-*tert*-butylphenyl)amine (10.0 g, 35.5 mmol), 1-bromo-4-iodobenzene (15.1 g, 53.3 mmol), and potassium carbonate (20.0 g, 145 mmol) in 1,2-dichlorobenzene (200 mL) under nitrogen was added copper powder (10.2 g, 160 mmol), and the reaction mixture was stirred continuously at 190 °C for 24 h (Scheme 1). The crude mixture was cooled to ambient temperature and filtered to remove inorganic solids. The combined organic phase was poured into water and extracted with methylene chloride three times. The organic solution was dried over anhydrous Na_2SO_4 and filtered. After removal of the solvent, the residue was purified by silica column chromatography with *n*-hexane to give a white solid (8.20 g, 18.8 mmol, 53%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.31 (s, 18H, *tert*-butyl), 6.90−7.30 (m, 12H, aromatic). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.4 ($C(CH_3)_3$), 34.3 ($C(CH_3)_3$), 113.7, 124.0, 124.3, 126.1, 131.9, 144.6, 146.1, 147.3. MS (EI): m/z 435.75 (M^+).

4,4′-Vinylphenyl-*N*,*N*-bis(4-*tert*-butylphenyl)benzenamine (B). The same procedure was followed, as described above for **A**, using *N*,*N*-bis(4-*tert*-butylphenyl)-4-bromobenzenamine (8.00 g, 18.3 mmol), 4-vinylphenylboronic acid (4.10 g, 27.5 mmol), tetrakis(triphenylphosphine)palladium(0) (1.00 g), THF (120 mL), and aqueous 2 M K_2CO_3 (40 mL). The coupling reaction was continued at 80 °C for 24 h under a nitrogen atmosphere (Scheme 1). The residue was purified by silica column chromatography with *n*-hexane and methylene chloride (9.5:0.5) to give a white solid (5.10 g, 11.1 mmol, 61%, mp = 195 °C). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.31 (s, 18H, *tert*-butyl), 5.23−5.26 (d, 1H, $CH_2=$ trans, J = 11.0 Hz), 5.74−5.79 (d, 1H, $CH_2=$ cis,

Scheme 1. Synthesis of 4,4′-Vinylphenyltriphenylamine (A) and 4,4′-Vinylphenyl-*N*,*N*-bis(4-*tert*-butylphenyl)benzenamine (B)

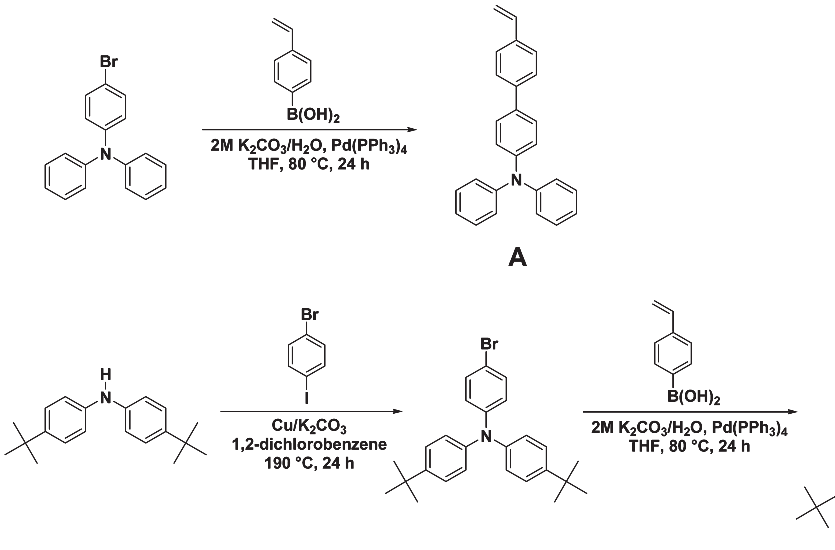


Table 1. Anionic Polymerization of 4,4′-Vinylphenyltriphenylamine (A) and 4,4′-Vinylphenyl-*N*,*N*-bis(4-*tert*-butylphenyl)benzenamine (B) in Tetrahydrofuran at Various Temperatures

run	monomer (mmol)	initiator type (mmol)	temp (°C)	time (h)	$M_n \times 10^{-3}$ calcd[a]	$M_n \times 10^{-3}$ obsd[b]	M_w/M_n[b]	yield (%)
1	**A**, 1.10	*sec*-BuLi, 0.0142	−78	5 min	19.0	21.4	g	70.6
2	**A**, 0.741	*sec*-BuLi, 0.0112	−78	0.5	23.0	29.2	g	100
3	**A**, 2.23	*sec*-BuLi, 0.0995	−78	1	7.8	6.2	g	100
4	**A**, 2.05	*sec*-BuLi, 0.0541/α-MeSt,[c] 0.370	−78	1	14.0	16.1	g	100
5	**A**, 1.23	*sec*-BuLi, 0.0601/LiCl,[d] 0.0609	−78	1	7.1	9.8	g	100
6	**A**, 2.14	Ph_2CHK,[e] 0.0334	−78	1	22.3	21.6	g	100
7	**B**, 0.722	*sec*-BuLi, 0.0701	−78	0.5	4.7	4.8	1.05	100
8	**B**, 1.15	*sec*-BuLi, 0.0368	−78	0.5	14.4	14.1	1.11	100
9	**B**, 0.623	K-Naph,[f] 0.0895	−78	0.5	6.4	6.2	1.10	100
10	**B**, 1.13	K-Naph, 0.0642	−78	0.5	16.2	16.3	1.09	100
11	**B**, 1.94	K-Naph, 0.0771	−78	0.5	23.1	23.3	1.06	100
12	**B**, 1.03	K-Naph, 0.0321	−78	0.5	29.5	30.0	1.09	100
13	**B**, 0.558	K-Naph, 0.0317	−78	10 min	12.0	13.2	1.06	73.9
14	**B**, 1.04	K-Naph, 0.0650	25	10 min	14.7	14.3	g	100
15	**B**, 0.465	K-Naph, 0.0638	0	10 min	6.7	6.9	g	100

[a] M_n(calcd) = (molecular weight of monomer) × [monomer] × f/[initiator]; f = 1 or 2, corresponding to the functionality of the initiators. [b] M_n(obsd) and M_w/M_n were gained by size exclusion chromatography calibration by using polystyrene standards in tetrahydrofuran solution containing 2% triethylamine as the eluent at 40 °C. [c] α-Methylstyrene. [d] Lithium chloride. [e] (Diphenylmethyl)potassium. [f] Potassium naphthalenide. [g] The M_w/M_n was bimodal, presumably due to the intermolecular side reaction.

Table 2. Block Copolymerization of 4,4′-Vinylphenyl-*N*,*N*-bis(4-*tert*-butylphenyl)benzenamine (B) with Styrene (St) and 2-Vinylpyridine (2VP) with *sec*-BuLi in Tetrahydrofuran at −78 °C[a]

run	initiator, mmol	monomer 1st, mmol	monomer 2nd, mmol	block copolymer (homopolymer) $M_n \times 10^{-3}$ calcd[b]	block copolymer (homopolymer) $M_n \times 10^{-3}$ obsd[c]	block copolymer (homopolymer) M_w/M_n[c]
1	*sec*-BuLi, 0.0699	**B**, 0.763	St,[d] 3.05	10.0 (5.0)	f (5.0)	f (1.07)
2	*sec*-BuLi, 0.0251	St, 2.94	**B**, 0.601	24.4 (12.2)	22.7 (13.2)	1.09 (1.13)
3	*sec*-BuLi, 0.0461	**B**, 1.19	2VP,[e] 5.90	28.3 (11.8)	29.7 (12.0)	1.08 (1.11)

[a] Polymer yields were quantitative in all cases. Polymerization times were total 1 h, 0.5 h for **B**, and 0.5 h for St and 2VP. [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 tetrahydrofuran solution containing 2% triethylamine as the eluent at 40 °C. [d] Styrene. [e] 2-Vinylpyridine. [f] The initiation efficiency was not quantitative, forming a mixture of homopolymer and resulting block copolymer.

J = 17.6 Hz), 6.70−6.77 (dd, 1H, =CH trans, J = 11.0 and 17.6 Hz), 7.04−7.54 (m, 16H, aromatic). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.4 (C(CH$_3$)$_3$), 34.3 (C(CH$_3$)$_3$), 113.4 (CH$_2$=), 122.9, 124.1, 126.1, 126.5, 126.6, 127.4, 133.7, 135.9, 136.5 (=CH), 140.2, 144.9, 145.8, 147.6. FT-IR (KBr, cm^{-1}): 3034−2871, 1598, 1506, 1497, 1364, 1324, 1299, 985, 879, 827, 741. Anal. Calcd for $C_{34}H_{37}N$: C, 88.84; H, 8.11; N, 3.05. Found: C, 88.69; H, 8.26; N, 2.96. MS (EI): m/z 459.20 (M$^+$).

Purification of Monomers. After silica column chromatography of **A** and **B**, the monomers were freeze-dried from their benzene solutions under reduced pressure for 12 h and then dried over phosphorus(V) oxide (P_2O_5) at 25 °C for 24 h in an glass apparatus equipped with break-seals on a vacuum line. The resulting monomers were diluted with dry THF and stored at −30 °C in glass ampules under high vacuum prior to anionic polymerization.

Anionic Polymerization of A. The anionic polymerization of **A** was carried out with *sec*-BuLi, *sec*-BuLi with some additives, and Ph_2CHK in THF at −78 °C under high vacuum (10^{-6} Torr) in all-glass reactors equipped with break-seals. The additives included α-MeSt and LiCl. The reactor was prewashed with the initiator solution after sealing from the vacuum line. The polymerization was usually performed by addition of monomer into the initiator solution. The reaction mixture immediately turned to deep violet after **A** was added to the initiator solution. The polymerization was terminated with methanol, and the reaction solution was poured into a large excess of methanol to precipitate the polymer. The polymer was purified by reprecipitation in THF/methanol and freeze-dried from a benzene solution under vacuum. The polymers were characterized by SEC.

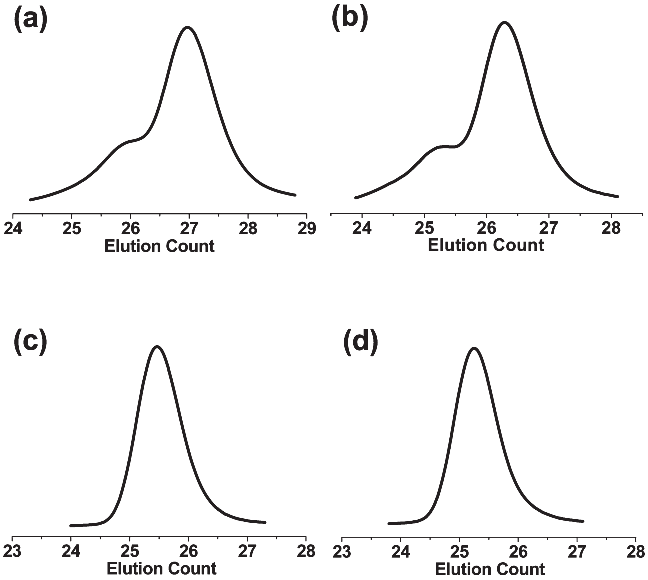


Figure 1. SEC curves of (a) poly(4,4′-vinylphenyltriphenylamine) prepared with *sec*-BuLi at −78 °C for 5 min (Table 1, run 1), (b) poly(4,4′-vinylphenyltriphenylamine) prepared with *sec*-BuLi at −78 °C for 0.5 h (Table 1, run 2), (c) poly(4,4′-vinylphenyl-*N,N*-bis(4-*tert*-butylphenyl)-benzenamine) prepared with *sec*-BuLi at −78 °C for 0.5 h (Table 1, run 8), M_n(obsd) = 14 100 and M_w/M_n = 1.11, and (d) poly(4,4′-vinylphenyl-*N*,*N*-bis(4-*tert*-butylphenyl)benzenamine) prepared with K-Naph at −78 °C for 0.5 h (Table 1, run 10), M_n(obsd) = 16 300 and M_w/M_n = 1.09.

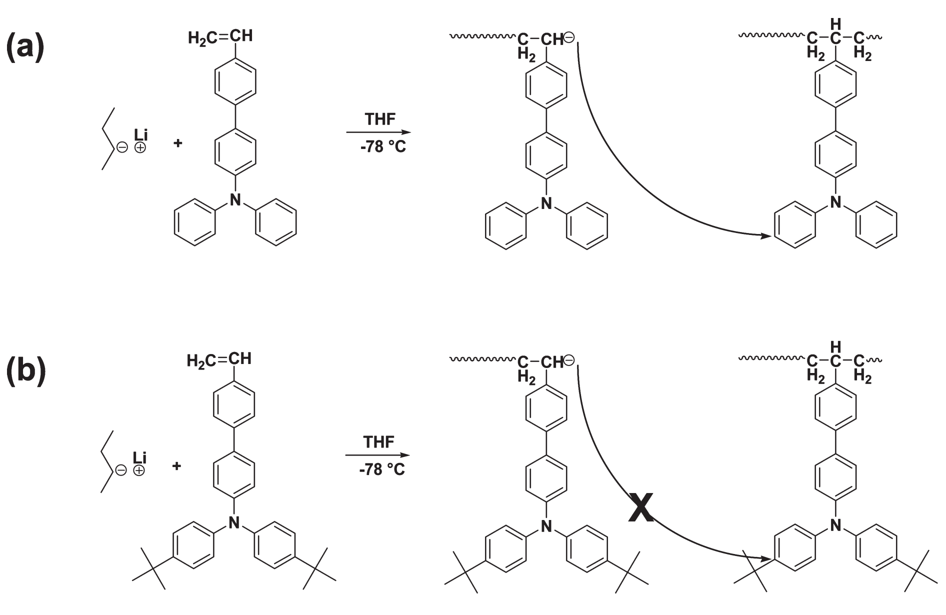
Anionic Polymerization of B. The same polymerization procedure was followed, as described above for anionic polymerization of **A**, using *sec*-BuLi and K-Naph in THF at −78 °C for 0.5 h. The color of polymerization solution was deep violet. The resulting polymer was characterized by ^{1}H NMR, SEC, elemental analysis (EA), and FT-IR spectroscopy with the following results. Poly(**B**) (M_n(obsd) = 30 000, M_w/M_n = 1.09 (Table 1, run 12)). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (18H, *tert*-butyl), 1.32−2.30 (3H, CH_2-CH), 6.45−7.46 (16H, aromatic). FT-IR (KBr, cm^{-1}): 3033−2868, 1602, 1511, 1496, 1365, 1322, 1296, 1190, 1112, 1015, 822, 746. Anal. Calcd for $(C_{34}H_{37}N)_n$: C, 88.84; H, 8.11; N, 3.05. Found: C, 87.89; H, 8.03; N, 2.84.

Block Copolymerization. The first-stage polymerization of St was performed with *sec*-BuLi in THF at −78 °C for 0.5 h in an all-glass apparatus equipped with break-seals under high vacuum (10^{-6} Torr). After a portion of the living poly(St) was sampled to characterize the poly(St), **B** was poured into the living poly(St) solution and the mixture reacted at −78 °C for 0.5 h. After termination with methanol, the reaction solutions were poured into a large excess of methanol to obtain both poly(St) and poly(St)-*b*-poly(**B**). The block copolymerization of **B** with 2VP was carried out by addition of 2VP into living poly(**B**) solution at −78 °C for 0.5 h. The resulting block polymers were characterized by means of ^{1}H NMR and SEC with the following results. Poly(St)-*b*-poly(**B**) (M_n(obsd) = 22 700, M_w/M_n = 1.09 (Table 2, run 2)). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.05−2.25 (CH_2-CH of poly(St) and poly(**B**), *tert*-butyl of poly(**B**)), 6.25−7.38 (phenyl of poly(St) and triphenylamine of poly(**B**)). Poly(**B**)-*b*-poly(2VP) (M_n(obsd) = 29 700, M_w/M_n = 1.08 (Table 2, run 3)). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19 (*tert*-butyl of poly(**B**)), 1.30−2.11 (CH_2-CH of poly(**B**) and poly(2VP)), 2.15−2.40 (CH_2-CH of poly(2VP)), 6.10−7.25 (triphenylamine of poly(**B**) and pyridine of poly(2VP)), 8.08−8.35 ($CH{=}N$ of poly(2VP)).

Results and Discussion

Anionic Polymerization of A. The results of the anionic polymerization of **A** are summarized in Table 1. First, the polymerization of **A** was carried out with *sec*-BuLi for 0.5 h. The yield of the polymer was quantitative, but the size exclusion chromatography (SEC) curve of the resulting polymer showed a bimodal peak and the molecular weight distribution (MWD) was relatively broad, as shown in Figure 1b.

Scheme 2. Proposed Anionic Polymerization Behaviors of (a) 4,4′-Vinylphenyltriphenylamine and (b) 4,4′-Vinylphenyl-*N*,*N*-bis(4-*tert*-butylphenyl)benzenamine



In the SEC curve, there was a shoulder in the higher M_n region that matched well with the double M_n of the main peak. For the 5 min reaction time, the results from SEC curve (Figure 1a) were identical with those of the polymerization performed for 0.5 h, although the polymer yield was 70.6%. Next, additives (α-MeSt and LiCl), introduced to lower the reactivity of *sec*-BuLi, and Ph_2CHK were used to synthesize the well-defined poly(**A**) with predictable molecular weight and narrow MWD. In all cases, however, the analysis of SEC curve showed identical results to that of the polymerization using *sec*-BuLi, even though the resulting polymer was obtained quantitatively.

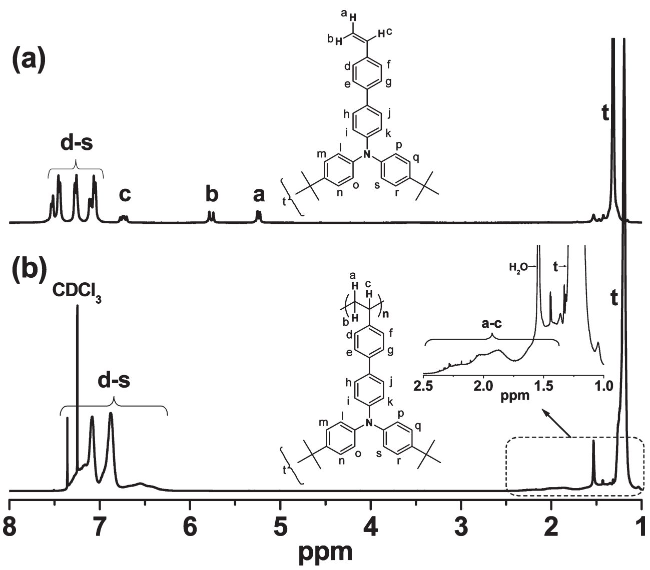


Figure 2. ^{1}H NMR spectra of (a) 4,4′-vinylphenyl-*N*,*N*-bis(4-*tert*-butylphenyl)benzenamine and (b) poly(4,4′-vinylphenyl-*N*,*N*-bis(4-*tert*-butylphenyl)benzenamine) in $CDCl_3$.

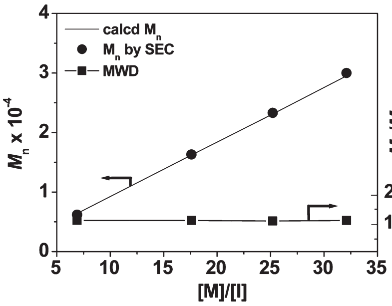


Figure 3. Plot of the feed ratio of 4,4′-vinylphenyl-*N*,*N*-bis(4-*tert*-butylphenyl)benzenamine to K-Naph vs M_n and M_w/M_n.

These results suggest that the intermolecular side reaction probably took place between the polymer chains during the course of the polymerization of **A** under the conditions employed here, as shown in Scheme 2a.[39] Accordingly, this undesirable side reaction, which does not occur in the anionic polymerization of 4-vinyltriphenylamine in THF at −78 °C for 12 h with *sec*-BuLi,[19] may support that electron-withdrawing nature, possibly indicated by the chemical shifts of the vinyl *β*-carbon in their ^{13}C NMR spectra of 4-vinyltriphenylamine (112.4 ppm)[17] and **A** (113.6 ppm), greatly affects their anionic polymerization behaviors.[40]

Living Anionic Polymerization of B. In the previous study, it was found that the living anionic polymerization of **A** was not successful when carried out at −78 °C due to the intermolecular side reaction. Thus, monomer **B** was prepared for the protection against the unwanted intermolecular side reaction. In monomer **B**, the site (Scheme 2a) attacked by the propagating chain-end carbanion at −78 °C was protected by the introduction of a *tert*-butyl group. The polymerization of **B** was carried out successfully with *sec*-BuLi and K-Naph at −78 °C, and the results are summarized in Table 1. The yields of polymers were always quantitative. As shown in Figure 2, the ^{1}H NMR spectrum of the monomer and resulting polymer clearly shows that polymerization proceeded exclusively because the signal of vinyl group of monomer disappeared, and the broad signal of the main polymer chain and the broad characteristic singlet of the *tert*-butyl group (1.23 ppm) appeared. Therefore, the study of the polymer using ^{1}H NMR spectroscopy proves the success of the anionic polymerization of **B** and the structure of poly(**B**).

As illustrated in Figure 1c,d, SEC measurements clearly showed unimodal curves with narrow MWDs for the resulting poly(**B**)s. The MWDs of the resulting polymers, M_w/M_n values, were around 1.10. Moreover, the observed M_n values agreed well with calculated molecular weights based on monomer-to-initiator ratios. These results mean that no intermolecular side reaction took place during the polymerization. For instance, the polymerization proceeded quantitatively with *sec*-BuLi (Table 1, run 8). The molecular weight (M_n = 14 100) detected from SEC was in good agreement with the calculated molecular weight (14 400), and the M_w/M_n ratio was 1.11. Thus, these results, as shown in Table 1 and Figure 1c,d, indicate strongly that the anionic polymerizations of **B** with *sec*-BuLi and K-Naph at −78 °C proceed without intermolecular side reactions, suggesting that the site attacked by propagating chain-end carbanion corresponds with the one shown in Scheme 2a. In other words, it is demonstrated that the nucleophilic attack of propagating chain-end carbanion of the living poly(**B**) on

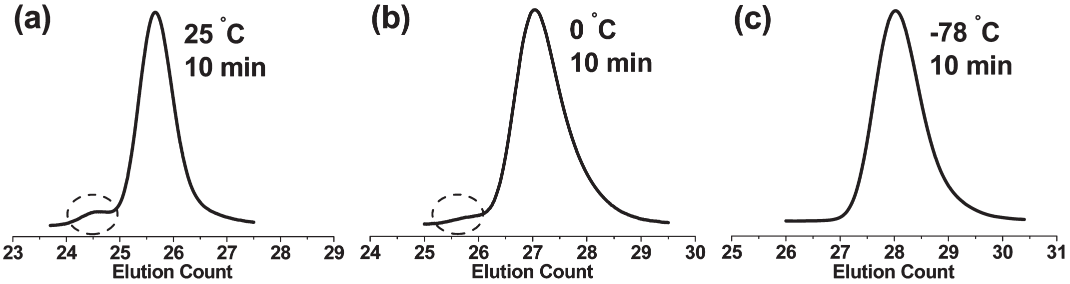


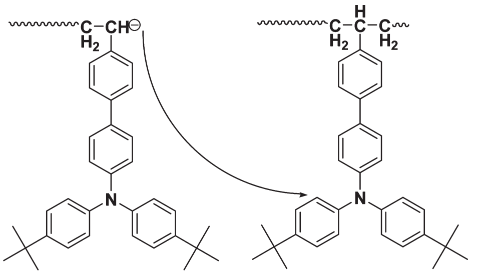
Figure 4. SEC curves of (a) poly(4,4′-vinylphenyl-*N*,*N*-bis(4-*tert*-butylphenyl)benzenamine) prepared with K-Naph at 25 °C for 10 min (Table 1, run 14), (b) poly(4,4′-vinylphenyl-*N*,*N*-bis(4-*tert*-butylphenyl)benzenamine) prepared with K-Naph at 0 °C for 10 min (Table 1, run 15), and (c) poly(4,4′-vinylphenyl-*N*,*N*-bis(4-*tert*-butylphenyl)benzenamine) prepared with K-Naph at −78 °C for 10 min (Table 1, run 13): M_n(obsd) = 13 200 and M_w/M_n = 1.06.

the triphenylamine moiety (*para* position) can be entirely suppressed at −78 °C by the introduction of a *tert*-butyl protecting group, as proposed in Scheme 2b.

In addition, poly(**B**)s were synthesized by using diverse molar ratios of **B** to K-Naph to substantiate the living nature of poly(**B**) (Table 1, runs 9−12). As shown in Figure 3, the MWDs were less than 1.10, and the M_n values were increased with increasing feed ratio of **B** to K-Naph. Such a good linear relationship between M_n and the feed ratio of **B** to K-Naph highlights the living nature of poly(**B**).

Effect of Polymerization Temperature. The anionic polymerization of **B** has been carried out with K-Naph in THF at 25, 0, and −78 °C for 10 min to investigate the temperature dependence of the anionic polymerization. The polymerization results are summarized in Table 1. The yields of polymers were quantitative after termination. It was confirmed from SEC analysis, however, that the resulting polymer prepared at 25 °C showed a bimodal SEC curve with relatively broad MWD, as shown in Figure 4a. There was a shoulder at the high-M_n region with the main peak having a narrow MWD. The observed M_n of the main peak agreed fairly well with the calculated molecular weight, and the double M_n of the main peak matched well with the peak in the higher M_n region. These results are probably due to an intermolecular side reaction between the polymer chains after the polymerization. For the possible side reaction, we now consider that the nucleophilic attack of propagating chain-end carbanion of the living poly(**B**) on the triphenylamine moiety (*ortho* position) might take place to some extent,[39] as shown in Scheme 3. This intermolecular side reaction could not be suppressed completely at 0 °C, even though the shape of the shoulder at the high-M_n region was very small (Figure 4b). At −78 °C, the polymerization of **B** was not complete within 10 min, and the yield of polymer was 73.9%. The SEC curve of the resulting polymer showed unimodal shape with narrow MWD (M_w/M_n = 1.06), and the observed M_n was in agreement with calculated molecular weight based on monomer-to-initiator ratio, indicating that there was no intermolecular side reaction. This result also supports that the side reaction might occur not during propagation but after the polymerization.[41] The results obtained here indicate that the polymerization temperature should be −78 °C for controlled anionic polymerization of **B**.

Scheme 3. Proposed Anionic Polymerization Behavior of 4,4′-Vinylphenyl-*N*,*N*-bis(4-*tert*-butylphenyl)benzenamine with K-Naph in Tetrahydrofuran at 25 and 0 °C



Block Copolymerization of B with Styrene (St) and 2-Vinylpyridine (2VP). From the synthetic viewpoint, the living anionic polymerization by sequential addition of comonomers is one of the best methods to create block copolymer because it offers a well-defined block copolymer with predictable molecular weight and narrow MWD. The results summarized in Table 1 highlight the living character of **B** in THF at −78 °C. Therefore, the achievement of the living anionic polymerization of **B** enables the well-defined block copolymer possessing poly(**B**) block to be produced by the sequential block copolymerization. Additionally, the relative reactivity of **B** and the terminal carbanion of the resulting living

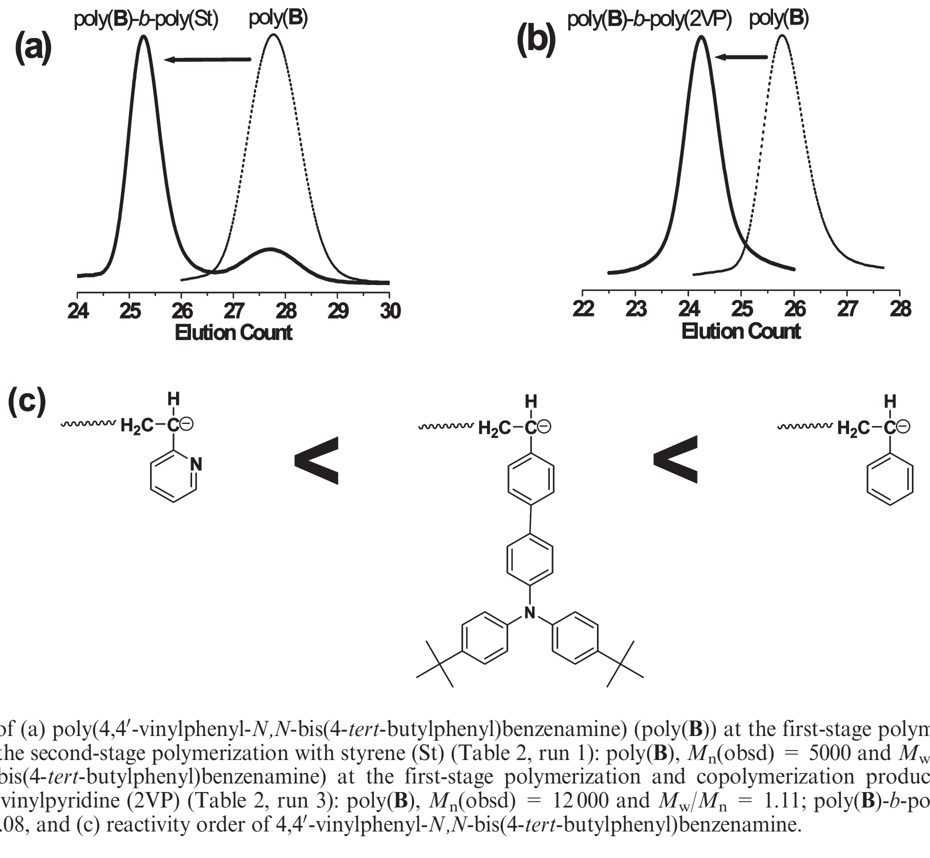


Figure 5. SEC curves of (a) poly(4,4′-vinylphenyl-*N*,*N*-bis(4-*tert*-butylphenyl)benzenamine) (poly(**B**)) at the first-stage polymerization and copolymerization product at the second-stage polymerization with styrene (St) (Table 2, run 1): poly(**B**), M_n(obsd) = 5000 and M_w/M_n = 1.07, (b) poly(4,4′-vinylphenyl-*N*,*N*-bis(4-*tert*-butylphenyl)benzenamine) at the first-stage polymerization and copolymerization product at the second-stage polymerization with 2-vinylpyridine (2VP) (Table 2, run 3): poly(**B**), M_n(obsd) = 12 000 and M_w/M_n = 1.11; poly(**B**)-*b*-poly(2VP), M_n(obsd) = 29 700 and M_w/M_n = 1.08, and (c) reactivity order of 4,4′-vinylphenyl-*N*,*N*-bis(4-*tert*-butylphenyl)benzenamine.

Scheme 4. Block Copolymerization of 4,4′-Vinylphenyl-*N*,*N*-bis(4-*tert*-butylphenyl)benzenamine with 2-Vinylpyridine in Tetrahydrofuran at −78 °C with *sec*-BuLi

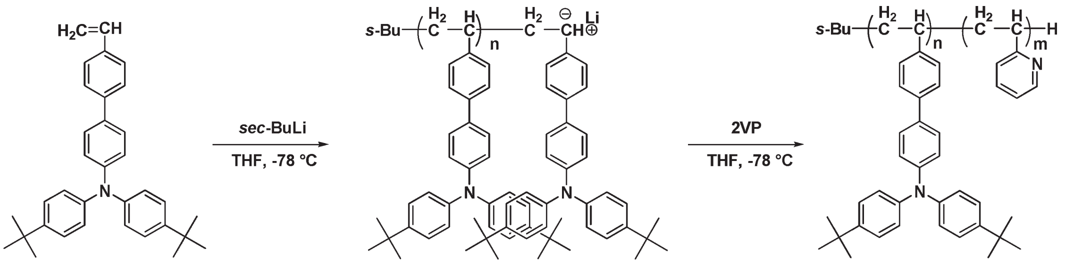


Table 3. Solubility of Poly(4,4′-vinylphenyl-*N*,*N*-bis(4-*tert*-butylphenyl)-benzenamine) (Poly(B))[a]

solvent	poly(**B**)	solvent	poly(**B**)
n-hexane	I	tetrahydrofuran	S
benzene	S	1,2-dichloroethane	S
toluene	S	1,2-dichlorobenzene	S
diethyl ether	S	*N*,*N*-dimethylformamide	I
ethyl acetate	S	dimethyl sulfoxide	I
chloroform	S	ethanol	I
acetone	I	methanol	I
1,4-dioxane	S	water	I

[a] Key: S, soluble; I, insoluble.

polymer can be provided by the results of the block copolymerization. As shown in Table 2, two traditional comonomers, styrene (St) and 2-vinylpyridine (2VP), were selected for the block copolymerization to evaluate the reactivity of **B**.

The block copolymerization of St with **B** was carried out successfully by sequential addition of St as the first monomer and **B** as the second monomer. As listed in Table 2, the block copolymer with predictable molecular weight and narrow MWD was obtained quantitatively. The observed M_n values of poly(St) and poly(St)-*b*-poly(**B**) detected from SEC were 13 200 ($M_w/M_n = 1.13$) and 22 700 ($M_w/M_n = 1.09$), respectively, were similar to the calculated values of 12 200 and 24 400. The SEC curve of block copolymer was sharp and symmetrical, and completely shifted from elution volume of poly(St) toward higher M_n. This result means that the propagating carbanion of St is stable at −78 °C for 0.5 h and propagating chain end derived from St can certainly polymerize **B** under the polymerization condition employed here. In contrast, a well-defined block copolymer was not synthesized by the reverse addition of two monomers. As shown in Figure 5a, the SEC curve in the polymerization of St with living poly(**B**) showed that the bimodal peak consisted of poly(**B**) and the block copolymer possessing M_n value much higher than predicted one because of partial initiation with rapid consumption of St by the newly formed polystyryl anion.[41] This result suggests that living poly(**B**) is not nucleophilic enough to polymerize St quantitatively, meaning that living poly(**B**) cannot be used to prepare well-defined block copolymers with St.

We were also able to synthesize the block copolymer, poly(**B**)-*b*-poly(2VP), with *sec*-BuLi without any additives (Scheme 4). The polymerization result is summarized in Table 2. The well-defined block copolymer with controlled molecular weight and narrow MWD was synthesized quantitatively. Figure 5b shows the SEC curves of poly(**B**) and poly(**B**)-*b*-poly(2VP). The SEC curve of the resulting block copolymer was unimodal and symmetrical and shifted from the starting poly(**B**) toward the higher molecular side. Accordingly, it can be demonstrated that the polymerization of 2VP was carried out successfully by living poly(**B**) without any side reaction. From the results of sequential block copolymerization of **B** with St and 2VP, the reactivity of living poly(**B**) was found to be between that of St and 2VP, as shown in Figure 5c.

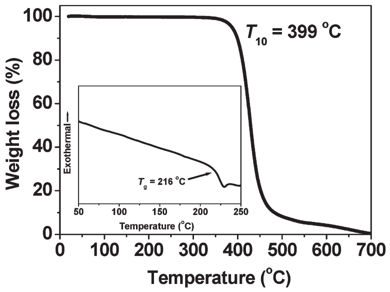


Figure 6. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) thermograms of poly(4,4′-vinylphenyl-*N*,*N*-bis(4-*tert*-butylphenyl)benzenamine) (M_n = 30 000) under nitrogen with a heating rate of 10 °C/min.

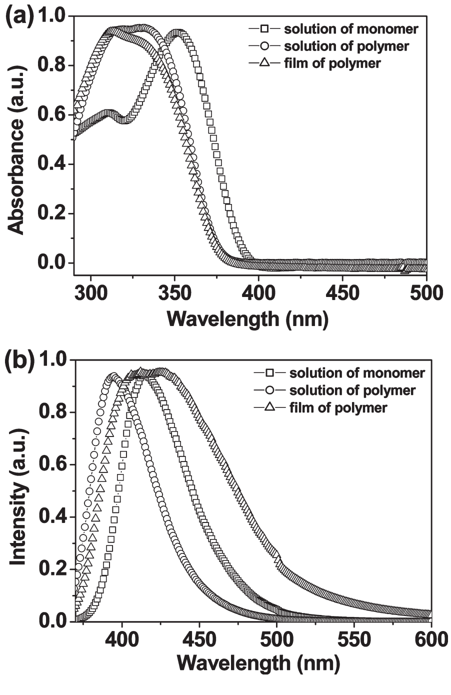


Figure 7. Absorption (a) and photoluminescence (PL) (b) spectra of 4,4′-vinylphenyl-*N*,*N*-bis(4-*tert*-butylphenyl)benzenamine and poly-(4,4′-vinylphenyl-*N*,*N*-bis(4-*tert*-butylphenyl)benzenamine) (4,4′-vinylphenyl-*N*,*N*-bis(4-*tert*-butylphenyl)benzenamine in toluene (□), poly-(4,4′-vinylphenyl-*N*,*N*-bis(4-*tert*-butylphenyl)benzenamine) in toluene (○), and film of poly(4,4′-vinylphenyl-*N*,*N*-bis(4-*tert*-butylphenyl)-benzenamine) (Δ)).

Solubility. The test of solubility of poly(**B**) was carried out using the various organic solvents at 25 °C and is summarized in Table 3. The polymer was soluble in benzene, toluene, diethyl

Table 4. Photophysical Properties of 4,4′-Vinylphenyl-*N*,*N*-bis-(4-*tert*-butylphenyl)benzenamine (B) and Poly(4,4′-vinylphenyl-*N*,*N*-bis(4-*tert*-butylphenyl)benzenamine) (Poly(B))

	solution^a		film	
material	UV−vis λ_{max} (nm)	PL λ_{max} (nm)	UV−vis λ_{max} (nm)	PL λ_{max} (nm)
B	311, 352	415		
poly(**B**)	332	395	314	412

^{a} In toluene dilute solution.

ether, ethyl acetate, chloroform, 1,4-dioxane, tetrahydrofuran, 1,2-dichloroethane, and 1,2-dichlorobenzene. On the other hand, it was not soluble in *n*-hexane, cyclohexane, acetone, *N*,*N*-dimethylformamide, dimethyl sulfoxide, ethanol, methanol, and water. Poly(**B**) was spin-coated successfully from the toluene solution. Consequently, this thin film can be a potential candidate for practical applications of organic electronic devices.

Thermal Properties. The thermal stability of poly(**B**) (M_n = 30 000) was investigated by thermogravimetric analysis (TGA) under nitrogen. The TGA thermogram and the value of the 10% weight loss temperature (T_{10}) of poly(**B**) are shown in Figure 6. Poly(**B**) exhibited good thermal stability with decomposition temperature at 399 °C. We next observed the glass transition temperatures (T_g) of poly(**B**) (M_n = 30 000) using differential scanning calorimetry (DSC). The T_g value of poly(**B**) was estimated as high as 216 °C, as shown in Figure 6. This temperature is almost 110 °C higher than the T_g value of polystyrene (~100 °C). The large improvement in T_g for poly(**B**) may result from the incorporation of the bulky triphenylamine moiety with *tert*-butyl group, causing the reduction in chain mobility. Therefore, this relatively high T_g value can be a thermal advantage for material used in organic electronic devices.

Photophysical Properties. The absorption and emission spectra of **B** and poly(**B**) (M_n = 30 000) are shown in Figure 7, and their photophysical properties are summarized in Table 4. For poly(**B**) in toluene solution, the maximum absorption peak was observed at 332 nm, which is slightly blue-shifted compared to its monomer **B**, presumably due to reduction in π-conjugation caused by the twisted conformation of vinyl backbone.[42] This absorption spectrum is ascribed to the $\pi-\pi^*$ transition of the triphenylamine moiety. The absorption spectrum of poly(**B**) in the solid state was almost identical to that in toluene solution.

In the solid state, the maximum emission peak of poly(**B**) was observed at 412 nm, as shown in Figure 7b. This emission spectrum was red-shifted by 17 nm from the corresponding solution spectrum. Such a phenomenon probably occurred due to intermolecular interactions between polymer chains leading to better conjugation in solid state than in solution. More studies on the luminescence properties will be undertaken in the near future.

Conclusions

The anionic polymerization of the styrene derivatives containing triphenylamine moieties, 4,4′-vinylphenyltriphenylamine (**A**) and 4,4′-vinylphenyl-*N*,*N*-bis(4-*tert*-butylphenyl)benzenamine (**B**), was carried out with various initiators in THF at −78 °C, but an intermolecular side reaction took place between the polymer chains during the course of the polymerization of **A**. In contrast, the anionic polymerization of **B**, in which the site where propagating chain-end carbanion attacks was protected by the introduction of a *tert*-butyl group, was carried successfully out with *sec*-BuLi and K-Naph as initiators in THF at −78 °C without any intermolecular side reaction. These results indicate strongly that the intermolecular side reaction was completely suppressed by the introduction of the *tert*-butyl protecting group to the triphenylamine moiety without any additives. The block copolymerization of **B** with styrene and 2-vinylpyridine was performed sequentially to estimate the reactivity of **B** and to find its living nature. The well-defined polystyrene-*b*-poly(**B**) and poly(**B**)-*b*-poly(2-vinylpyridine) with predictable molecular weights and narrow MWDs were synthesized, and it was confirmed that reactivity of living poly(**B**) was between that of styrene and 2-vinylpyridine. The poly(**B**) (M_n = 30 000) showed good solubility and excellent thermal stability for potential applications in electronic devices.

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