Anionic Polymerization of 4-Diphenylaminostyrene: Characteristics of the Alkyllithium/*N,N,N′,N′*-Tetramethylethylenediamine System for Living Anionic Polymerization

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ABSTRACT: A well-controlled anionic polymerization of 4-diphenylaminostyrene (DAS) with alkyllithium (RLi) has been achieved for the first time. The nucleophilicity and solubility of RLi, 4-diphenylaminostyryllithium (DASLi), and poly(4-diphenylaminostyryl)lithium (PDASLi) were very important controlling factors. An initiator system of *tert*-butyllithium (*t*-BuLi)/*N,N,N′,N′*-tetramethylethylenediamine (TMEDA) in toluene was found to be very effective. In this system, the *t*-BuLi/TMEDA complex reacts with toluene to form the benzyllithium (BzLi)/TMEDA complex, and this complex initiates the anionic polymerization of DAS. The DASLi/TMEDA and PDASLi/TMEDA complexes have sufficient nucleophilicity and stability as propagating species, without the metalation of toluene, and as a result, living anionic polymerization was achieved. The high molecular weight poly(4-diphenylaminostyrene) (PDAS), synthesized using the RLi/TMEDA system, had a syndiotactic-rich configuration, independent of the polymerization solvent.

Introduction

Anionic polymerization is a very important method for the synthesis of homopolymers, copolymers, block copolymers, and ω-functionalized polymers. Various monomers, such as styrene (St) (derivatives), methacrylic acid derivatives, and diene monomers have been polymerized using this method, and they have provided a variety of polymer chain structures and properties.

Among the St derivatives, 4-diphenylaminostyrene (DAS, also known as 4-vinyltriphenylamine) has been considered a favorable monomer for the synthesis of triphenylamine- (TPA-) containing polymers, because excellent charge transport properties are expected for such polymer structures.[1,2] To obtain poly(DAS) (PDAS) with a well-defined polymer chain structure, a number of polymerization studies have been carried out using anionic,[3,4] radical and living radical[3,5–9] methods. However, only high molecular weight polymers ($M_n \geq 10000$) were provided by the (living) radical polymerization (PDAS yield = 60–80 wt %; polydispersity index (PDI) = 1.20–4.30),[5–9] and quite limited information has been reported concerning the anionic polymerization of DAS (Scheme 1).

Feast et al. attempted the anionic polymerization of DAS in benzene with *s*-butyllithium (*s*-BuLi) as an initiator.[3] Although the molar ratio of $[\text{DAS}]_0/[s\text{-BuLi}]_0$ was 170, the PDAS obtained showed considerably lower molecular weight (number average molecular weight (M_n): 9500) than that of M_n, as estimated from the $[\text{DAS}]_0/[s\text{-BuLi}]_0$ molar ratio ($170 \times 271 = 46070$). Furthermore, the yield of PDAS remained at 80%. Therefore, this polymerization system is not controlled, and several side reactions, such as transfer and termination reactions, are thought to occur in this polymerization. Tew et al. reported the anionic polymerization of DAS in benzene/tetrahydrofuran (THF) with *n*-butyllithium (*n*-BuLi) as an initiator (DAS, 3.40 g; *n*-BuLi, 2.11 mL).[4] Although the $[\text{DAS}]_0/[n\text{-BuLi}]_0$ molar ratio was only 4.96, the yield of PDSA remained at 88%. That is, the side reactions preventing the anionic polymerization of DAS seem to occur in this polymerization system. Thus, to date, there has been no successful example of a well-controlled anionic polymerization of DAS for the synthesis of PDAS with a well-defined polymer chain structure.

Recently we reexamined the possibility of the anionic polymerization of DAS in order to develop a new method for the synthesis of TPA-containing polymers with well-defined polymer chain structures. With regard to anionic polymerization, the reaction and microstructure of the polymers are strongly affected by the initiators, solvents, and additives used. In order to reveal the characteristics of polymerization, the anionic polymerization of DAS was attempted under various polymerization conditions, and the nature of the polymerization was found to be considerably different from St, due to the bound diphenylamino group on the benzene ring of the St unit. As a result, it was discovered that a specific initiator system consisting of alkyllithium (RLi) and amine was particularly active for the anionic polymerization of DAS.

In the present paper, the characteristics of the anionic polymerization of DAS initiated by various RLi, RLi/THF, and RLi/amine systems are discussed in detail. The first successful example of living anionic polymerization of DAS with the RLi/*N,N,N′,N′*-tetramethylethylenediamine (TMEDA) system and the stereoregularity of PDAS obtained are also described.

Experimental Section

Materials. Cyclohexane (≥99.5%), toluene (≥99.8%), THF (≥99.9%), and TMEDA (≥99.5%) were refluxed over calcium hydride (CaH_2, 95%) and then distilled under dry argon. St, stirred with neutral aluminum oxide at room temperature, was degassed by argon bubbling to remove air and then distilled under reduced pressure over CaH_2. 1,4-Diazabicyclo[2,2,2]octane (DABCO, 98%), methyltriphosphonium bromide (MPB, ≥98.0%), and 4-(diphenylamino)benzaldehyde (DAB, ≥98.0%) were dried under reduced pressure in dry argon. *n*-BuLi (1.60 mol/L in *n*-hexane), *s*-BuLi (1.40 mol/L in cyclohexane), *tert*-butyllithium (*t*-BuLi; 1.70 mol/L in pentane), methanol (MeOH, ≥99.9%), dichloromethane (≥99.9%), and *n*-hexane (≥95%) were used without further purification. MPB and DAB were purchased from Tokyo Chemical. All other reagents were purchased from Aldrich.

DAS was synthesized via a standard Wittig reaction, as summarized in the following. Triphenylphosphonium methylide was prepared with MPB (12.5 g, 35.0 mmol) and *n*-BuLi (35.0 mmol)

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Scheme 1. Anionic Polymerization of 4-Diphenylaminostyrene with Alkyllithium

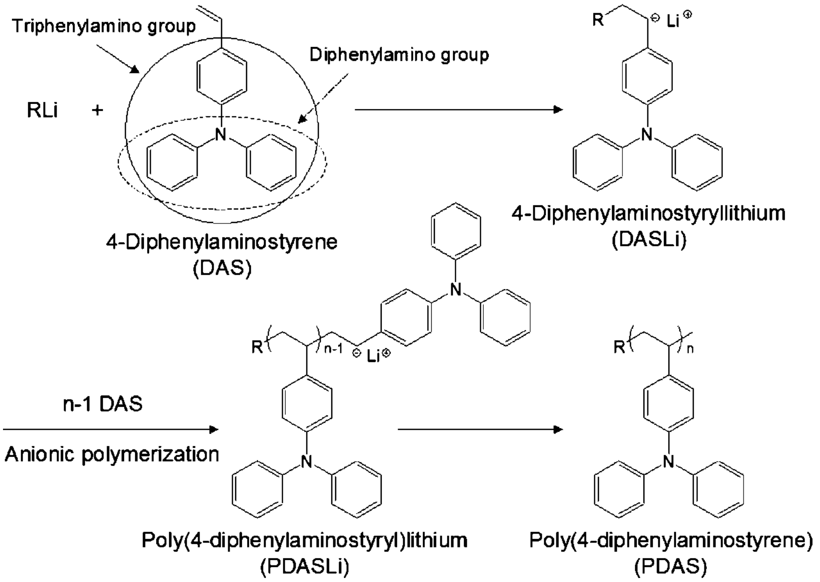


Table 1. Effects of Diphenylamino Group and Solvents on the Anionic Polymerization[a]

no.	initiator	solvent	$[DAS]_0/[Li]_0$	$[St]_0/[Li]_0$	polymerization time (h)	yield (wt %)	M_n[b]	PDI[b]
1	*n*-BuLi	cyclohexane	7.50		24	4.2	2680	4.13
2	*s*-BuLi	cyclohexane	7.50		24	1.8	970	1.47
3	*t*-BuLi	cyclohexane	7.50		24	55	2410	1.62
4	*s*-BuLi	cyclohexane		22.0	2	100	2380	1.09
5	*n*-BuLi	toluene	7.50		24	56	4500	1.72
6	*s*-BuLi	toluene	7.50		24	100	1300	1.15
7	*t*-BuLi	toluene	7.50		24	91	3720	1.51
8	*s*-BuLi	toluene	13.4		24	93	2440	1.22
9	*s*-BuLi	toluene	22.7		24	90	4360	1.49
10	*s*-BuLi	toluene	41.2		24	58	3230	1.42
11	*n*-BuLi	THF	7.50		24	96	3220	1.98
12	*s*-BuLi	THF	7.50		24	97	3670	2.65
13	*t*-BuLi	THF	7.50		24	93	3710	2.30

[a] Polymerization was carried out under dry argon at room temperature. Monomer/solvent = 0.500 g/15.0 mL. [b] M_n and PDI were estimated by GPC, using PSt as standard.

at room temperature (*ca.* 25 °C) in dry THF for 2 h under dry argon. DAB (9.56 g, 35.0 mmol) was then added to this solution, and the reaction mixture was magnetically stirred under dry argon at room temperature for 24 h. The crude DAS obtained was purified using column chromatography with *n*-hexane/dichloromethane = 3/1 as a developing mixed solvent at room temperature. Pure DAS was obtained in 92% yield.

Anionic Polymerization of DAS. A well-dried 50 mL Schlenk tube was purged with dry argon, and 5.0 mL of polymerization solvent (cyclohexane, toluene, or THF) was added at room temperature (*ca.* 25 °C) using a hypodermic syringe. RLi was then supplied to this solution with a hypodermic syringe under dry argon. If necessary, an additive (THF, DABCO, or TMEDA) was then added to this solution under dry argon and the mixture was stirred for 10 min. DAS (0.185 mol/L solution in polymerization solvent) was added to this solution, and the reaction mixture was magnetically stirred under dry argon at room temperature. After the polymerization, dry MeOH was added to the reaction mixture in an equimolar amount to the lithium (Li) atoms present in the reaction mixture, in order to terminate the reaction. The polymerization mixture was then poured into a large volume of MeOH to precipitate the polymer, which was then separated by filtration. The product was dried under reduced pressure in dry argon at room temperature for 24 h, resulting in a white powdery polymer.

Measurements. M_n, the weight average molecular weight (M_w), and PDI (M_w/M_n) were determined by using a gel permeation chromatography (GPC) apparatus equipped with a differential refractometer detector and a Shimadzu Shim-pack GPC-80 M column (column length: 300 mm, column diameter: 8 mm, effective molecular weight range of 100−4000000) at 40 °C. THF was used as the eluent, and the flow rate was 1.0 mL/min. A molecular weight calibration curve was obtained using polystyrene (PSt) standards. The Mark−Houwink−Sakurada constants for PSt/THF system were used. ^{1}H NMR spectra of the polymers were measured in deuterated chloroform ($CDCl_3$) at 500 MHz using a Jeol JNM α−500 spectrometer.

Results and Discussion

Effect of Diphenylamino Group on Anionic Polymerization. As shown in Scheme 1, DAS has a diphenylamino group with a nitrogen atom (a strong electron-donor) adjoining the benzene ring of the St unit. Therefore, although DAS is a St derivative, it was expected that the nature of the anionic polymerization would be considerably different from St. The anionic polymerization of DAS was carried out in cyclohexane (a typical aliphatic hydrocarbon solvent) with three types of RLi ($[DAS]_0/[Li]_0 = 7.50$) at room temperature under dry argon for 24 h, in order to reveal the effect of the diphenylamino group on the anionic polymerization of DAS (Scheme 1). As a comparison, the anionic polymerization of St was performed in cyclohexane with *s*-BuLi ($[St]_0/[Li]_0 = 22.0$) at room temperature under dry argon for 2 h. The results obtained are summarized in Table 1 (nos. 1−4).

In cyclohexane, the anionic polymerization of DAS initiated by RLi was very difficult in comparison with that of St. When *n*-BuLi and *s*-BuLi were used as initiators, the yield of PDAS

Table 2. Effects of Polar Additives on the Anionic Polymerization of DAS in Cyclohexane[a]

no.	initiator system (Li/additive)	$[\mathrm{DAS}]_0/[\mathrm{Li}]_0$	polymerization time (h)	yield (wt %)	M_{n}[b]	PDI[b]
14	*n*-BuLi/THF (1.00/1.25)	6.30	24	98	1870	1.19
15	*s*-BuLi/THF (1.00/1.25)	6.30	24	100	1690	1.16
16	*t*-BuLi/THF (1.00/1.25)	6.30	24	98	1740	1.15
17	*n*-BuLi/DABCO (1.00/1.25)	6.30	24	78	2530	1.81
18	*s*-BuLi/DABCO (1.00/1.25)	6.30	24	47	1710	2.12
19	*t*-BuLi/DABCO (1.00/1.25)	6.30	24	72	3380	1.64
20	*n*-BuLi/TMEDA (1.00/1.25)	6.30	24	100	1130	1.11
21	*s*-BuLi/TMEDA (1.00/1.25)	6.30	24	100	1150	1.16
22	*t*-BuLi/TMEDA (1.00/1.25)	6.30	24	98	1210	1.17
23	*n*-BuLi/TMEDA (1.00/0.250)	6.30	24	91	1320	1.16
24	*n*-BuLi/TMEDA (1.00/0.500)	6.30	24	100	1180	1.14
25	*n*-BuLi/TMEDA (1.00/1.25)	7.80	2	100	1570	1.12
26	*n*-BuLi/TMEDA (1.00/1.25)	10.9	2	100	2320	1.11
27	*n*-BuLi/TMEDA (1.00/1.25)	29.1	24	86	5860	1.28
28	*n*-BuLi/TMEDA (1.00/1.25)	29.1	120	96	5970	1.27
29	*n*-BuLi/TMEDA (1.00/1.25)	38.5	120	82	7180	1.44
30	*n*-BuLi/TMEDA (1.00/1.25)	148	120	71	8400	1.86

[a] Polymerization was carried out under dry argon at room temperature.DAS/solvent = 0.500 g/15.0 mL. [b] M_{n} and PDI were estimated by GPC, using PSt as standard.

was only 4.2 and 1.8 wt %, respectively (Table 1, nos. One and 2). The anionic polymerization of DAS was relatively improved by using *t*-BuLi as an initiator; however, the yield remained at 55 wt % (Table 1, no. 3). On the other hand, the anionic polymerization of St with *s*-BuLi gave yield of 100 wt % PSt. Therefore, the diphenylamino group on the benzene ring of the St unit is thought to strongly inhibit the anionic polymerization of DAS.

To our knowledge, the necessary condition for vinyl monomers to undergo anionic polymerization is the presence of vinyl groups with low electron density. With respect to DAS, the electron density of the benzene ring of the St unit seems to be increased by the diphenylamino group bound with a nitrogen atom (a strong electron-donor) (Scheme 1). Consequently, the vinyl group of DAS is thought to have a higher electron density than that of St. As a result, the initiation reaction of DAS with RLi is considerably impeded (Table 1, nos. 1 and 2). In addition, side reactions such as transfer and termination reactions are thought to occur as competitive reactions to the propagation reaction in the anionic polymerization of DAS in cyclohexane. The propagation reaction seems to be also prevented by the large steric hindrance of the bulky diphenylamino group of DAS. For these reasons, the anionic polymerization of DAS with RLi in an aliphatic hydrocarbon solvent is very difficult in contrast to that of St. In addition, it was expected that improvement of the nucleophilicity of RLi, 4-diphenylaminostyryllithium (DASLi), and PDASLi would be a very important factor for the well-controlled anionic polymerization of DAS.

Effect of Solvents on the Anionic Polymerization of DAS. It is well-known that anionic polymerization of conventional monomers, such as butadiene (Bd), isoprene (Ip), St, and methyl methacrylate (MMA), are strongly affected by the types of solvents used. RLi becomes monomeric in polar solvents, and the metal−carbon bond is polarized. Consequently, it was expected that a polar solvent would be more favorable for the anionic polymerization of DAS.

In order to reveal the effect of solvents, the anionic polymerization of DAS was performed with three types of RLi ($[\mathrm{DAS}]_0/[\mathrm{Li}]_0 = 7.50$) in toluene (a typical aromatic hydrocarbon solvent) and THF (a typical polar solvent) at room temperature under dry argon for 24 h. The polymerization results are summarized in Table 1 (nos 5−13).

When the anionic polymerization of DAS with RLi was carried out in toluene (Table 1, nos. 5−7), each RLi provided a considerably higher yield of PDAS than that in cyclohexane (Table 1, nos. 1−3). In particular, the anionic polymerization of DAS with *s*-BuLi in toluene (Table 1, no. 6) provided a 100 wt % yield of PDAS with a relatively narrow PDI range. Thus, an aromatic hydrocarbon solvent is an appropriate polymerization solvent for DAS. However, this polymerization system was not a well-controlled anionic polymerization. As shown in Table 1 (nos. 8−10), the yield of PDAS decreased, while the PDI of PDAS became broad with the increase of the $[\mathrm{DAS}]_0/[s\text{-BuLi}]_0$ molar ratios. Therefore, although the initial stage of that polymerization seems to be controlled, side reactions such as transfer and termination reactions are also thought to occur as competitive reactions to the propagation reaction in the anionic polymerization of DAS with *s*-BuLi in toluene.

In the case of the anionic polymerization of DAS with RLi in THF, a high yield of PDAS (≥93 wt %) was also obtained as in the case of toluene as a polymerization solvent, as displayed in Table 1 (nos. 11−13). However, all the PDAS obtained showed a broad PDI range. In THF, it is known that aggregation is substantially reduced for RLi compounds and the reactivity is very high. The broad distribution obtained for PDAS in THF without additive seems to be related to higher reaction temperature (room temperature) and the instability of anions.

Effects of Polar Additives on the Anionic Polymerization of DAS in an Aliphatic Hydrocarbon Solvent. With respect to anionic polymerization, polar additives such as amine and ether are regarded as strong complexing agents for organolithium compounds. In general, these complexing agents strongly affect the polymerization reactions and microstructure of the polymers.[10−12]

The effects of polar additives were examined to obtain fundamental information for the anionic polymerization of DAS. The anionic polymerization of DAS was performed with three types of RLi ($[\mathrm{DAS}]_0/[\mathrm{Li}]_0 = 6.30$) in cyclohexane with several different additives at room temperature under dry argon for 24 h. The results are displayed in Table 2 (nos. 14−22).

Under these polymerization conditions, the color of the PDASLi solution was a deep red. When THF was used as an additive, a high yield of PDAS with a relatively narrow PDI range was obtained (Table 2, nos. 14−16). The addition of DABCO to the polymerization system somewhat improved the yield of PDAS, compared with the anionic polymerization of DAS with RLi in cyclohexane containing no additive (Table 1, nos. 1−3); however, the polymers obtained showed a broad PDI range (Table 2, nos. 17−19). Among the three kinds of polar additives, TMEDA (a typically strong complexing agent) provided the best polymerization results (Table 2, nos. 20−22). A high yield of PDAS with a relatively narrow PDI range was obtained for each RLi/TMEDA (1.00/1.25) system. In particular,

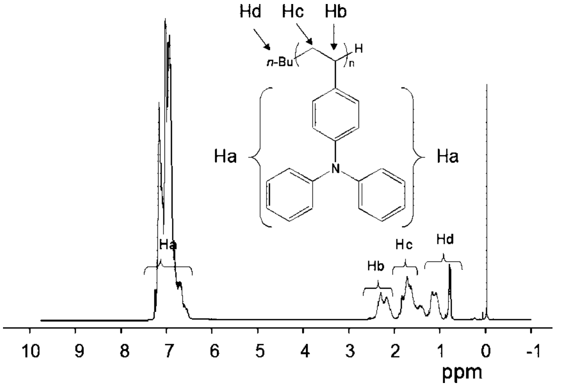


Figure 1. ^{1}H NMR spectrum of poly(4-diphenylaminostyrene) obtained using the *n*- butyllithium/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (1.00/1.25) system in cyclohexane ($M_n = 1130$, PDI = 1.11), measured in a 3.0 wt % solution of $CDCl_3$ at 50 °C.

the anionic polymerization of DAS with the *n*-BuLi/TMEDA (1.00/1.25) system in cyclohexane gave PDAS with a 100 wt % yield and narrow PDI range (Table 2, no. 20).

For the *n*-BuLi/TMEDA system, *n*-BuLi and TMEDA easily form a complex. This *n*-BuLi/TMEDA complex is monomeric in solution,[13] and the metal−carbon bond is thought to be strongly polarized. This complex easily causes the metalation reaction of organic compounds with acidic hydrogens (e.g., benzene, toluene, and *p*-xylene)[14,15] and the polymerization reaction of olefins such as ethylene, St, Bd, Ip, and 1,3-cyclohexadiene (1,3-CHD).[10−13,16,17] Therefore, as shown in Scheme 1 (RLi = *n*-BuLi/TMEDA), the *n*-BuLi/TMEDA complex is thought to have an sufficient nucleophilicity to form the DASLi/TMEDA complex with a quantitative yield as an initiation reaction. Furthermore, the DASLi/TMEDA and PDASLi/TMEDA complexes as propagating species seem to have sufficient nucleophilicity for the anionic polymerization of DAS. As a result, a 100 wt % yield of PDAS with a narrow PDI range is expected to be obtained.

Figure 1 shows a typical ^{1}H NMR spectrum of PDAS synthesized by anionic polymerization with the *n*-BuLi/TMEDA (1.00/1.25) system in cyclohexane (Table 2, no. 20). The peaks from 6.5 to 7.3 ppm (H_a) are assigned to aromatic protons on the triphenylamino groups. The peaks around 2.3 ppm (H_b) are assigned to methine protons in the main chain. The peaks around 1.7 ppm (H_c) are assigned to methylene protons in the main chain. The peaks from 0.6 to 1.3 ppm are assigned to methyl, methylene, and methine protons in the butyl residues from *n*-BuLi. Good agreement was obtained between the observed M_n calculated from the ^{1}H NMR spectrum of Figure 1 ($M_{n,NMR} = 1690$)[18] and the expected M_n estimated from the molar ratio of $[DAS]_0/[n\text{-BuLi}]_0 = 6.30$ ($M_{n,exp} = 1710$), indicating that every initiator (*n*-BuLi/TMEDA complex) produced one polymer molecule.

Anionic Polymerization of DAS with the *n*-BuLi/TMEDA System in Cyclohexane. The *n*-BuLi/TMEDA system is a good initiator system for the anionic polymerization of DAS. To reveal the characteristics of the *n*-BuLi/TMEDA system, the anionic polymerization of DAS was performed with various molar ratios of the *n*-BuLi/TMEDA system in cyclohexane for 24 h. The polymerization results obtained are summarized in Table 2(nos. 20, 23, and 24).

The anionic polymerization of DAS was remarkably improved by the addition of TMEDA as a polar additive. The yield of PDAS was increased, while the PDI range of PDAS became narrow with the increase of the *n*-BuLi/TMEDA molar ratio. Therefore, the nucleophilicity of the initiator system (e.g., the *n*-BuLi/TMEDA complex) and the propagating species (e.g., the DASLi/TMEDA and PDASLi/TMEDA complex) is concluded to be a very important factor for the well-controlled anionic polymerization of DAS (Scheme 1 (RLi = *n*-BuLi/TMEDA)).

Subsequently, the anionic polymerization of DAS with the *n*-BuLi/TMEDA (1.00/1.25) system was then carried out in cyclohexane with various $[DAS]_0/[n\text{-BuLi}]_0$ molar ratios to examine the nature of this polymerization system. The polymerization results obtained are shown in Table 2 (nos. 20 and 25−30).

When the $[DAS]_0/[n\text{-BuLi}]_0$ molar ratio was below 10.9 (Table 2, nos. 20, 25, and 26), PDAS was obtained in a quantitative yield with a narrow PDI range, indicating well-controlled anionic polymerization. However, the solubility of PDASLi decreased with the increase in the M_n of PDASLi. When the $[DAS]_0/[n\text{-BuLi}]_0$ molar ratio was higher than 29.1, the color of the reaction system changed from deep red to orange and became an opaque solution. After some time, the reaction system gradually became heterogeneous and an orange colored powder appeared. At the same time, the rate of the polymerization reaction became very slow. In addition, the yield of PDAS decreased, while the PDI range of PDAS became broad with the increase of the $[DAS]_0/[n\text{-BuLi}]_0$ molar ratio (Table 2, nos. 27−30). Therefore, for the well-controlled anionic polymerization of DAS, improvement in the solubility of PDASLi is thought to be required.

Table 3. Effects of Polar Additives on the Anionic Polymerization of DAS in Toluene[a]

no.	initiator system (Li/additive)	$[DAS]_0/[Li]_0$	yield (wt %)	M_n[b]	PDI[b]
31	*n*-BuLi/THF (1.00/1.25)	6.30	92	1900	1.17
32	*s*-BuLi/THF (1.00/1.25)	6.30	90	9250	1.21
33	*t*-BuLi/THF (1.00/1.25)	6.30	91	2470	1.21
34	*n*-BuLi/DABCO (1.00/1.25)	6.30	97	1880	1.17
35	*s*-BuLi/DABCO (1.00/1.25)	6.30	97	2230	1.22
36	*t*-BuLi/DABCO (1.00/1.25)	6.30	93	2450	1.26
37	*n*-BuLi/TMEDA (1.00/1.25)	6.30	97	2150	1.15
38	*s*-BuLi/TMEDA (1.00/1.25)	6.30	97	7190	1.31
39	*t*-BuLi/TMEDA (1.00/1.25)	6.30	100	1310	1.10
40	*t*-BuLi/TMEDA (1.00/1.25)	11.0	100	2550	1.10
41	*t*-BuLi/TMEDA (1.00/1.25)	19.5	100	4880	1.11
42	*t*-BuLi/TMEDA (1.00/1.25)	38.5	100	10600	1.11
43	*t*-BuLi/TMEDA (1.00/1.25)	73.9	99	21550	1.12
44	*t*-BuLi/TMEDA (1.00/1.25)	148	98	41600	1.18
45	*t*-BuLi/TMEDA (1.00/1.25)	195	96	55900	1.27

[a] Polymerization was carried out under dry argon at room temperature for 24 h.DAS/solvent = 0.500 g/15.0 mL. [b] M_n and PDI were estimated by GPC, using PSt as standard.

Effects of Polar Additives on the Anionic Polymerization of DAS in an Aromatic Hydrocarbon Solvent. The nucleophilicity and solubility of the initiator (system) and propagating species are very important factors for the well-controlled anionic polymerization of DAS. In order to improve the solubility of PDASLi, the anionic polymerization of DAS was performed with three types of RLi ($[DAS]_0/[Li]_0$=6.30) in toluene with several different additives at room temperature under dry argon for 24 h. The polymerization results obtained are summarized in Table 3(nos. 31−39).

In the case of THF as an additive, the yield of PDAS was around 90 wt % with a somewhat broad PDI range (Table 3, nos. 31−33), indicating the occurrence of some side reactions, such as transfer and termination reactions. The addition of DABCO to the polymerization system improved the yield of PDAS; however, the polymers obtained had a somewhat broad PDI range (Table 3, nos. 34−36). Among the three kinds of polar additives, TMEDA provided the best polymerization results (Table 3, nos. 37−39). A high yield of PDAS with a relatively narrow PDI range was obtained for each RLi/TMEDA

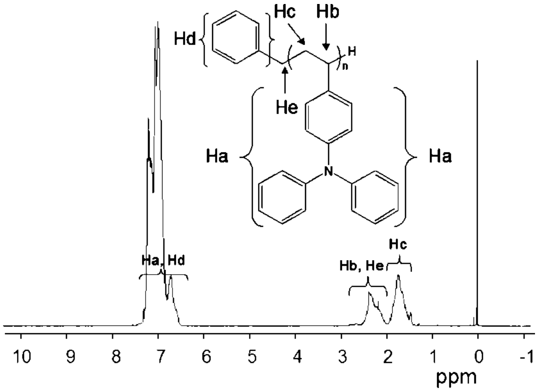


Figure 2. ^{1}H NMR spectrum of poly(4-diphenylaminostyrene) obtained using the *tert*-butyllithium/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (1.00/1.25) system in toluene (M_n = 1310, PDI = 1.10), measured in a 3.0 wt % solution of $CDCl_3$ at 50 °C.

(1.00/1.25) system. In particular, the anionic polymerization of DAS with the *t*-BuLi/TMEDA (1.00/1.25) system in toluene gave 100 wt % yield of PDAS with a narrow PDI range (Table 3, no. 39).

With respect to the anionic polymerization of DAS with the *t*-BuLi/TMEDA system, the color of the polymerization solution was changed twice. At first, the color of the toluene solution containing *t*-BuLi in a Schlenk tube became orange when TMEDA was added. Subsequently, the color of the toluene solution was changed from orange to deep red (the color of PDASLi) when DAS was supplied into the solution. In order to reveal the polymerization mechanism of DAS initiated by the *t*-BuLi/TMEDA system in toluene, ^{1}H NMR measurement of the obtained PDAS was conducted. As a result, it was noted that there was no ^{1}H NMR spectral peak from butyl residues in this polymer, in contrast to the ^{1}H NMR spectra of PDAS initiated by the *n*-BuLi/TMEDA system in cyclohexane (Figure 1).

The *n*-BuLi/TMEDA complex in the *n*-BuLi/TMEDA system is monomeric in solution,[13] and the metal−carbon bond is thought to be strongly polarized. This complex easily causes the metalation of organic compounds with acidic hydrogens (e.g., benzene, toluene, and *p*-xylene).[14,15] Eberhardt et al. found that toluene undergoes quantitative metalation with the *n*-BuLi/TMEDA complex to give benzyllithium (BzLi).[15]

The *t*-BuLi/TMEDA complex in the *t*-BuLi/TMEDA system is thought to be a stronger reagent for the metalation of toluene than the *n*-BuLi/TMEDA complex, because *t*-BuLi seems to have greater nucleophilicity than that of *n*-BuLi. The *t*-BuLi/TMEDA complex is thought to react rapidly with toluene, and to form the BzLi/TMEDA complex. (This seems to be an actual initiator system for DAS, showing an orange color in toluene solution.) When DAS is added into a solution of the BzLi/TMEDA complex, the initiation reaction of DAS is thought to occur with very high efficiency, and the DASLi/TMEDA complex is formed in a quantitative yield. Furthermore, DASLi/TMEDA and the PDASLi/TMEDA complexes as propagating species seem to have sufficient nucleophilicity for DAS. On the other hand, the DASLi/TMEDA and PDASLi/TMEDA complexes are thought to lack the ability for metalation of toluene, in contrast to the *t*-BuLi/TMEDA complex. As a result, PDAS was expected to be obtained in 100 wt % yield with a narrow PDI range (Table 3, no. 39).

Figure 2 shows a typical ^{1}H NMR spectrum of PDAS synthesized by anionic polymerization with the *t*-BuLi/TMEDA (1.00/1.25) system in toluene (Table 3, no. 39). The peaks from 6.5 to 7.4 ppm (Ha, Hd) seem to be assignable to aromatic protons on the triphenylamino groups (Ha) and the benzyl residues from BzLi (Hd). The peaks around 2.3 ppm (Hb, He) are assigned to methine protons in the main chain (Hb) and methylene protons in the benzyl residues from BzLi (He). The peaks around 1.7 ppm (Hc) are assigned to methylene protons in the main chain. Peaks from butyl residues were not observed due to the metalation of toluene by the *t*-BuLi/TMEDA complex.

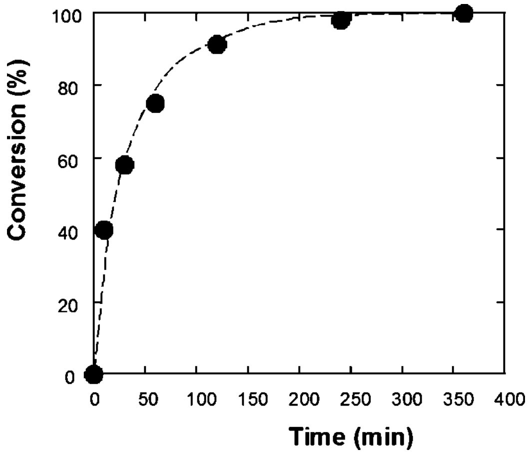


Figure 3. Time−conversion relationship for the anionic polymerization of 4-diphenylaminostyrene with the *tert*-butyllithium/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (1.00/1.25) system in toluene. Polymerization was performed under dry argon at room temperature (*ca*. 25 °C). [4-diphenylaminostyrene]$_0$/[*tert*-butyllithium]$_0$ = 36.9. 4-diphenylaminostyrene/toluene = 0.500 g/15.0 mL.

Synthesis of a High Molecular Weight PDAS with the *t*-BuLi/TMEDA System in Toluene. From the results in Table 3 (nos. 31−39), it was expected that the *t*-BuLi/TMEDA system in toluene would be an excellent initiator system for the well-controlled anionic polymerization of DAS. That is, this polymerization system was expected to provide significant nucleophilicity for the initiator system (i.e., the BzLi/TMEDA complex) and propagating species (i.e., the DASLi/TMEDA and PDASLi/TMEDA complexes), and provide PDASLi with good solubility. To examine the characteristics of the *t*-BuLi/TMEDA system in toluene, the anionic polymerization of DAS was carried out under dry argon at room temperature with various [DAS]$_0$/[*t*-BuLi]$_0$ molar ratios. The polymerization results obtained are summarized in Table 3 (nos. 39−45).

With respect to the anionic polymerization of DAS with the *t*-BuLi/TMEDA system in toluene, the polymerization system displayed a homogeneous solution with a deep red color during the polymerization. The M_n of PDAS was increased with the increase in the [DAS]$_0$/[Li]$_0$ molar ratio, indicating a well-controlled anionic polymerization. The PDAS obtained showed almost quantitative yield (96−100 wt %) and a relatively narrow PDI range (1.10−1.27). In addition, this polymerization system enabled the synthesis of a high molecular weight PDAS by anionic polymerization. The polymers of nos. 42−45 in Table 3 have a M_n of over 10 000. These are the first successful examples of anionic polymerized DAS that have yielded PDAS with a high molecular weight.

Living Nature of the Anionic Polymerization of PDAS with the *t*-BuLi/TMEDA System in Toluene. From the results summarized in Table 3 (nos. 39−45), the *t*-BuLi/TMEDA system in toluene appears to cause the well-controlled anionic polymerization of DAS. That is, the *t*-BuLi/TMEDA system in toluene seems to have the ability for the living anionic polymerization of DAS. The anionic polymerization of DAS with the *t*-BuLi/TMEDA system was carried out in toluene under dry argon at room temperature in order to examine the living nature of this polymerization system ([DAS]$_0$/[Li]$_0$ = 36.9). As shown in Figure 3, the conversion of DAS to PDAS

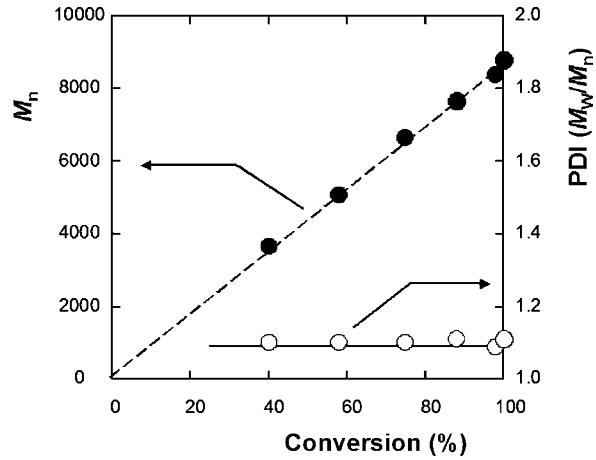
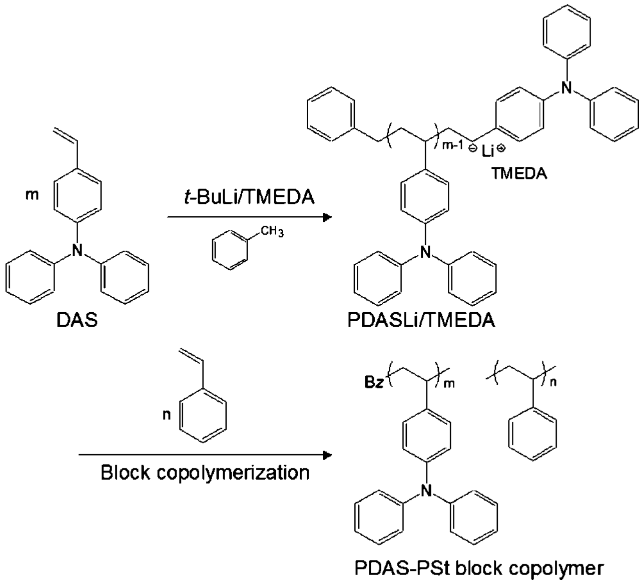


Figure 4. Polymerization of 4-diphenylaminostyrene with the *tert*-butyllithium/*N,N,N′,N′*-tetramethylethylenediamine (1.00/1.25) system in toluene at room temperature ([4-diphenylaminostyrene]$_0$/[*n*-BuLi]$_0$ = 36.9 with a M_n(PDI) conversion relationship. M_n and PDI were obtained by GPC calibrated using polystyrene standards.

Scheme 2. Block Copolymerization of 4-Diphenylaminostyrene and Styrene with the *tert*-Butyllithium/*N,N,N′,N′*-Tetramethylethylenediamine (1.00/1.25) System in Toluene



was 40% at 10 min, 58% at 30 min, 75% at 60 min, 92% at 120 min, 98% at 240 min, and 100% at 360 min. The M_n of these polymers increased linearly with conversion of DAS to PDAS, retaining a narrow PDI range (Figure 4).

In order to confirm the living nature of this polymerization system, the synthesis of a block copolymer of DAS and St with a narrow PDI range was then attempted, as shown in Scheme 2. A toluene solution of DAS was added to a toluene solution of the *t*-BuLi/TMEDA (1.00/1.25) system ([DAS]$_0$/[Li]$_0$ = 8.70), and the polymerization was carried out under dry argon at room temperature for 120 min. The conversion of DAS to PDAS was 100%, and the M_n and PDI of the PDAS prepolymer were 1910 and 1.10, respectively (Figure 5a). Subsequently, St was added to the reaction mixture ([St]$_0$/[Li]$_0$ = 70.5) and the polymerization was continued under dry argon at room temperature for 120 min. 100% conversion of St to the PDAS−PSt block copolymer was achieved after 120 min, and the resulting white powdery polymer product was obtained in almost quantitative yield. This block copolymer showed a sharp GPC chromatogram, and the M_n of the polymer increased from 1910 to 9260, while retaining a narrow PDI (M_w/M_n = 1.09, Figure 5(b)). ^{1}H NMR confirmed that the block copolymer obtained consisted of DAS and St units (Figure 6). Therefore, from the results in Figures 4–6, the polymerization of DAS with the *t*-BuLi/TMEDA system in toluene is thought to be a living anionic polymerization.

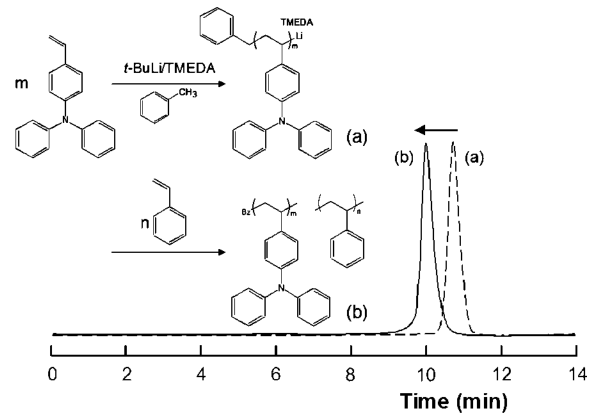


Figure 5. Block copolymerization of 4-diphenylaminostyrene and styrene with the *tert*-butyllithium/*N,N,N′,N′*-tetramethylethylenediamine (1.00/1.25) system in toluene at room temperature ([4-diphenylaminostyrene]$_0$/[styrene]$_0$/[*tert*-butyllithium]$_0$ = 8.70/70.5/1.00). GPC chromatograms of the prepolymer of poly(4-diphenylaminostyrene) (a: M_n = 1910; PDI = 1.10) and the block copolymer of 4-diphenylaminostyrene and styrene (b: M_n = 9260; PDI = 1.09). M_n and PDI were obtained by GPC calibrated using polystyrene standards.

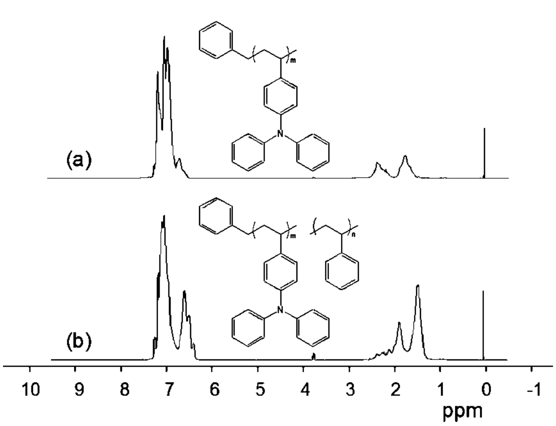


Figure 6. ^{1}H NMR spectra of poly(4-diphenylaminostyrene) (a: M_n = 1910; PDI = 1.10) and poly(4-diphenylaminostyrene)-polystyrene block copolymer (b: M_n = 9260; PDI = 1.09) obtained using the *tert*-butyllithium/*N,N,N′,N′*-tetramethylethylenediamine (1.00/1.25) system in toluene, measured in a 3.0 wt % solution of $CDCl_3$ at 50 °C.

Polymer Chain Structure of PDAS Initiated by the RLi/TMEDA System. As shown in Table 2 (nos. 20 and 25−30), the solubility of PDASLi decreased with the increase in the molecular weight of PDASLi. When the M_n of PDASLi was higher than 5000, the color of the cyclohexane solution changed from deep red to orange and became heterogeneous. Therefore, it was expected that the polymer chain structure changed during the increase of the polymer chain length. ^{1}H NMR measurements of PDAS with different M_n were then conducted in order to examine the relationship between the molecular weight and the polymer chain structure. Figure 7 shows the ^{1}H NMR spectra of PDAS obtained using the *n*-BuLi/TMEDA system in cyclohexane (Table 2, nos. 20, 26, and 28). The peaks of each proton from PDAS were remarkably affected by the increase in the molecular weight (i.e., the length of polymer chain). The aromatic proton signals (from 6.4 to 7.4 ppm) become sharper peaks with the increase in the molecular

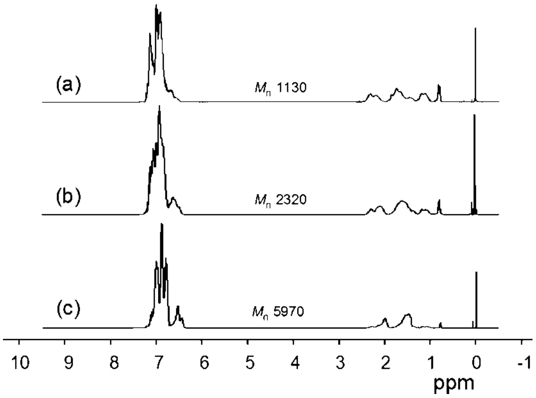


Figure 7. ^{1}H NMR spectra of poly(4-diphenylaminostyrene) obtained using the *n*-butyllithium/*N,N,N′,N′*-tetramethylethylenediamine (1.00/1.25) system in cyclohexane: (a) $M_n = 1130$, PDI = 1.11; (b) $M_n = 2320$, PDI = 1.11; (c) $M_n = 5970$, PDI = 1.27. Values were measured in a 3.0 wt % solution of $CDCl_3$ at 50 °C.

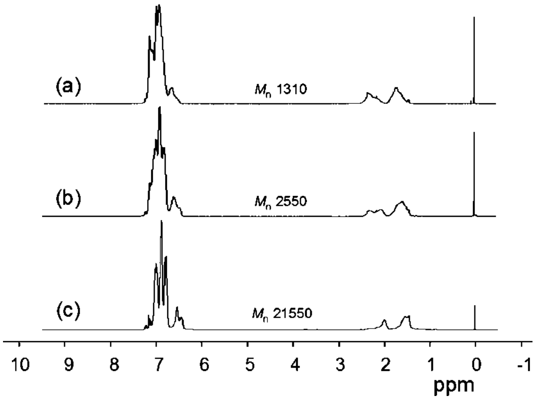


Figure 8. ^{1}H NMR spectra of poly(4-diphenylaminostyrene) obtained using the *tert*-butyllithium/*N,N,N′,N′*-tetramethylethylenediamine (1.00/1.25) system in toluene: (a) $M_n = 1310$, PDI = 1.10; (b) $M_n = 2550$, PDI = 1.10; (c) $M_n = 21550$, PDI = 1.12. The values were measured in a 3.0 wt % solution of $CDCl_3$ at 50 °C.

weight. The methine proton signals around 2.3 ppm (Figure 7, parts a and b), are shifted to higher magnetic field (around 2.0 ppm, Figure 7c). The methylene proton signals around 1.7 ppm (Figure 7, parts a and b) are shifted to higher magnetic field (around 1.5 ppm, Figure 7(c)).

Matsuzaki et al. reported that the methine proton signals of PSt are shifted to higher magnetic field in the order of isotactic-, atactic-, and syndiotactic-rich polymer.[19] The methine proton signals of isotactic PSt and syndiotactic PSt were around 2.3 and 2.1 ppm, respectively. In addition, Ishihara et al. showed that the methylene proton signals of PSt are shifted to higher magnetic field in the order of isotactic-, atactic-, and syndiotactic-rich polymer.[20] The methylene proton signals of isotactic PSt and syndiotactic PSt were around 1.6 and 1.4 ppm, respectively.

Therefore, the changes in the ^{1}H NMR spectra, as shown in Figure 7, seem to reflect the stereoregularity of PDAS as for PSt. That is, the low molecular weight of PDAS ($M_n \approx 1000$) has an isotactic-rich configuration, as shown in Figure 7a. The stereoregularity becomes an atactic-rich configuration when the M_n of PDAS is increased to around 2500 (Figure 7b). PDAS has a syndiotactic-rich configuration when the M_n is higher than 5000 (Figure 7b), due to the large steric hindrance of each adjoining bulky triphenylamino group.

Figure 8 shows the ^{1}H NMR spectra of PDAS obtained by the *t*-BuLi/TMEDA system in toluene (Table 3, nos. 39, 40, and 43). The peaks of each proton from PDAS were remarkably changed by the increasing molecular weight, as was the case for PDAS obtained by the *n*-BuLi/TMEDA system in cyclohexane (Figure 7).

Therefore, the high molecular weight PDAS synthesized by the RLi/TMEDA system has a syndiotactic-rich configuration, independent of the polymerization solvent.

Conclusion

The anionic polymerization of DAS with RLi was examined in detail. The diphenylamino group on the benzene ring of the St unit strongly inhibited the anionic polymerization of DAS. In an aliphatic hydrocarbon solvent, the anionic polymerization of DAS by RLi was very difficult in comparison with that of St. The nucleophilicity and solubility of RLi, DASLi, and PDASLi were very important factors for the anionic polymerization of DAS, which was remarkably improved when the solvents and polar additives used were taken into account. The anionic polymerization of DAS with the *n*-BuLi/TMEDA system in cyclohexane was a good polymerization system. However, the synthesis of high molecular weight PDAS was very difficult, due to the low solubility of PDASLi in the aliphatic hydrocarbon solvent. The *t*-BuLi/TMEDA system in toluene was found to be an excellent initiator system for the anionic polymerization of DAS. The *t*-BuLi/TMEDA complex reacted with toluene and formed the BzLi/TMEDA complex, and this complex initiated the anionic polymerization of DAS. The DASLi/TMEDA and the PDASLi/TMEDA complexes, as propagating species, had sufficient nucleophilicity for DAS. Furthermore, the DASLi/TMEDA and PDASLi/TMEDA complexes lacked the ability for metalation of toluene. As a result, the anionic polymerization of DAS with the *t*-BuLi/TMEDA system in toluene became a living anionic polymerization. High molecular weight PDAS and PDAS-PSt block copolymers were obtained using this polymerization method. The high molecular weight PDAS synthesized by the RLi/TMEDA system had a syndiotactic-rich configuration, independent of the polymerization solvent.

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