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Preparation of diblock copolymer based on poly(4-*n*-butyltriphenylamine) via palladium coupling polymerization

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ABSTRACT

A self-condensing monomer 4-(4′-bromophenyl)-4″-*n*-butyldiphenylamine (**1**) was synthesized, and successfully converted to poly(4-*n*-butyltriphenylamine) (PBTPA) by arylamination using palladium catalyst. PBTPAs can be functionalized at both terminals separately by adding an aryl bromide or arylamine derivatives as a terminator, which enabled us to prepare the diblock copolymer PBTPA-*block*-PEO. Polymer characterization was performed by ^{1}H NMR, ^{13}C NMR, and DSC, which confirmed that the PEO segment was successfully introduced at the terminal of PBTPA. The surface morphology in a thin film of PBTPA-*block*-PEO was examined by AFM, revealing that a microphase-separated structure or cup-shaped structure with PEO sphere domains formed when the film was spin-cast from 1,1,2,2-tetrachloroethane solutions of different concentrations.

1. Introduction

Triphenylamine (TPA) derivatives have been known as candidates for hole transport materials to be used in organic electroluminescent (EL) and photovoltaic cell devices. Many compounds containing the TPA moiety for EL devices have been reported for decades [1–4]. In the meantime, some researchers employed triphenylamine as a polymer backbone for building up the π-conjugated structure of poly(triphenylamine) (PTPA) [5–8]. PTPA takes an advantage for simple wet processes such as spin-coating or ink-jet printing to fabricate the devices in contrast to low molecular weight TPA derivatives that are generally supposed to be adopted by costly chemical vapor deposition process. General methods to synthesize PTPA can be classified as oxidative polymerization of TPA [5,6] and nickel(0)-catalyzed coupling polymerization [7,8] of dibromotriphenylamine. Sato et al. reported that the poly(4-alkyltriphenylamine) prepared by oxidative polymerization showed higher photoconductivity than poly(*N*-vinylcarbazole), a well-known hole transport material, promising the benefit to apply PTPA for electric devices [9].

Recently self-assembled materials with nano-scale structures, especially microphase separation of block copolymers, have attracted significant attention for a bottom-up technique in device manufacture [10,11]. Tailoring ordered structures of polymeric materials with nano-size domains have potential to improve the performance of organic electronic devices. For examples, the interpenetrating polymer network structure based on a blend of poly(*p*-phenylenevinylene)s exhibited high efficiency in charge dissociation at the interface between electron and hole transport polymers [12]. Furthermore, Hiramoto et al. demonstrated that elaborately prepared organic semiconductor lattice structures which stand vertical to electrodes showed high internal photocurrent quantum efficiency [13]. Hole and electron transport layers were laminated alternatively, and each layer with desired width was prepared by spin coating. Layer width in a vertical lattice had an effect on the quantum efficiency that reached a maximum value of 41% when the layer width was 5 nm.

On the other hand, arylamination reactions of aryl halides with amines using palladium catalyst developed by Hartwig and Buchwald are a powerful way for the preparation of arylamine derivatives [14–16]. Some researchers applied this manner for polymer syntheses to prepare a series of poly(aniline)s with good regioregularity [17–19]. Hartwig et al. demonstrated that the poly(*N*-arylaniline)s, which contain a triphenylamine moiety in the polymer backbone, were synthesized and showed tunability of the redox potential by varying the side chain [20]. In this article, we chose Hartwig–Buchwald arylamination to build up the polymer structure containing triphenylamine, and prepared diblock copolymers consisting of poly(4-butyltriphenylamine) (PBTPA) and poly(ethylene oxide) (PEO) segments by the polymerization of a self-condensing monomer with PEO modified terminators.

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2. Experimental section

2.1. Materials

Toluene was distilled over sodium and benzophenone, and stored under nitrogen atmosphere. Dimethylformamide was distilled under reduced pressure over calcium hydride, and stored under nitrogen atmosphere. Poly(ethylene oxide) monomethyl ethers with number average molecular weights of 1900 and 5300, and polydispersity indices of 1.03 and 1.02, respectively, were kindly donated by NOF corporation, and used without further purification. The other reagents and solvents were used as received.

2.2. Synthesis of 4-(4′-bromophenyl)-4″-n-butyldiphenylamine (1)

To a solution of 4-*n*-butylaniline (3.73 g, 25.0 mmol), 4,4′-dibromobiphenyl (7.80 g, 25.0 mmol), and sodium *tert*-butoxide (3.35 g, 35.0 mmol) in dry toluene (50 mL) was added [1,1′-bis-(diphenylphosphino)ferrocene]dichloropalladium(II) (Pd(dppf)Cl_2) (0.204 g, 0.25 mmol) under nitrogen atmosphere. The mixture was stirred under reflux for 24 h. After the reaction, the resulting solution was washed with 1 N HCl and saturated brine, and then dried with $MgSO_4$. Toluene was removed by rotary evaporator, and the residue was purified by silica column chromatography with toluene/hexane (1/1 in volume ratio). The crude product was recrystallized from hexane affording 4.35 g of yellow crystals (46%). Mp: 116 °C (DSC). ^{1}H NMR ($CDCl_3$): δ 7.51 (d, $J = 8.8$ Hz, 2H), 7.43 (d, $J = 8.8$ Hz, 2H), 7.41 (d, $J = 8.8$ Hz, 2H), 7.11 (d, $J = 8.8$ Hz, 2H), 7.07 (d, $J = 4.8$ Hz, 2H), 7.04 (d, $J = 4.8$ Hz, 2H), 5.71 (s, 1H), 2.57 (t, $J = 7.2$ Hz, 2H), 1.59 (m, $J = 8.4$ Hz, 2H), 1.37 (m, $J = 6.8$ Hz, 2H), 0.93 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 143.91, 140.02, 139.90, 136.80, 131.94, 131.75, 129.40, 128.18, 127.93, 120.65, 119.38, 116.94, 35.06, 33.92, 22.44, 14.09. Anal. Calcd for $C_{22}H_{22}BrN$: C, 69.48; H, 5.83; N, 3.68. Found: C, 69.54; H, 5.87; N, 3.71.

2.3. Tosylation of poly(ethylene oxide) monomethyl ether ($M_n = 2000$) (2)

To the two-necked flask equipped with an addition funnel was added poly(ethylene oxide) monomethyl ether (2.0 g, $M_n = 1900$, $M_w/M_n = 1.03$, 1.0 mmol), and it was dried at 50 °C under vacuum. After cooling to room temperature, the solid was dissolved in triethylamine (0.70 mL, 5.0 mmol) and dichloromethane (10 mL). To this solution was added tosyl chloride (0.953 g, 5.0 mmol) in dichloromethane (10 mL) dropwise at 0 °C. The mixture was stirred for 12 h at room temperature then the solution was washed with water (three times) and saturated brine. The organic layer was dried with $MgSO_4$, and concentrated by rotary evaporator. The resulting solid was washed with diethyl ether, then filtered and dried. The yield was 2.0 g (93%). Mp: 54 °C (DSC). ^{1}H NMR ($CDCl_3$): δ 7.80 (d, $J = 7.8$ Hz, 2H), 7.34 (d, $J = 7.8$ Hz, 2H), 4.16 (t, $J = 4.8$ Hz, 2H), 3.66–3.62 (m, 160H), 3.38 (s, 3H), 2.45 (s, 3H).

2.4. Synthesis of 4-bromophenyl terminated poly(ethylene oxide) ($M_n = 2000$) (3)

To a dispersion of sodium hydride (0.020 g, 0.50 mmol) in dimethylformamide (1 mL) was added 4-bromophenol (0.087 g, 0.50 mmol) under nitrogen atmosphere. After stirring for 1 h at room temperature, a solution of **2** (1.0 g, 0.50 mmol) in dimethylformamide (3 mL) was added, and the mixture was stirred for 12 h. Water was added to the solution to quench the remaining sodium hydride, and the mixture was extracted with chloroform. The organic layer was dried with $MgSO_4$, and concentrated by rotary evaporator. The residue was washed with diethyl ether and dried. The yield was 0.83 g (83%). Mp: 55 °C (DSC). ^{1}H NMR ($CDCl_3$): δ 7.36 (d, $J = 8.8$ Hz, 2H), 6.80 (d, $J = 8.8$ Hz, 2H), 4.10 (t, $J = 4.8$ Hz, 2H), 3.85 (t, $J = 4.8$ Hz, 2H), 3.74–3.58 (m, 160H), 3.38 (s, 3H). Anal. Calcd for $C_{97}H_{187}BrO_{46}$: C, 52.65; H, 8.89. Found: C, 53.94; H, 8.51.

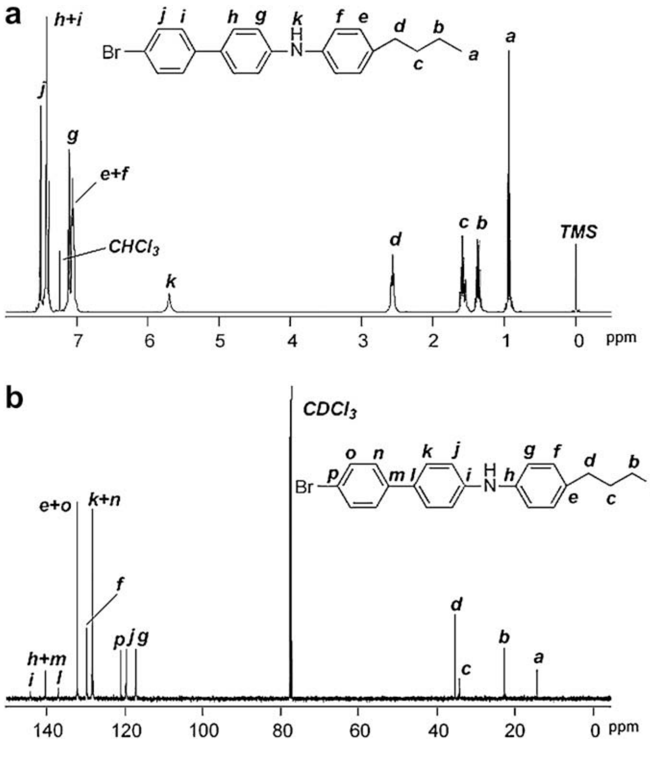
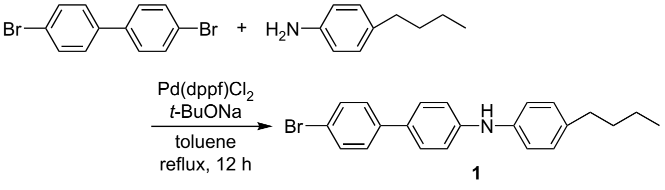


Fig. 1. (a) ^{1}H and (b) ^{13}C NMR spectra of monomer **1**.



1

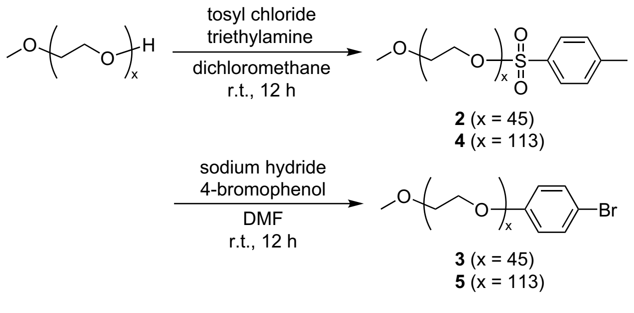
Scheme 1. Synthesis of self-condensing monomer **1**.

2.5. Tosylation of poly(ethylene oxide) monomethyl ether ($M_n = 5400$) (4)

Tosylation was carried out by the same procedure as the synthesis of **2** using poly(ethylene oxide) monomethyl ether (2.5 g, $M_n = 5300$, $M_w/M_n = 1.02$, 0.5 mmol). The yield was 2.4 g (95%). Mp: 61 °C (DSC). ^{1}H NMR ($CDCl_3$): δ 7.80 (d, $J = 7.8$ Hz, 2H), 7.34 (d, $J = 7.8$ Hz, 2H), 4.16 (t, $J = 4.8$ Hz, 2H), 3.66–3.62 (m, 160H), 3.38 (s, 3H), 2.45 (s, 3H).

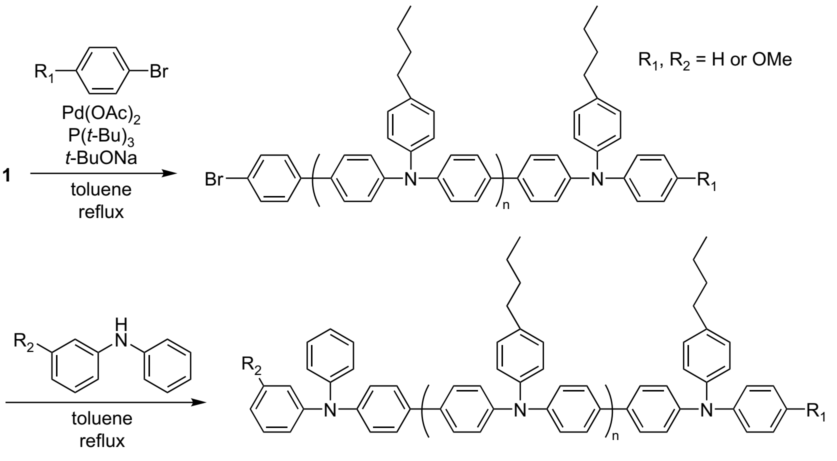
2.6. Synthesis of 4-bromopheyl terminated poly(ethylene oxide) ($M_n = 5400$) (5)

Etherification was carried out by the same procedure as the synthesis of **3** using **4** (2.4 g, 0.47 mmol). The yield was 2.0 g (85%).



2 (x = 45)
4 (x = 113)
3 (x = 45)
5 (x = 113)

Scheme 2. Syntheses of PEO modified aryl bromide terminators.



Scheme 3. Polymerization of **1** by arylamination.

Mp: 62 °C (DSC). ^{1}H NMR (CDCl$_3$): δ 7.36 (d, $J = 8.8$ Hz, 2H), 6.80 (d, $J = 8.8$ Hz, 2H), 4.10 (t, $J = 4.8$ Hz, 2H), 3.85 (t, $J = 4.8$ Hz, 2H), 3.74–3.58 (m, 160H), 3.38 (s, 3H). Anal. Calcd for $C_{233}H_{459}BrO_{114}$: C, 54.18; H, 8.96. Found: C, 54.39; H, 8.75.

2.7. Polymerization of 1 (PBTPA)

To the solution of **1** (0.10 g, 0.27 mmol), sodium *tert*-butoxide (0.028 g, 0.30 mmol), and palladium(II) acetate (0.0012 g, 0.0054 mmol) in dry toluene (1 mL) was added tri-*tert*-butylphosphine (0.0044 g, 0.022 mmol) under nitrogen atmosphere. The mixture was stirred under reflux for 24 h. After the reaction, the resulting solution was poured into methanol. The precipitate was filtered and washed with methanol and water. The polymer was dissolved in chloroform, and then reprecipitated in methanol. After filtration, 0.078 g (99%) of white polymer was obtained. ^{1}H NMR (CDCl$_3$): δ 7.43 (d, $J = 7.5$ Hz, 4H), 7.15–7.03 (m, 8H), 2.58 (t, $J = 7.0$ Hz, 2H), 1.61 (m, $J = 7.5$ Hz, 2H), 1.38 (m, $J = 7.0$ Hz, 2H), 0.94 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (CDCl$_3$): δ 147.08, 145.45, 138.29, 134.87, 129.49, 127.46, 125.18, 124.07, 124.03, 35.22, 33.74, 22.54, 14.02.

2.8. Preparation of PBTPA-block-PEO

To the solution of **1** (0.10 g, 0.27 mmol) and sodium *tert*-butoxide (0.028 g, 0.30 mmol) in dry toluene (0.5 mL) was added a solution of **3** or **5** (0.0054 mmol), palladium(II) acetate (0.0012 g, 0.0054 mmol), and tri-*tert*-butylphosphine (0.0044 g, 0.022 mmol) in toluene (0.5 mL) under nitrogen atmosphere. After the mixture was stirred under reflux for 24 h, a solution of diphenylamine (0.0054 mmol) in toluene (0.5 mL) was added. Stirring continued for 1 h. The resulting solution was poured into methanol. The precipitate was filtered and washed with methanol and water. The polymer was dissolved in chloroform, and then reprecipitated in methanol. After filtration, a white polymer was obtained. Hot extraction of the polymer with acetone was performed by Soxhlet

Table 1
Polymerization of **1** under various conditions.[a]

Run	Aryl bromide[b]	Diphenylamine[b]	Yield[c] (%)	M_n[d] (kDa)	M_w[d] (kDa)	M_w/M_n[d]
1	None	None	94	7.1	36	5.0
2	None	3-Methoxy diphenylamine	99	6.7	31	4.6
3	4-Bromobenzene	3-Methoxy diphenylamine	99	8.6	36	4.2
4	4-Bromoanisole	Diphenylamine	99	8.0	33	4.1
5	4-Bromoanisole	3-Methoxy diphenylamine	99	9.0	36	4.0
6	3	Diphenylamine	92	6.5	20	3.1

[a] Polymerization was carried out with **1** (1.0 equiv.), Pd(OAc)$_2$ (2.0 mol%), t-BuONa (1.1 equiv.), and P(t-Bu)$_3$ (8.0 mol%) in toluene.
[b] Added 2 mol%.
[c] Yield of the polymer before hot extraction.
[d] Determined by GPC eluted with chloroform using polystyrene standards.

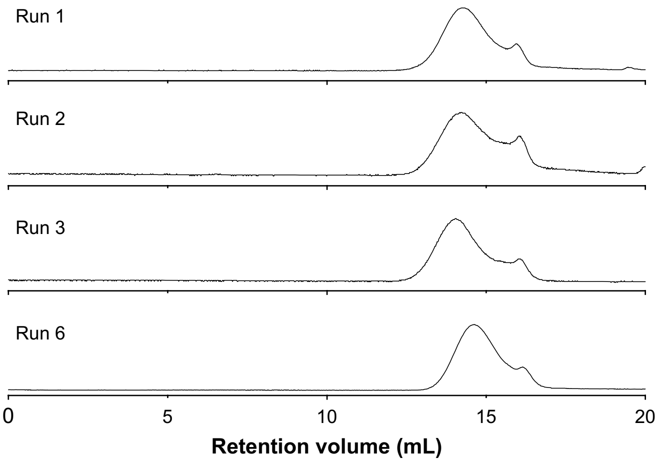


Fig. 2. GPC traces of PBTPAs obtained under various conditions (Table 1).

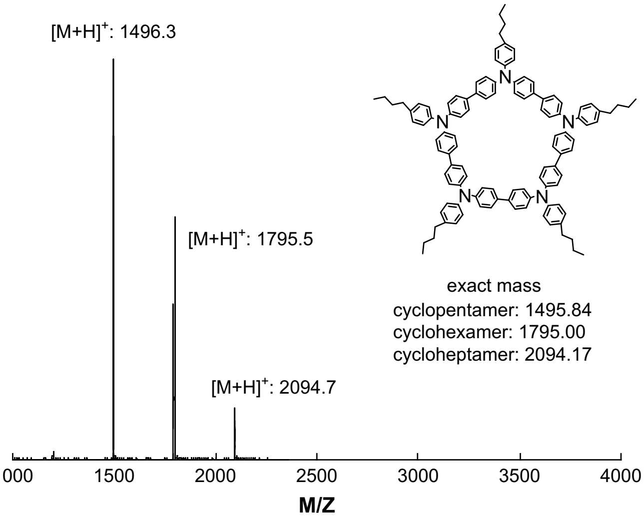
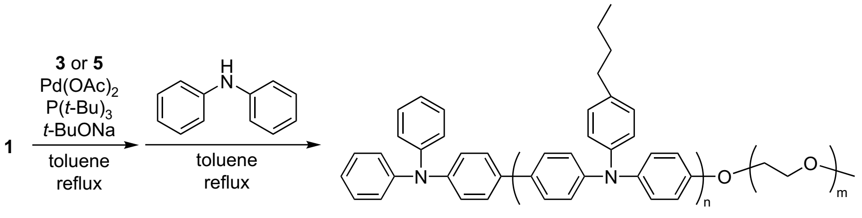


Fig. 3. MALDI-TOF MS spectrum of the low molecular weight fraction of PBTPA.



Scheme 4. Synthesis of PBTPA-*block*-PEO.

Table 2
PBTPA-*block*-PEOs with different PEO contents.[a]

PBTPA-*block*-PEO	Aryl bromide	M_n[b] (kDa)	M_w[b] (kDa)	M_w/M_n[b]	PEO content[c] (wt%)
BP1[d]	3[e]	12	22	1.88	9.1
BP2	5[e]	10	22	2.14	7.5
BP3	5[f]	10	17	1.66	23

[a] Polymerization was carried out with **1** (1.0 equiv.), $Pd(OAc)_2$ (2.0 mol%), *t*-BuONa (1.1 equiv.), $P(t\text{-}Bu)_3$ (8.0 mol%), and diphenylamine (2.0 mol%) in toluene.

[b] Determined by GPC eluted with chloroform using polystyrene standards after hot extraction with acetone.

[c] Estimated by ^1H NMR.

[d] Same polymer as Run 6 in Table 1.

[e] Added 2 mol%.

[f] Added 5 mol%.

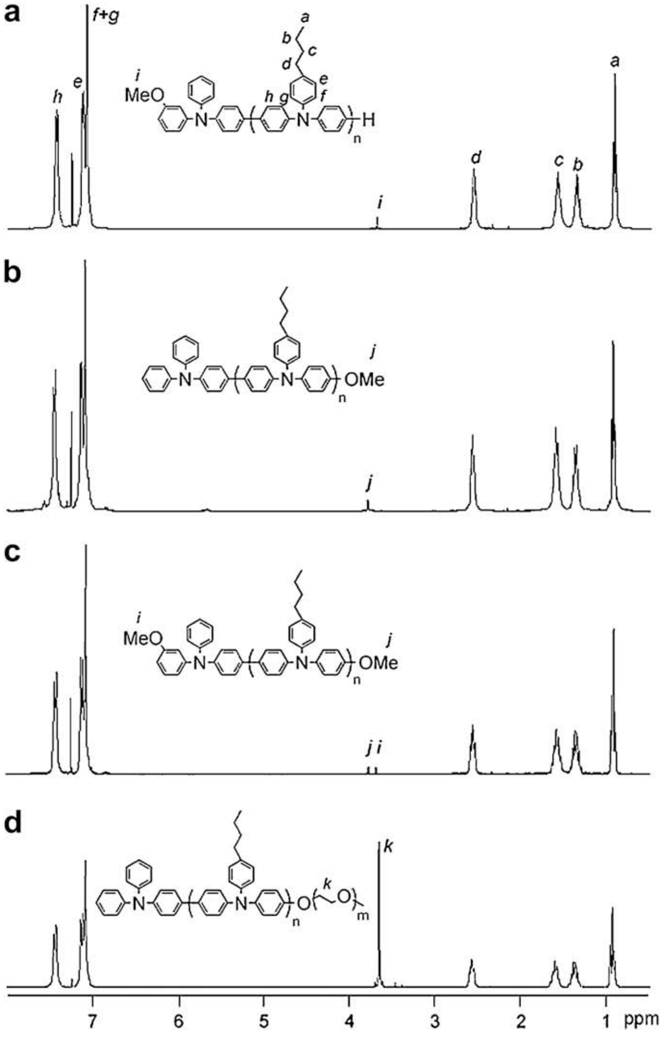


Fig. 4. ^1H NMR spectra of PBTPAs for (a) Run 3, (b) Run 4, (c) Run 5, and (d) Run 6 in Table 1.

extractor apparatus for 24 h to get rid of small amount of cyclic oligomers. The residue in a conical filter was collected and dried under vacuum.

2.9. Measurements

^1H and ^{13}C NMR spectra were obtained on a JEOL ALPHA500 instrument at 500 and 125 MHz, respectively. Deuterated chloroform was used as a solvent with tetramethylsilane as an internal standard. Number- and weight-average molecular weights (M_n and M_w) were determined by gel permeation chromatography (GPC) analysis with a JASCO RI-2031 detector eluted with chloroform at a flow rate of 1.0 mL min^{-1} and calibrated by standard polystyrene samples. Differential scanning calorimetric (DSC) analyses were performed on a Rigaku DSC-8230 under a nitrogen atmosphere at heating and cooling rates of 10 °C/min. The matrix assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectrum was obtained on a Kratos Kompact MALDI instrument operated in linear detection mode to generate positive ion spectrum using 2,5-dihydroxybenzoic acid (DHBA) as a matrix. Atomic force

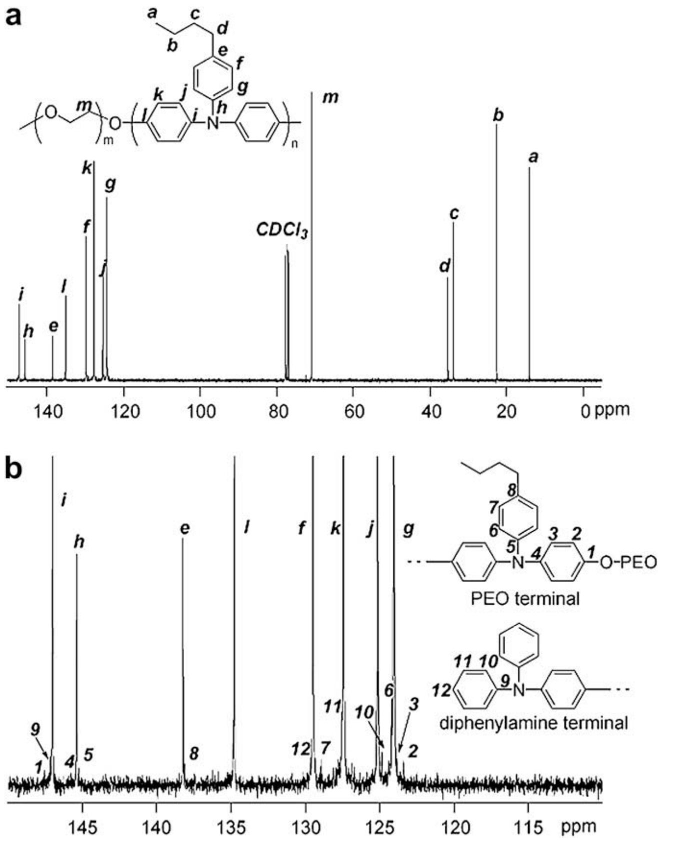


Fig. 5. (a) ^{13}C NMR spectrum of PBTPA-*block*-PEO (BP1) and (b) expanded spectrum of the aromatic region.

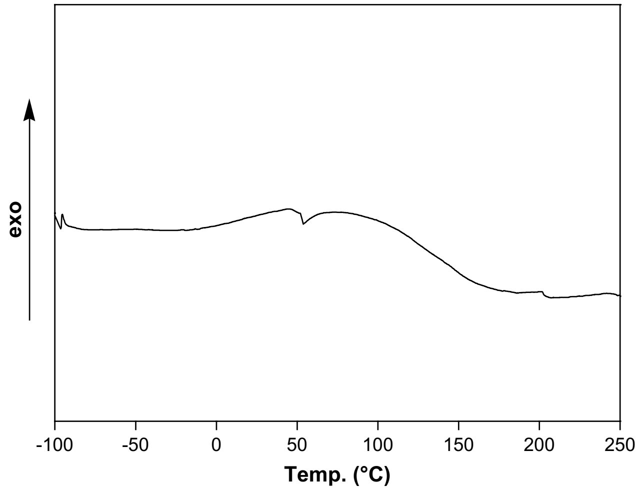


Fig. 6. The DSC curve of BP3 (second heating).

microscopic (AFM) measurements were performed on a JEOL JSPM-4200 system in tapping mode (phase and topographic modes) with an MPP-11100-10 silicon probe (resonant frequency: 300 kHz, force constant: 40 N/m). All thin films of polymers were spin-cast onto glass slide by a MIKASA 1H-D7 spin coater from 1,1,2,2-tetrachloroethane solutions at 1500 rpm for 30 s.

3. Results and discussion

3.1. Monomer synthesis

PTPA prepared by the polymerization of self-condensing monomer possesses two different terminal groups, namely aryl bromide and secondary arylamine, which would make it possible to modify each terminal unit separately. Modification of PTPA can create diblock or hetero triblock copolymers having PTPA segment. Therefore, as a self-condensing monomer, 4-(4′-bromophenyl)-4″-*n*-butyldiphenylaniline (**1**) was prepared by coupling 4,4′-dibromobiphenyl with 4-*n*-butylaniline using [1,1′-bis(diphenylphosphino)ferrocene] dichloropalladium (II) (Pd(dppf)Cl_2) as a catalyst (Scheme 1). The structure of **1** was confirmed by ^{1}H and ^{13}C NMR spectra, in which all the protons and carbons of **1** are assignable to all signals (Fig. 1). The characteristic signals assignable to the carbon next to bromo atom (*p* position) as well as the *ortho*-carbons of secondary amine moiety (*g*, *j* positions) are observed from 117 to 120 ppm in ^{13}C NMR.

Some researches revealed that block copolymers possessing PEO segment showed unique nanostructures such as vertically ordered cylindrical domains [21,22]. Therefore, aryl bromide terminators **3** and **5** modified by PEO segments with 1900 and 5300 of M_n respectively were prepared as shown in Scheme 2 in order to prepare diblock copolymers of PBTPA and PEO. The degrees of functionalization of **3** and **5** by 4-bromophenol were estimated as 97% and 95% from ^{1}H NMR spectra, respectively.

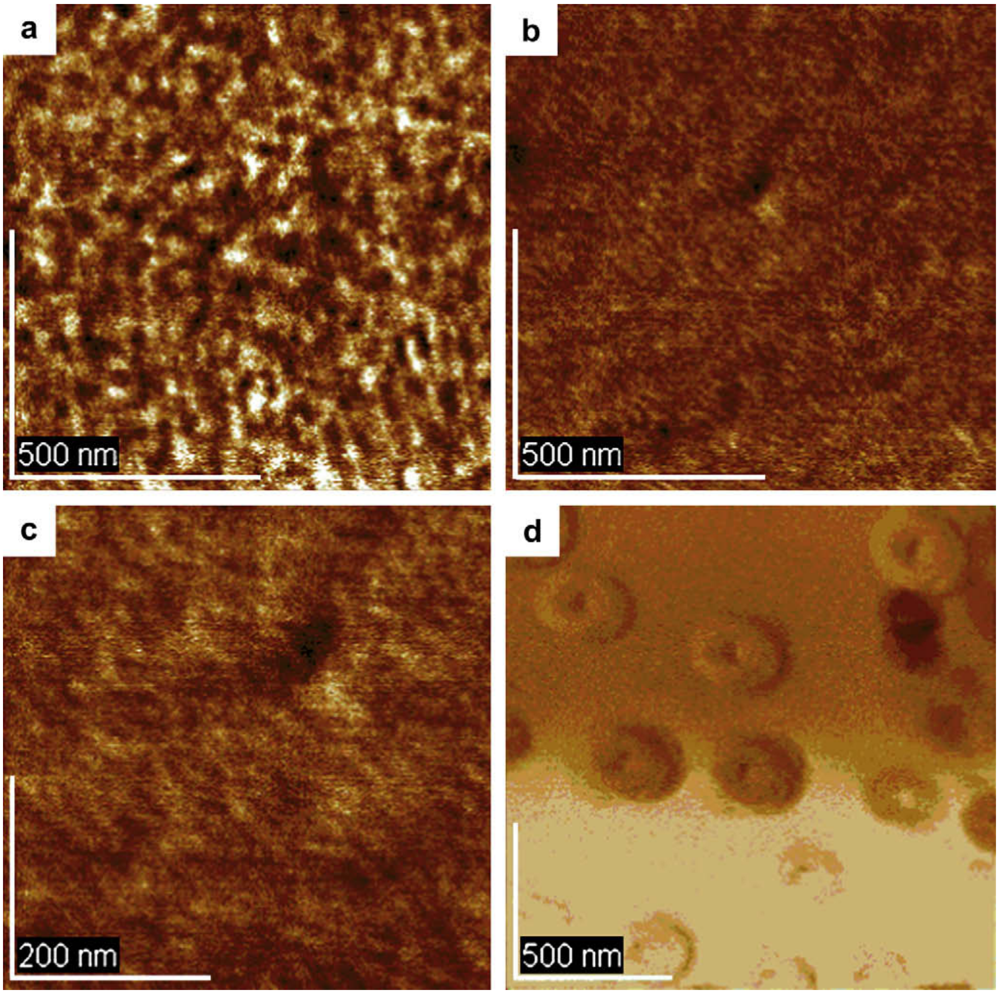


Fig. 7. The phase mode AFM images of BP1 films prepared from (a) 10 wt%, (b, c) 1 wt%, and (d) 0.5 wt% 1,1,2,2-tetrachloroethane solutions.

3.2. Polymer synthesis

We examined the polymerization of **1** by arylamination as well as terminal modification of the resulting PTPA with aryl bromide and arylamine derivatives. The self-condensing polymerizations of **1** were carried out using Pd(II) acetate, sodium *tert*-butoxide, and tri(*tert*-butyl)phosphine in toluene solution (Scheme 3). Aryl bromide derivatives were used to modify the diphenylamine terminal; on the other hand the polymerization was terminated by adding diphenylamine derivatives at the end of the reaction. Table 1 shows the results of polymerization with various terminal groups. Polymers with weight-average molecular weights (M_w) over 30,000 were obtained, but the polydispersity index (M_w/M_n) broadened. Furthermore, **3** was used to prepare diblock copolymer consisting of PBTPA and PEO segments (Table 1, Run 6). The apparent M_w value was slightly lower than that of homopolymer because the PEO segment showed relatively poor solubility in toluene. All the polymers show bimodal profiles in GPC as shown in Fig. 2, which involves a major peak and a small peak corresponding to a high molecular weight of 20,000–25,000 at peak top and a low molecular weight of 2200 at peak top, respectively. All the polymers give almost the same retention volume of the small peak for the low molecular weight fraction. This result can be attributed to the formation of cyclic polymers as discussed in the literature [15]. Hot extraction with acetone allowed us to collect only the low molecular weight fraction. MALDI-TOF mass analysis of this fraction was performed to investigate the structure as shown in Fig. 3. A dominant peak is found at m/z 1496.3 with minor peaks at m/z 1795.5 and 2094.7, which correspond to the molecular weights of the cyclic pentamer, hexamer, and heptamer, respectively. Cyclic oligomers can be generated in our polymerization conditions, but the yield of this fraction was negligible (less than 5%) as well as removable by a hot extraction. Notably, all the polymers in Table 1 showed narrower polydispersity indexes around 2.0 after the removal of cyclic oligomers by the extraction.

Block copolymers with different PEO contents were synthesized using **3** and **5** (Scheme 4 and Table 2). All the polymers showed M_n higher than 10,000 and narrower M_w/M_n after hot extraction with acetone. PEO contents in block copolymers were estimated by ^{1}H NMR. Although the amount of PEO incorporation in BP2 is slightly low, PBTPA-*block*-PEOs with different PEO segment lengths can be prepared (BP1 and BP2). Furthermore, higher PEO content can be achieved by increasing PEO terminator from 2 mol% to 5 mol% for BP3.

3.3. Polymer characterization

The structures of PBTPAs were confirmed by ^{1}H and ^{13}C NMR spectra. Fig. 4 shows ^{1}H NMR spectra of the polymers, and all the signals were assigned to the protons of polymer backbone. In addition, the protons of methoxy groups at the terminal units are clearly observed at 3.70 and 3.78 ppm, which were derived from 3-methoxydiphenylamine and 4-bromoanisole, respectively. Both methoxy groups are confirmed for the PBTPA obtained in Run 5, indicating that each terminal can be functionalized independently using different terminators. The ^{1}H NMR spectrum of PBTPA-*block*-PEO is shown in Fig. 4(d), and it is obvious that a signal at 3.67 ppm assignable for methylene protons of PEO implies the incorporation of the PEO segment into the polymer backbone.

Moreover, the ^{13}C NMR spectrum of PBTPA-*block*-PEO is shown in Fig. 5. All the signals can be assigned, including the carbon of PEO segment at 70.8 ppm. The small signals derived from the triphenylamine moiety at the terminal are observed in the aromatic region in Fig. 5(b). In the meantime, no other signals assignable to the bromo or secondary arylamine terminals can be found from 117 to 120 ppm, which implies that PBTPA homopolymer does not exist in PBTPA-*block*-PEO.

The thermal properties of the polymers were measured by differential scanning calorimetry (DSC). In the DSC profile of the homopolymer PBTPA (Table 1, Run 3), the glass transition temperature (T_g) is observed at 215 °C. The DSC curve of BP3 showed a melting point (T_m) at 56 °C as well as a glass transition temperature at 200 °C (Fig. 6). The T_m is attributed to the melting point of the PEO segment in addition to the T_g of PBTPA, which is evidence for co-existence of both PBTPA and PEO domains.

3.4. Surface morphology of polymer films

Finally, the surface morphology of the PBTPA-*block*-PEO thin films was investigated by the atomic force microscopy (AFM). The sample films were prepared by spin coating from 1,1,2,2-tetrachloroethane solutions of BP1 or PB3, and then annealed at 200 °C for 24 h. The phase mode AFM images of the annealed polymer films are shown in Fig. 7. Microphase separation with 20–50 nm spherical domains of PEO segment is clearly observed in the film with 1 μm thickness (Fig. 7(a)), while thinner film with 50 nm thickness showed smaller PEO domains with a size of 10 nm (Fig. 7(b) and (c)). Because the PBTPA-*block*-PEO has a broad polydispersity index, all the films gave microphase-separated structures without any ordered orientation. Interestingly, cup-shaped structures are observed in the film prepared from the diluted condition (Fig. 7(d)). Fig. 8 shows the topographic mode AFM image of Fig. 7(d), and the height profile was performed on this structure through the blue line. The height of the centered black area is lower

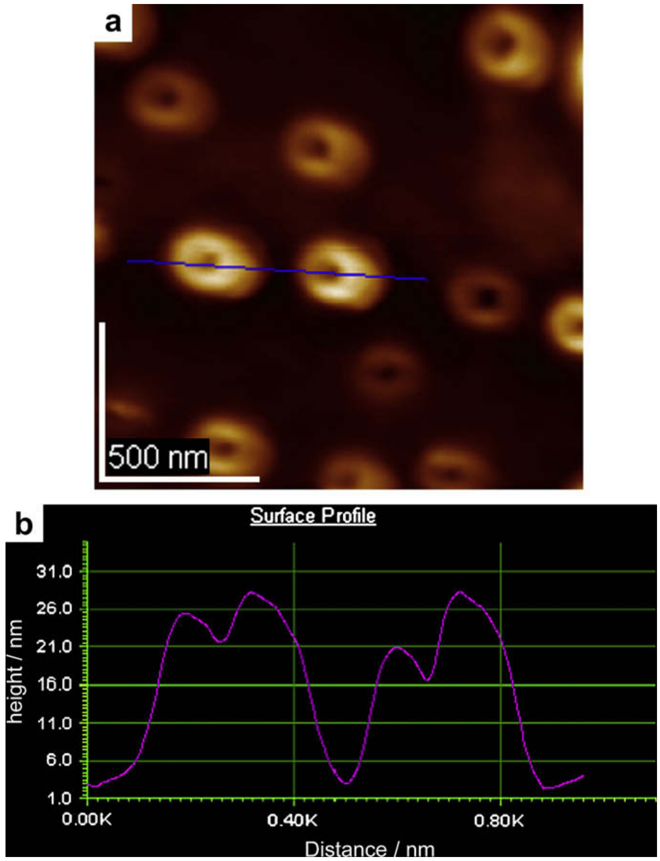


Fig. 8. (a) The topographic mode AFM image of BP1 film prepared from 0.5 wt% 1,1,2,2-tetrachloroethane solution and (b) the height profile through the blue line. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

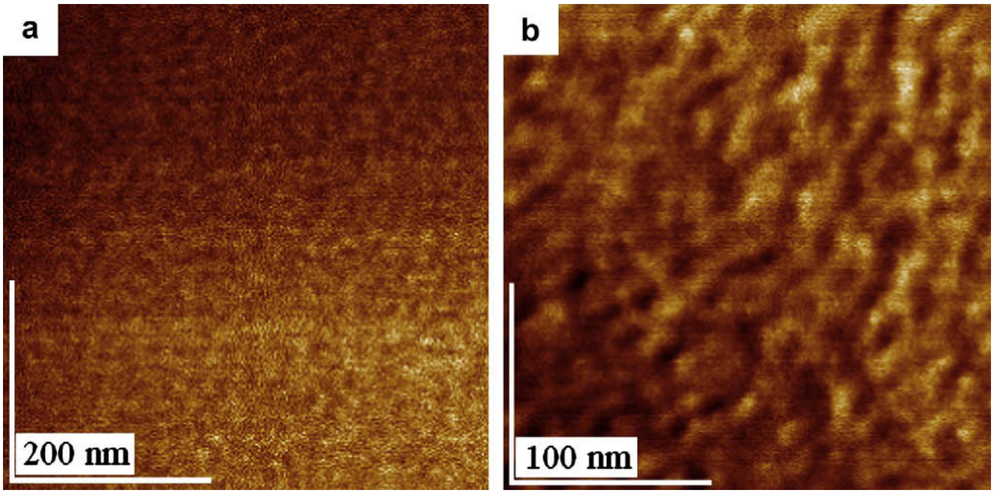


Fig. 9. (a) The phase mode AFM images of BP3 films prepared from 1 wt% 1,1,2,2-tetrachloroethane solution and (b) the magnified image of (a).

than that of the spherical area, which means that the centered area consists of the soft PEO segment. This morphology may be explained as micelles with a PEO core formed in dilute condition and squashed on the glass slide during the spin-coating process. Thus, the PEO domain in Fig. 7 should be assumed to be a spherical domain that is reasonable in terms of PEO weight ratio ($W_{PBTPA}:W_{PEO} = 0.91:0.09$). On the other hand, the morphology in the films of BP3, which possesses higher PEO content ($W_{PBTPA}:W_{PEO} = 0.77:0.23$), was investigated by AFM as shown in Fig. 9. The similar phase-separated structure with a size of 10–20 nm was observed in thin films. It was found that the PEO domains were partially connected as shown in the magnified image (Fig. 9(b)) because the PEO weight ratio of BP3 is higher than that of BP1. No unique morphology was obtained in the film of BP3 when the film thickness was changed.

4. Conclusions

In order to build up diblock copolymers comprising hole transporting triphenylamine backbone, we have successfully demonstrated that the polymerization of a self-condensing monomer, 4-(4-bromophenyl)-4′-*n*-butyldiphenylamine (**1**), by means of arylamination using palladium catalyst afforded PBTPA with a high molecular weight. Adding aryl bromide or secondary arylamine derivatives as a terminator during the polymerization enabled respective functionalization at each terminal of PBTPA, which can be applied for the synthesis of diblock copolymer PBTPA-*block*-PEO using PEO with an aryl bromide moiety. The thin films of PBTPA-*block*-PEO showed a phase-separated morphology including cup-shaped structures in AFM images, promising for nano-scaled device architecture. In an effort to apply the microphase-separated structures of functional diblock copolymers containing PTPA segment for EL and photovoltaic cell devices, further study on the structural control of the block copolymers, namely the preparation of PBTPA-*block*-PEO with narrow polydispersity as well as the combination of PBTPA with electron transport materials and/or light emitting materials, is under investigation.

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