Synthesis and Characterization of Poly(ethylene oxide)-*b*-poly(4-butyltriphenylamine)-*b*-poly(ethylene oxide) Triblock Copolymers

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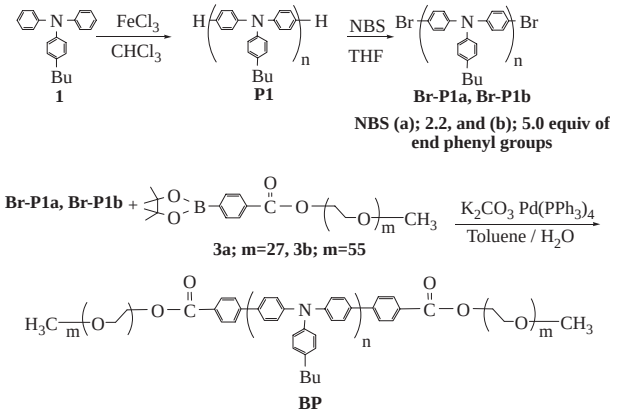
The synthesis and characterization of poly(ethylene oxide)-*b*-poly(4-butyltriphenylamine)-*b*-(polyethylene oxide) triblock copolymers (PEO-*b*-PBTPA-*b*-PEO) with different block ratio are described. The optical properties of block copolymers were investigated by UV–vis absorption, and photoluminescence (PL) spectroscopy. From atomic force microscopy (AFM) observation of the annealed thin films of block copolymers, microphase-separated morphology was observed.

We reported that polytriarylamines were simply prepared by chemical oxidative polymerization using iron(III) chloride as an oxidant.[1,2] Poly(4-butyltriphenylamine) (PBTPA) sensitized with fullerene showed the excellent photoconductivity compared with a conventional poly(*N*-vinylcalbazole).[1] Apart from triarylamine, block copolymers are attractive materials because their microphase-separated structure can improve device performance. However, the microdomains in thin films generally have no preferred orientation. Recently, it has been reported that the thin films of poly(ethylene oxide) (PEO)[3,4] based block copolymers spontaneously formed well-defined nanostructure, where cylindrical domains of PEO are oriented normal to the surface of a film over large areas.

This specific nature allows us to utilize the polymers with PEO segment for photovoltaic applications. Orthogonal cylinder structure can function as definite carrier path. Chemical modification of PBTPA to the block copolymer makes the photoconductors with nanostructures possible. In this study, we have established the synthetic route for novel polymers, poly(ethylene oxide)-*block*-poly(4-butyltriphenylamine)-*block*-poly(ethylene oxide) triblock copolymers, as the one essential component for photovoltaic applications. Synthesized polymers were characterized by ^{1}H and ^{13}C NMR spectroscopy and GPC. The optical properties and morphologies were also investigated.



Scheme 1. Synthetic route of poly(ethylene oxide)-*b*-poly(4-butyltriphenylamine)-*b*-poly(ethylene oxide) block copolymers.

4-Butyltriphenylamine (BTPA) (compound **1**) was synthesized as described in Ref. 2. Polymer **P1** was prepared by oxidative coupling. Then, **P1** was reacted with NBS in THF to obtain end brominated PBTPA. The amount of NBS was adjusted to 2.2 (**Br–P1a**), or 5 (**Br–P1b**) equivalent to the end phenyl groups in **P1**. Finally, PEO-*b*-PBTPA-*b*-PEO were synthesized by the Suzuki coupling of end brominated PBTPA and PEO with pinacol borate moiety (**3a** or **3b**), affording triblock copolymers with different PEO contents (as shown in Scheme 1 and Table 1).

In ^{13}C NMR, **P1** reacted with 2.2 equiv. of NBS (**Br–P1a**) afforded the signal for the ipso carbon with bromo substituents (114.48 ppm) at the chain end. The signal at 122.44 ppm for the carbon at 4-position in end phenyl groups almost diminished (93%). This result indicates that bromination almost completely proceeded in the presence of 2.2 equiv. of NBS. The brominated product (**Br–P1b**) with excess amount of NBS (5 equiv.) gave unassignable signals in 121–124 ppm, suggesting that bromination reaction also occurred at other positions of aromatic rings in polymer main chain as well as at end phenyl groups. Table 1 summarized the characteristics of block copolymers prepared by the Suzuki coupling of brominated PBTPA with PEO containing pinacol borate moiety. Chemical composition of each resulting block copolymer was calculated from ^{1}H NMR spectrum. Theoretical PEO contents were calculated assuming that both the end phenyl groups are monobrominated, and then brominated phenyl groups are completely reacted with PEO derivatives. The PEO content in **BP-1** is consistent with calculated values. It is re-

Table 1. Characteristics of synthesized homo- and block polymers

Product	Reactant[a]	Yield /%	M_n[b] ($\times 10^3$)	PDI[c]	PEO content /wt %	
					Calc.[d]	Exp.[b]
P1	—	71	15.0	2.5	—	—
BP-1	**Br–P1a**, **3a**	84	17.4	2.5	0.14	0.14
BP-2	**Br–P1b**, **3a**	84	20.0	2.9	0.14	0.24
BP-3	**Br–P1b**, **3b**	83	25.0	3.5	0.24	0.39

[a]**Br–Ps 1a**, **1b**; Brominated PBTPA with NBS (**a**; 2.2, and **b**; 5.0 equiv. of end phenyl groups), **3a** and **3b**; PEO functionalized with boron derivative (M_n = 1000, and 2000, respectively), [b]Determined by ^{1}H NMR. [c]Determined by GPC. [d]Based on the assumption that both the end phenyl groups are monobrominated, and then brominated phenyl groups are completely reacted with PEO derivatives.

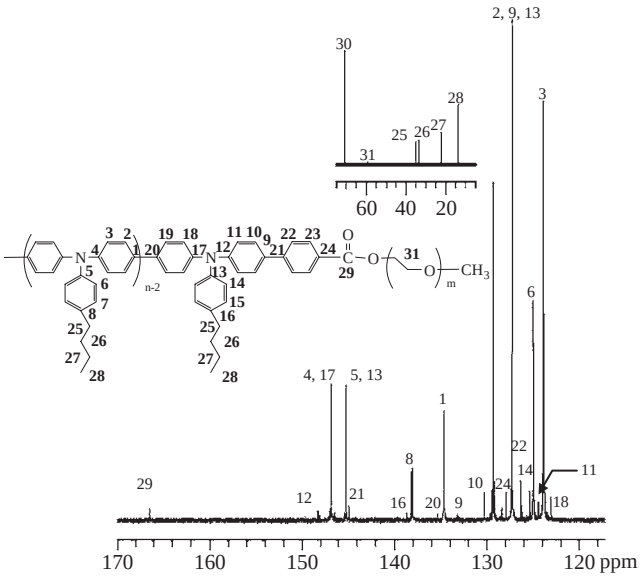


Figure 1. ^{13}C NMR spectrum of **BP-1**.

vealed that bromination with NBS and the subsequent Suzuki coupling reactions proceeded quantitatively to afford designed triblock copolymers. Block copolymers (**BP-2** and **BP-3**) were synthesized utilizing brominated PBTPA (**Br–P1b**) with 5 equiv. of NBS. These copolymers have higher PEO contents compared with calculated values. Assumed that the Suzuki coupling proceeded perfectly, it can be concluded that bromination occurred at other positions including main chain ring as well as at end phenyl groups. Taking the PEO content into consideration, the numbers of PEO branches in **BP-2** and **BP-3** are 1.43 and 1.25, respectively. ^{13}C NMR spectrum of **BP-1** is shown in Figure 1. The signal for the ipso carbon with bromo substituent at the chain end completely disappeared and that for carbonyl carbon appeared at 166.48 ppm. The other signals including those in PBTPA block ends were assigned based on the assignments for dimer of BTPA with PEO moiety prepared with a similar method. The assignments of other signals for **BP-1** are shown in Figure 1.

The optical properties of synthesized copolymers were investigated with UV–vis absorption and photoluminescence spectroscopy. In a solution state, the UV–vis spectra for block copolymers were similar to that of the parent **P1**, which exhibited an absorption maximum at 370 nm. In the case of block copolymers, phenyl units substituted with carbonyl group exist at the junction points between PBTPA and PEO blocks. Carbonyl group leads to bathochromic shift due to its electron-accepting nature and/or extended conjugation. In fact, the model compound, the dimer of BTPA substituted with PEO moiety, showed absorption maximum at 368 nm. The effect of carbonyl groups on spectra for block copolymers was, however, almost negligible because of the low concentration of the groups. In a film state, the absorption maxima for all polymers were bathochromically shifted to 375–381 nm compared with those in a solution state.

The excitation wavelengths of PL measurement for solutions and films were 370 and 375 nm, respectively. The solution of **P1** exhibited blue emission at 426 nm. All block copolymers showed additional emission peaks at 473 and 503 nm. To confirm the origin of longer wavelength emission, photoluminescence for the above-mentioned model compound was examined for comparison. Emission maxima at 479 and 509 nm were observed for this compound, suggesting that the longer wavelength emission for block copolymers results from the end phenyl groups functionalized with carbonyl group. In a film state, the emission from junction parts, i.e., the end functionalized moieties of PBTPA block, was emphasized compared with the solution state. This resulted from the efficient energy transfer to the junction parts in a condensed state.

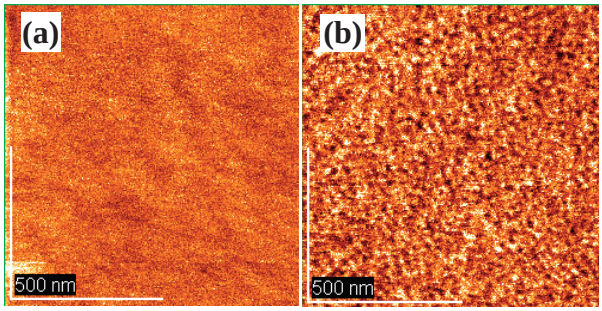


Figure 2. AFM images of thin film of **BP-3** (a) before annealing, (b) after annealing. Preparation condition; 2 mg/mL toluene solution, 1000 rpm film thickness 60–80 nm on Si wafer.

DSC trace for **BP-3** upon heating showed two distinct thermal transitions. Endothermic peak observed at 20 °C and baseline shift at 142 °C are attributed to the melting of PEO segment and the glass transition of PBTPA segment, respectively. Both transitions occurred at lower temperature compared with corresponding homopolymers (PEO; 60 °C, PBTPA; 175 °C).[5]

The AFM images of **BP-3** films with thickness of 60–80 nm are shown in Figure 2. As shown in Figure 2a, as-cast film shows homogeneous morphology. After annealing at 170 °C for 7 days, films exhibited the microphase-separated structure (Figure 2b). Dark and bright parts represent PEO and PBTPA domains, respectively. However, well-defined microdomains, long range order, and the orientation of microdomains were not observed. The disordered morphology is probably due to the polydispersed nature of block copolymers and/or the existence of PEO branches in PBTPA block, which disturb the regular packing of PBTPA blocks, and the orientation of the PEO domains.

In conclusions, we have established here the synthetic route for novel triblock copolymers consisting of photoconducting PBTPA block and inert PEO. The morphological and photovoltaic studies are in progress for the blend of synthesized block copolymers with PEO functionalized with electron-accepting moiety. Our ultimate purpose is to design the block copolymers suitable for the creation of nanostructured bulk heterojunctions, and the macroscopic alignment of the nanostructures in photovoltaic applications.

References and Notes

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6 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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