3546 *Macromolecules* **2006,** *39,* 3546−3552

Synthesis of n-Type Poly(benzotriazole)s Having p-Conducting and Polymerizable Carbazole Pendants

Akitoshi Tanimoto and Takakazu Yamamoto*

Chemical Resources Laboratory, Tokyo Institute of Technology. 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Received December 16, 2005; Revised Manuscript Received March 14, 2006

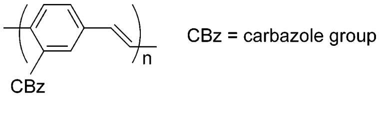
ABSTRACT: Poly(benzotriazole)s, **P(BTz)s**, having an n-type benzotriazole-π-conjugated main chain and p-type and electrochemically polymerizable carbazole (CBz) pendant groups, $-(CH_2)_m-$CBz ($m = 12$ or 6) groups, were synthesized by Ni− (for homopolymers) and Pd-promoted (for a copolymer) organometallic polycondensations. The copolymer between benzotriazole with the $-(CH_2)_{12}-$CBz pendant and *p*-phenylene was soluble in organic solvents and showed a number-average molecular weight (M_n) of 27000 in the GPC analysis. The homopolymers ($m = 12$, 6) were less soluble, and about half of the polymer was soluble in $CHCl_3$ in the case of $m = 12$; the soluble part gave an M_n value of 4700. The polymers were photoluminescent with quantum yields of 50−70%. Cyclic voltammograms of the polymers revealed that the polymers were active in electrochemical n-doping in accord with the electron-accepting nature of the benzotriazole main chain. Application of electrochemical oxidation potential to the polymer made the polymer insoluble due to occurrence of electrochemical polymerization of the CBz unit.

Introduction

π-Conjugated polymers are the subjects of recent interest.[1] Various π-conjugated polymers have been synthesized and some of them are industrialized.[2]

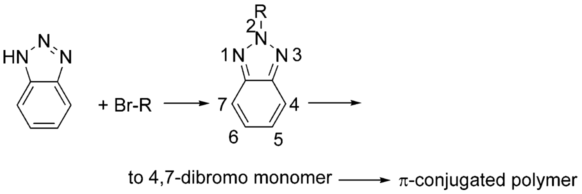
Electron-donating aromatic heterocyclics such as pyrrole, thiophene, and carbazole give p-type poly(arylene)s, whereas electron-accepting heterocycles such as pyridine, quinoxaline, and thiadiazole afford n-type poly(arylene)s.

Recently, another type of π-conjugated polymers or oligomers containing both a p-type conducting unit and an n-type conducting unit are also attracting interest. Such polymers and oligomers are expected to give simpler electronic devices (e.g., monolayer type polymer light emitting diode[3]) and/or ambipolar electronic devices.[4] For example, poly(*p*-phenylenevinylene)[5a] with a carbazole pendant group[5] has been synthesized. In the polymer, the poly(*p*-phenylenevinylene) main chain is the electron-accepting unit[6] and the carbazole pendant is the electron-donating unit. Other types of π-conjugated polymers with the carbazole pendant group have also been reported.[5b−g]



Benzazoles such as benzimidazole and benzothiadiazole contain electron-withdrawing imine $-C{=}N-$ nitrogen(s), and their polymers afford a class of n-type π-conjugated polymer materials.[7−9]

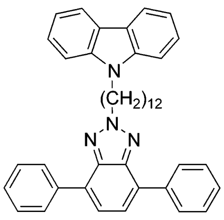
Among the poly(benzazole)s shown in Chart 1, poly(benzotriazole)s, **P[BTz(R)]s**, can receive easy chemical modification. Various dibromo monomers, which have various R side chains and are suited for organometallic polycondensations,[1] can easily be obtained.



(1)

By using the chemical modification reaction, we have synthesized new poly(benzotriazole)s with a carbazole pendant. The polymers have an n-conducting benzotriazole main chain[9] and an electron-donating CBz group in the R side chain. Scheme 1 depicts outline of the synthetic routes of the polymers and further chemical modification (or electrochemical polymerization of the side CBz unit) of the polymers.

For better understanding of the polymers, the following model compound **Ph—BTz(C12—CBz)—Ph** has also been synthesized.



Ph-BTz(C12-CBz)-Ph

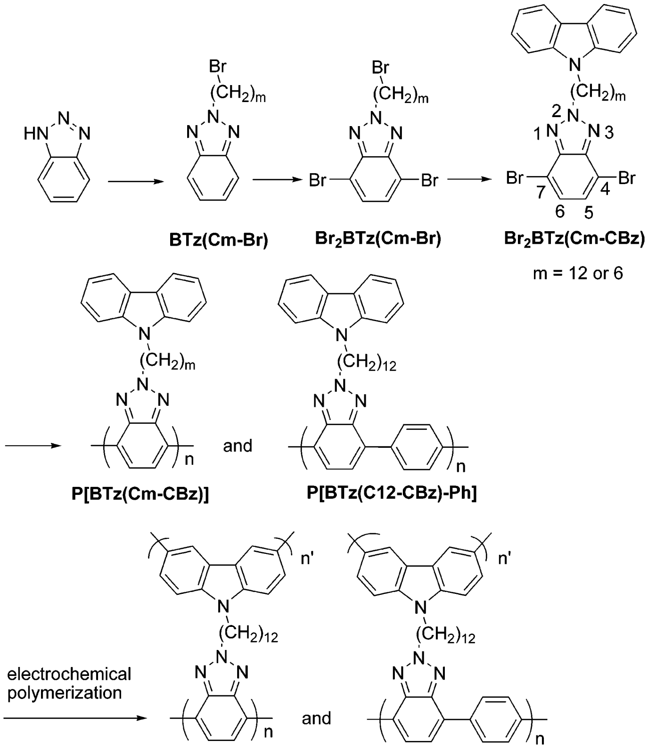
Herein we report results of the synthesis of the polymers and chemical properties of the polymers. Although various π-conjugated polymers consisting of benzothiadiazole unit (cf. Chart 1) have been reported,[8] π-conjugated polymers composed of the isoelectronic benzotriazole unit have received less attention.[9] A π-conjugated polythiophene with a benzotriazole pendant has

---

* Corresponding author. E-mail: tyamamot@res.titech.ac.jp.

10.1021/ma052688b CCC: $33.50

Scheme 1. Preparation of Poly(benzotriazole)s and Electrochemical Polymerization of the Side Carbazole Unit



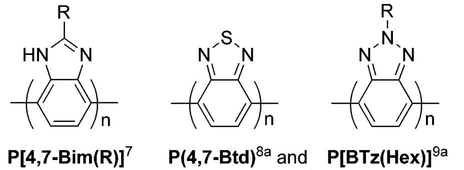
been synthesized, and electron-accepting effect of the benzotriazole unit in the polymer has been reported.[9b]

Results and Discussion

Synthesis. Scheme 1 exhibits the synthetic route of poly(benzotriazole)s, **P(BTz)s**. The monomers were synthesized by modification of a previously reported method applied to the synthesis of **P[BTz(Hex)]**.[9a] Alkylation of benzotriazole with RX usually gives a mixture of 1- and 2-alkyl isomers. In the present research, **BTz(C*m*—Br)** (m = 12 or 6) with the $-(CH_2)_m$Br group at the 2-position was isolated by column chromatography. Bromination of **BTz(C*m*—Br)** gave **Br$_2$BTz(C*m*—Br)**.

Panel a in Figure 1 shows ^{1}H NMR spectrum of **BTz(C6—Br)**. The two aromatic signals at δ 7.86 and 7.38 appear as a typical AA′BB′ peak pattern.[10] As depicted in Figure 1, a simulated ^{1}H NMR spectrum for the aromatic protons agrees well with the observed ^{1}H NMR spectrum, supporting isolation of the symmetrical 2-alkylated **BTz(C6—Br)**. Appearance of only one aromatic peak at δ 7.44 for **Br$_2$BTz(C6—Br)** in panel b supports the symmetrical 2-alkylated structure of the product. The ^{1}H NMR patterns of **BTz(C6—Br)** and **Br$_2$BTz(C6—Br)** resemble those of previously reported 2-hexyl analogues (the R groups is a hexyl group instead of the $-(CH_2)_6$Br group).[9a] **BTz(C12—Br)** and **Br$_2$BTz(C12—Br)** give analogous ^{1}H NMR results (cf. Figure S1). Because of the symmetrical structure of the monomer, the synthesized polymers have a simple symmetrical structure.

Chart 1. Examples of n-Type Poly(benzazole)s



P[4,7-Bim(R)][7] **P(4,7-Btd)**[8a] and its copolymers[8b-f] **P[BTz(Hex)]**[9a] Hex = hexyl

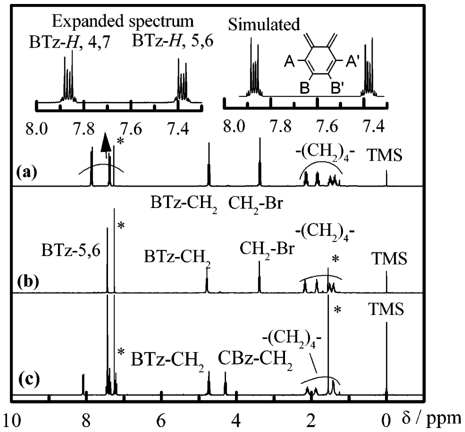
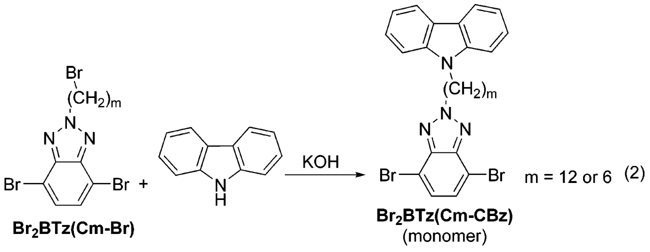


Figure 1. ^{1}H NMR (300 MHz) spectra of (a) **BTz(C6—Br)**, (b) **Br$_2$BTz(C6—Br)**, and (c) **Br$_2$BTz(C6—CBz)** in CDCl$_3$. The peaks with the $*$ are due to the solvent impurities (CHCl$_3$ and H$_2$O). The simulated spectrum agrees well with the observed aromatic signal patterns. The simulation is carried out with the following coupling constants: $J_{AB} = 8.96$ Hz, $J_{BB'} = 6.65$ Hz, $J_{AB'} = 1.16$ Hz, and $J_{AA'} = 0.90$ Hz. Analogous J values have been reported for benzoxadiazole, benzothiadiazole, and benzoselenadiazole.[10b]

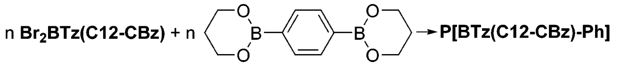
Scheme 2. Preparation of the Br$_2$BTz(C*m*−CBz) Monomers



It is known that *N*-alkylation of carbazole proceeds well with various R−Br,[11] and the reaction of **Br$_2$BTz(C*m*—Br)** with carbazole in the presence of KOH afforded the **Br$_2$BTz(C*m*—CBz)** monomer.

The homopolymers, **P[BTz(C*m*—CBz)]** (m = 12, 6), were prepared using an Ni(0)-bpy complex as the condensing reagent.[1,9a] The copolymer with *p*-phenylene, **P[BTz(C12—CBz)—Ph]**, was obtained according to Suzuki coupling using a Pd(PPh$_3$)$_4$ catalyst.

$$\text{n } \mathbf{Br_2BTz(Cm\text{-}CBz)} + \text{n Ni(0)-bpy complex} \longrightarrow \underset{m\,=\,12,\,6}{\mathbf{P[BTz(Cm\text{-}CBz)]}} \qquad (3)$$



$$\text{n } \mathbf{Br_2BTz(C12\text{-}CBz)} + \text{n } \mathrm{(C_3H_6O_2)B{-}C_6H_4{-}B(O_2C_3H_6)} \longrightarrow \mathbf{P[BTz(C12\text{-}CBz)\text{-}Ph]} \qquad (4)$$

Of the two hompolymers, **P[BTz(C12—CBz)]** showed some solubility in organic solvents, and about 50% of **P[BTz(C12—CBz)]** was extracted with a Soxhlet extractor using CHCl$_3$, and the extracted polymer was recovered and isolated by reprecipitation into methanol. The extracted and recovered polymer was soluble in organic solvents and gave a number-average molecular weight (M_n) of 4700 in the GPC analysis. Because the extracted part and unextracted part gave the same IR data, the two parts were considered to have the same molecular structure and the polymer molecules with lower molecular weights were considered to be extracted. **P[BTz(C6—CBz)]** was less soluble, and only a yellow colored solution was obtained by the extraction with CHCl$_3$ at room temperature.

P[BTz(C12—CBz)—Ph] was soluble in organic solvents such as toluene and chloroform, and gave an M_n value of 27000 in GPC analysis. The polymerization results are summarized in Table 1. Because boron was not detected in ICP

Table 1. Preparation of the Polymers

polymer	yield,%	color	M_n[a]	M_w/M_n[a]	T_d,[b] °C
P[BTz(C12—CBz)]	90	red	4700[c]	1.51	387
P[BTz(C6—CBz)]	52	red	2700[c]	1.23	422
P[BTz(C12—CBz)—Ph]	62	green	27 000	1.77	435

[a] Estimated from GPC (eluent: chloroform, vs polystyrene standards). M_n = number-average molecular weight. M_w = weight-average molecular weight. [b] 5% weight-loss temperature measured by TGA under N_2 with a heating rate of 10 °C min^{-1}. [c] For the chloroform soluble part (cf. the text).

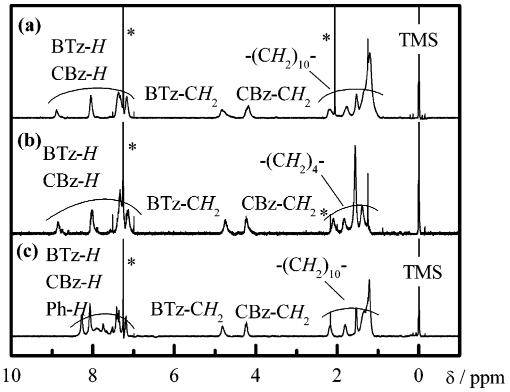


Figure 2. ^{1}H NMR spectra of (a) **P[BTz(C12—CBz)]** ($CHCl_3$ soluble part), (b) **P[BTz(C6—CBz)]** ($CHCl_3$ soluble part), and (c) **P[BTz-(C12—CBz)—Ph]** in $CDCl_3$. The peaks with the * are due to the solvent impurities ($CHCl_3$ and H_2O).

(inductively coupled plasma) emission spectrometry of **P[BTz-(C12—CBz)—Ph]**, the polymer is considered to have a polymer−Br and/or polymer−H group as the main terminal group; the latter polymer−H group is considered to be formed from a polymer−Pd group during workup. Data of elemental analysis indicated that the homopolymers, **P[BTz(C*m*—CBz)]**, did not contain Br, which suggested that the polymer had a polymer-H terminal groups, similar to cases of π-conjugated polymers prepared by using zerovalent nickel complexes.[1,9a]

Thermogravimetric analysis (TGA) revealed that the polymers had good thermal stability under N_2. The first major weight loss of the polymers started around 390 °C for **P[BTz-(C12—CBz)]** and **P[BTz(C12—CBz)—Ph]**. All the polymer gave residual weight of about 30−40% at 900 °C, and 5% weight loss temperatures (T_d) of the polymers are included in Table 1.

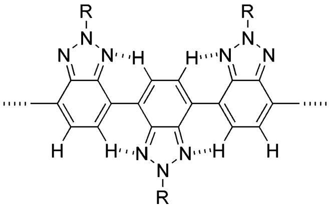
Figure 2 exhibits ^{1}H NMR spectra of the polymers. As shown in Figure 2, **P[BTz(C12—CBz)]** gives BTz-C*H*$_2$ (C*H*$_2$ attached at the benzotriazole unit) and CBz−C*H*$_2$ signals at δ 4.7 and 4.3, respectively. The aromatic signal pattern and other aliphatic signals are reasonable for the polymer structure, and the area ratio between the aromatic and aliphatic signals agrees with the structure of **P[BTz(C12—CBz)]**. ^{1}H NMR spectra of the other two polymers also agree with the structures of the polymers. IR spectra of the polymers (cf. Figure S2) show peaks originated from the BTz, CBz, and $(CH_2)_m$ units.

UV—Vis and Photoluminescence (PL) Data. Figure 3 indicates UV−vis spectra of the polymers and the model compound, **Ph—BTz(C12—CBz)—Ph**, and the UV−vis data are summarized in Table 2.

Both the polymers and the model compound show UV−vis peaks at 265 and 296 nm in chloroform, which are originated from the benzotriazole and carbazole units, respectively. 2-Hexylbenzotriazole[9a] and carbazole give UV−vis peaks at 279 and 292 nm, respectively.

As exhibited in Figure 3, the model compound **Ph—BTz-(C12—CBz)—Ph** gives an additional UV−vis peak at 333 nm, which is attributed to expansion of the π-conjugation system. **P[BTz(C12—CBz)]** affords a lowest energy absorption peak at 452 nm, and the absorption band is assigned to a π−π* transition mainly occurred in the π-conjugated polymer main chain. The UV−vis peak is located at a considerably longer wavelength compared with those of poly(*p*-phenylene) (λ_{max} = ca. 380 nm)[1] and poly(2,3-diheptylquinoxaline-5,8-diyl)s (λ_{max} = ca. 374 nm)[14] having an analogous main chain (cf. Chart 2), revealing formation of an effectively π-conjugated polymer main chain in **P[BTz(C12—CBz)]**.

A conceivable N−HC interaction[15] may assist coplanarization of the main chain to afford the effectively π-conjugated system.



In the UV−vis spectrum of **P[BTz(C12—CBz)—Ph]**, the lowest energy π−π* peak is moved to a shorter wavelength (λ_{max} = 398 nm), possibly due to weakening of the N−HC interaction and occurrence of *o*-hydrogen repulsion by intervention of the *p*-phenylene unit. **P[BTz(C6—CBz)]** showed UV−vis peak at a somewhat shorter wavelength (λ_{max} = 440 nm) than **P[BTz(C12—CBZ)]**, and this seems to be due to the lower degree of polymerization for its $CHCl_3$ soluble part (vide ante). The shape of the UV−vis spectrum and relative intensities between the peaks did not vary with the concentration of the benzotriazole polymers, indicating that the peaks were originated from single polymer molecule and there was no obvious intermolecular electronic interaction in the solution. The UV−vis peaks of **P[BTz(C*m*—CBz)]** (*m* = 12, 6) is somewhat shifted to a longer wavelength from that of previously reported

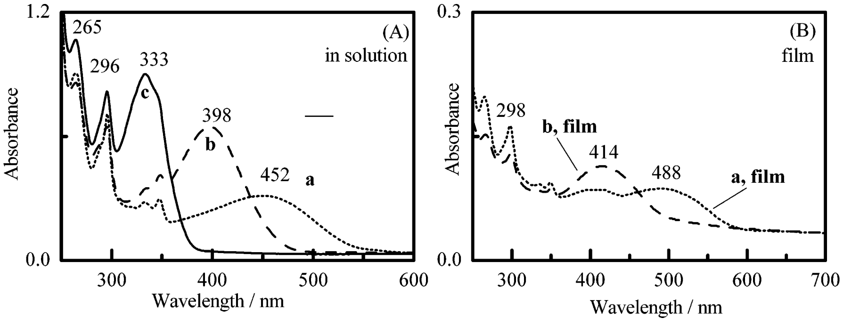


Figure 3. UV−vis spectra of (A) chloroform solutions and (B) cast films for (a) **P[BTz(C12—CBz)]** (···), (b) **P[BTz(C12—CBz)—Ph]** (- − -), and (c) the model compound **Ph—BTz(C12—CBz)—Ph** (-).

Table 2. Optical and Electrochemical Data of the Polymers, the Model Compound, and Previously Reported P[BTz(Hex)]

							redox potential (V vs Ag^+/Ag)[e]	
polymer	$\lambda_{max,sol}$,[a] nm	$\lambda_{max,film}$,[b] nm	$\lambda_{em,sol}$,[a] nm	$\lambda_{em,film}$,[b] nm	Φ^c, %	Φ^d, %	E_{red}	E_{ox}
P[BTz(C12—CBz)]	265, 296, 348,452	265, 298, 397, 488	542	585, 635[f]	67	28	−2.37[h]	0.95, 0.60
P[BTz(C6—CBz)]	265, 296, 348, 440		532		57	28		
P[BTz(C12—CBz)—Ph]	265, 296, 398	238, 266, 298, 414	489	496, 531[f]	60	36	−2.49	0.64, 1.02, 1.76
Ph-BTz(C12—CBz)—Ph	265, 296, 333		409		56	41		
P[BTz(Hex)][g]	265, 420		490		47			
carbazole	292		339, 353			1.6	0.80[i] (1.10)[j]	

[a] In chloroform. [b] Observed with cast film. [c] Quantum yield obtained by irradiation with light with the lowest $\pi-\pi^*$ transition energy. PL quantum yield was calculated by using a quinine sulfate standard (ca. 10^{-5} M solution in 0.5 M H_2SO_4, having a quantum yield of 54.6%).[12] [d] Quantum yield obtained by irradiation with light at 296 nm (absorption peak of the CBz unit). Irradiation with 296 nm light will cause electronic excitation of the CBz unit (at peak abosorption) and the benzotriazole unit (at the tail absorption). [e] Measured by cyclic voltammetry in an acetonitrile solution of $[(C_2H_5)_4N]BF_4$ (0.10 M) unless otherwise noted. E_{red} and E_{ox} stand for reduction (n-doping) peak and oxidation (p-doping) peak potentials, respectively. [f] Subpeak. [g] Data from ref 9a. [h] In an acetonitrile solution of $[(n\text{-}C_4H_9)_4N]ClO_4$ (0.10 M). [i] Data from ref 13. [j] Datum for *N*-alkyl carbazole.[13c]

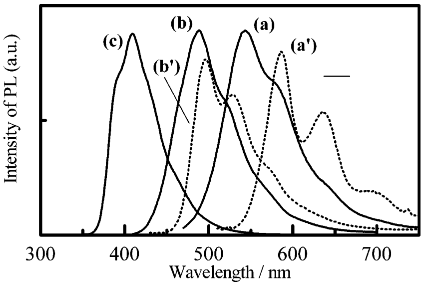


Figure 4. PL spectra of **P(BTz)s** and the model compound in chloroform (−) and in the solid state (···): (a and a′) **P[BTz-(C12—CBz)]**; (b and b′) **P[BTz(C12—CBz)—Ph]**; (c) **Ph—BTz-(C12—CBz)—Ph**.

P[BTz(Hex)], $\lambda_{max} = 420$ nm,[9a] which may be due to contribution of a charge-transferred (CT) electronic state because of the presence of the electron-accepting benzotriazole main chain and electron-donating carbazole unit. Effects of such a CT electronic state of π-conjugated polymers constituted of electron-accepting units and carbazole unit have been discussed.[16]

In the cast films of **P[BTz(C12—CBz)]** and **P[BTz-(C12—CBz)—Ph]**, the lowest-energy UV−vis peaks are shifted by 36 and 16 nm, respectively, to a longer wavelength, suggesting the presence of intermolecular electronic interaction and/or increase in coplanarity of the polymer in the solid. XRD (X-ray diffraction) patterns of the polymers (Figure S3) revealed that **P[BTz(C6—CBz)]** and **P[BTz(C12—CBz)—Ph]** were essentially amorphous; π-conjugated polymers with alkyl side chains usually exhibit broad XRD peak at about 20° which are assigned to a side-to-side distance between loosely aggregated alkyl chains.[1] **P[BTz(C12—CBz)]**, on the other hand, gave distinct XRD peaks and was considered to assume an ordered structure in the solid. The sharp XRD peak at $2\theta = 10°$ may be assigned to a distance between the π-conjugated main chains separated by the side alkyl chains.[1]

Figure 4 shows the PL spectra of the polymers.

The polymers and model compound are highly photoluminescent in the solution. As shown in Table 2, the PL quantum yield (cf. Φ in Table 2) of the polymers in chloroform is in a range of 57−67%. Their photoluminescence peaks, λ_{em}'s, appear at the onset position of the UV−vis absorption bands (e.g., around 540 nm for **P[BTz(C12—CBz)]** (cf. Figure 3)), as usually observed with π-conjugated aromatic compounds and polymers.[1] Excitation spectra of PL agree with the UV−vis data. For example, the excitation spectrum of **P[BTz(C12—CBz)—Ph]** in chloroform exhibits peaks at 265, 296, and 399 nm; the former two peaks revealing the occurrence of energy transfer from photoactivated benzotriazole and carbazole units to the π-conjugated polymer main chain.

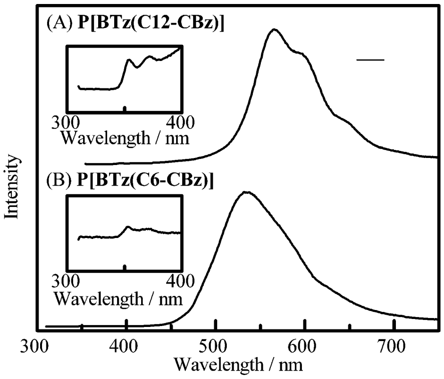


Figure 5. Comparison of PL spectra of **P[BTz(C*m*—CBz)]s** (m = 12, 6). The emission from the CBz unit (300−400 nm region) is expanded. Key: (A) **P[BTz(C12—CBz)]**; (B) **P[BTz(C6—CBz)]** (in chloroform and excited at 292 nm). Inset (300−400 nm region): intensity of PL was expanded by 100 times. Both PL spectra were obtained with the chloroform solution having the same absorbance of 0.11 at the UV−vis absorption peak positions (452 and 440 nm for **P[BTz(C12—CBz)]** and **P[BTz(C6—CBz)]**, respectively). Both PL spectra show almost the same main peak intensity, whereas the intensity of emission from the CBz unit at about 350 nm shows a large difference.

For the cast films of **P[BTz(C12—CBz)]** and **P[BTz-(C12—CBz)—Ph]** (Figure 4, parts a′ and b′), the PL peaks are shifted by 43 and 7 nm, respectively, toward a longer wavelength in accord with the shift of the UV−vis absorption band in the film. The larger shift observed with **P[BTz(C12—CBz)]** may originate from a stronger intermolecular electronic interaction in the solid because **P[BTz(C12—CBz)]** is considered to assume an ordered structure in the solid, as discussed above based on the XRD data. The PL spectrum of the film shows a substructure, which is assigned to vibronic coupling.[17]

Effect of $(CH_2)_m$ Length on Energy Transfer from the CBz Unit. As described above, irradiation with 296 nm light to the CBz center of **P[BTz(C*m*—CBz)]** leads to emission at about 540 nm, which is related to the $\pi^*-\pi$ transition occurred along the polymer main chain. These data indicate an effective energy transfer of the photoenergy captured by the CBz unit to the polymer main chain.

However, a detailed examination of the PL spectrum reveals certain contribution of the emission from the CBz unit (λ_{em} = 353 nm; cf. the last line in Table 2).

Intensity of the CBz emission at 353 nm is weaker in **P-[BTz(C6—CBz)]** than in **P[BTz(C12—CBz)]** as exhibited in Figure 5, suggesting that the photoenergy transfer from the CBz unit to the main chain occurs more effectively in **P[BTz-(C6—CBz)]**. It is reported that the efficiency of similar photoenergy transfer between two chromophores linked by a $(CH_2)_m$ group is strongly affected by the length of $(CH_2)_m$;[18]

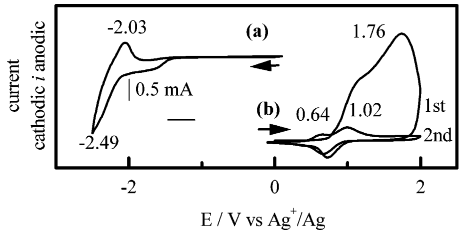


Figure 6. Cyclic voltammogram of the cast film of **P[BTz-(C12—CBz)—Ph]** on an ITO glass plate in an CH_3CN solution of $[Et_4N]BF_4$ (0.10 M). Scanning rate = 50 mV s^{-1}. Key: (a) for the reduction region; (b) for the oxidation region.

shorter length is advantageous for the photoenergy transfer and the present results agree with the previously reported results.

Electrochemical Redox and Electrochemical Polymerization of the CBz Unit. The electrochemical response of **P[BTz-(C12—CBz)]** and **P[BTz(C12—CBz)—Ph]** was investigated by cyclic voltammetry (CV) using their cast films, and the CV data are included in Table 2. Because of the low solubility of **P[BTz(C6—CBz)]**, its cast film suited for the CV measurement was not obtained. Figure 6 shows the CV curve of the film of **P[BTz(C12—CBz)—Ph]**. The film of **P[BTz(C12—CBz)]** gave analogous CV data.

P[BTz(C12—CBz)—Ph] exhibits a reduction (n-doping) peak at −2.49 V vs Ag^+/Ag, and this reduction is assigned to reduction of the electron-accepting benzotriazole main chain. The homopolymer, **P[BTz(C12—CBz)]**, also gives the n-doping peak near the potential (−2.37 V vs Ag^+/Ag; cf. Table 3). The n-doping potential is comparable to that of poly(quinoxaline-5,8-diyl)s (cf. Chart 2; n-doping peak = ca. −2.5 V vs Ag^+/Ag),[14] and lower than that of poly(benzthiadiazole-4,7-diyl) **P(4,7-Btd)** (−1.9 V vs Ag^+/Ag).[8a] These data reveal that the benzotriazole unit serves as a moderate electron-accepting unit. In the first sweep in the oxidation region, **P[BTz-(C12—CBz)—Ph]** exhibit two oxidation peaks at about 1.0 V (shoulder) and 1.76 V vs Ag^+/Ag. It is reported that oxidation of *N*-alkylcarbazole takes place at about 1.0 V vs Ag^+/Ag,[5f,g,13] and the oxidized carbazole (or cation radical of carbazole) undergoes oxidative polymerization. The shoulder peak observed at about 1.0 V vs Ag^+/Ag for **P[BTz(C12—CBz)—Ph]** is also assigned to the oxidative polymerization of the CBz unit. The oxidation peak at 1.76 V vs Ag^+/Ag is tentatively assigned to oxidation of the benzotriazole unit (e.g., p-doping of the π-conjugated main chain and/or partial removal of lone pair electrons at the *N*-$(CH_2)_m$ nitrogen). Similar irreversible electrochemical oxidation peaks have been reported for π-conjugated polymers with carbazole pendants.[5f,g]

Electrochemical Polymerization of the CBz Unit. As depicted in Figure 6, the CV chart in the second scanning shows two oxidation peaks at 1.02 and 0.64 V vs Ag^+/Ag. The two peaks are considered to be assigned to electrochemical polymerization of carbazole and p-doping of formed polycarbazole, respectively. Because electrochemical oxidative polymerization of *N*-alkylcarbazole in a side chain of a polymer has been carried out in an CH_3CN solution of $[Bu_4N]ClO_4$,[13c] the polymerization process of carbazole in **P[BTz(C12—CBz)—Ph]** has been examined in the same electrolytic solution. Figure 7 depicts CV curves in repeated scannings. As depicted in Figure 7, the two peaks, especially the peak at 0.64 V vs Ag^+/Ag grows in the repeated scanning.

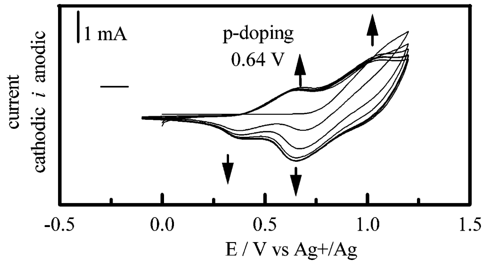


Figure 7. CV charts observed in repeated scanning for the film of **P[BTz(C12—CBz)—Ph]** on an ITO glass plate in an CH_3CN solution of $[Bu_4N]ClO_4$ (0.20 M). Scanning rate = 50 mV s^{-1}. Curves obtained in the first to fifth scanning are shown. At the first scanning, only the peak assigned to the electrochemical polymerization is observed.

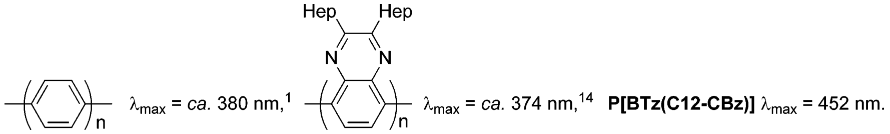
Because it is known that carbazole can be electrochemically polymerized and the formed polycarbazole receives electrochemical oxidation (or p-doping) at about 0.55 V vs Ag^+/Ag,[13] the growth of the peak at 0.64 V vs Ag^+/Ag is assigned to p-doping of the polymerized carbazole. In the repeated scanning, the amount of the formed polycarbazole is considered to increase.

The IR spectrum of **P[BTz(C12—CBz)—Ph]** shows peaks at 722 and 748 cm^{-1}, which are assigned to out-of-plane δ-(C−H) vibration of carbazole (cf. Figure S2-d).[13b] After the CV scanning, the IR spectrum of **P[BTz(C12—CBz)-Ph]** exhibits a strong ClO_4^- peak at 1100 cm^{-1} (Figure S2-e); ClO_4^- is considered to work as a p-dopant for the p-doped polycarbazole. After treatment with NH_3, which usually leads to quenching of p-doped states of π-conjugated polymers, the peak at 1100 cm^{-1} is weakened, and the IR spectrum exhibits peaks at 800 and 877 cm^{-1} (cf. Figure S2-f). These two peaks are assigned to δ(C−H) vibration of a trisubstituted benzene ring, and supports electrochemical polymerization of carbazole.[13] The remaining IR peaks at 722 and 748 cm^{-1}, however, suggest the presence of intact carbazole units. The electrochemically polymerized **P-[BTz(C12—CBz)—Ph]** exhibits a PL spectrum similar to that of **P[BTz(C12—CBz)—Ph]**, however, its intensity becomes significantly weaker (cf. Figure S4). After the electrochemical polymerization, the polymer became insoluble in organic solvents. This type of insolubilization of π-conjugated polymers on demand may provide a new tool for patterning of film of the polymer.

Conclusions

New poly(benzotriazole)s with the carbazole pendant have been prepared by organometallic polycondensations. The polymers are photoluminescent with quantum yields of 57−67%. Electrochemical response of the polymer indicates that the polymer receives n-doping because of electron-accepting nature of the benzotriazole main chain and the pendant carbazole unit can be polymerized electrochemically. CV data indicate that benzotriazole is a moderate electron-accepting unit. As described in the Introduction, synthesis of various π-conjugated poly(benzotriazole)s with various unique pendant groups seems to be possible.

Chart 2. Comparison of the λ_{Max} Position



Experimental Section

Materials. 1,2,3-Benzotriazole, benzene-1,4-diboronic acid, and phenylboronic acid were used as purchased. Bis(1,5-cyclooctadiene)nickel(0) (Ni(cod)$_2$)[19] and 1,4-bis(1,3,2-dioxaborinane)benzene[20] were prepared according to the literature.

2-(12-Bromododecyl)benzotriazole (BTz(C12—Br)): To a methanol solution of 1,2,3-benzotriazole (1.0 g, 8.4 mmol) and potassium *tert*-butoxide (1.4 g, 12.6 mmol), was added 1,12-dibromododecane (4.1 g, 12.6 mmol), and the mixture was stirred under reflux for 12 h. After removal of the solvent by evaporation, the residue was washed with H_2O and extracted with $CHCl_3$. The $CHCl_3$ solution was condensed by evaporation and the product was purified by column chromatography on a SiO_2 column (eluent = $CHCl_3$) to obtain **BTz(C12—Br)** as a colorless oil; Yield: 27%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80 (s, 2H), 7.45 (s, 2H), 4.75 (m, 2H, N$-$CH$_2$) 3.41 (t, 2H, CH$_2-$Br), 2.13 (br, 2H, CH$_2$), 1.85 (m, 2H, CH$_2$), 1.42$-$1.28 (br, 16H, (CH$_2$)$_8$).

2-(6-Bromohexyl)benzotriazole (BTz(C6—Br)) was prepared via an analogous route, and obtained as a colorless oil. Yield: 40%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86 (m, 2H), 7.38 (m, 2H), 4.74 (t, 2H, J = 7.0 Hz, N$-$CH$_2$), 3.38 (t, 2H, J = 6.8 Hz CH$_2-$Br), 2.14 (m, 2H, CH$_2$), 1.85 (m, 2H, CH$_2$), 1.50 (m, 2H, CH$_2$), 1.38 (m, 2H, CH$_2$).

2-(12-Bromododecyl)-4,7-dibromobenzotriazole (Br$_2$BTz(C12—Br)). BTz(C12—Br) (3.7 g, 10 mmol) and an aqueous HBr solution (5.8 M, 20 mL) were added to a flask, and the mixture was stirred for 1 h at 100 °C. Bromine (4.0 g, 25 mmol) was added, and the mixture was stirred for 12 h at 135 °C. After the mixture had cooled to room temperature, an aqueous solution of $NaHCO_3$ was added and the product was extracted with $CHCl_3$. The organic solution was condensed by evaporation, and the product was purified by column chromatography on a SiO_2 column (eluent = $CHCl_3$) to afford **Br$_2$BTz(C12—Br)** as a yellow oil. Yield: 76%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 (s, 2H), 4.78 (t, 2H, N$-$CH$_2$), 3.41 (t, 2H, CH$_2-$Br), 2.15 (m, 2H, CH$_2$), 1.85 (m, 2H, CH$_2$), 1.44$-$1.26 (br, 16H, (CH$_2$)$_8$).

2-(6-Bromohexyl)-4,7-dibromobenzotriazole (Br$_2$BTz(C6—Br)) was prepared via an analogous route, and obtained as a brown oil. Yield: 40%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44 (s, 2H), 4.79 (t, 2H, J = 7.3, N$-$CH$_2$), 3.39 (m, 2H, CH$_2-$Br), 2.17 (m, 2H, CH$_2$), 1.86 (m, 2H, CH$_2$), 1.52 (m, 2H, CH$_2$), 1.41 (m, 2H, CH$_2$).

2-(12-*N*-Carbazolyldodecyl)-4,7-dibromobenzotriazole (Br$_2$BTz(C12—CBz)). To a DMF solution of carbazole (0.14 g, 0.84 mmol) and KOH (0.07 g, 1.3 mmol) was added **Br$_2$BTz(C12—Br)** (0.49 g, 0.78 mmol), and the reaction mixture was stirred at 130 °C for 12 h. After cooling to room temperature, the reaction mixture was poured into H_2O, washed with H_2O, and extracted with $CHCl_3$. The $CHCl_3$ solution was condensed by evaporation and the product was purified by column chromatography on a SiO_2 column (eluent = $CHCl_3$) and HPLC to obtain **Br$_2$BTz(C12—CBz)** as a yellow oil. Yield: 15%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, 2H, J = 7.8 Hz, CBz), 7.47$-$7.38 (m, 6H, CBz and BTz), 7.21 (t, 2H, J = 7.3 Hz, CBz), 4.76 (t, 2H, J = 7.3 Hz, BTz-CH$_2^{\alpha}$), 4.29 (t, 2H, CBz-CH$_2^{\alpha}$), 2.11 (m, 2H, BTz-CH$_2^{\beta}$), 1.86 (m, 2H, CBz-CH$_2^{\beta}$), 1.25 (m, 16H, (CH$_2$)$_8$). ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.13 (d, 2H, J = 7.5 Hz, CBz), 7.61 (s, 2H, BTz), 7.56 (d, 2H, J = 8.3 Hz), 7.43 (m, 2H, CBz), 7.18 (t, 2H, J = 7.3, CBz), 4.80 (t, 2H, J = 7.0, BTz-CH$_2^{\alpha}$), 4.37 (t, 2H, J = 7.0, CBz-CH$_2^{\alpha}$), 2.01 (m, 2H, BTz-CH$_2^{\beta}$), 1.73 (m, 2H, CBz-CH$_2^{\beta}$), 1.21$-$1.11 (br, 16H, (CH$_2$)$_8$). Anal. Calcd for $C_{30}H_{34}Br_2N_4$: C, 59.03; H, 5.61; N, 9.18. Found: C, 59.00; H, 5.58; N, 9.04.

2-(6-*N*-Carbazolylhexyl)-4,7-dibromobenzotriazole (Br$_2$BTz(C6—CBz)) was prepared via an analogous route and obtained as a yellow oil. Yield: 11%. ^{1}H NMR (300 MHz, $CDCl_3$), δ 8.07 (d, 2H, J = 7.9 Hz, CBz), 7.47$-$7.35 (m, 4H, CBz), 7.44 (s, 2H, BTz), 7.24$-$7.19 (m, 2H, CBz), 4.74 (t, 2H, BTz-CH$_2^{\alpha}$), 4.30 (t, 2H, CBz-CH$_2^{\alpha}$), 2.10 (m, 2H, BTz-CH$_2^{\beta}$), 1.89 (m, 2H, CBz-CH$_2^{\beta}$), 1.42 (m, 4H, (CH$_2$)$_2$). HRMS (FAB): found, 526.0195; calcd for $C_{24}H_{22}Br_2N_4$, 526.0192.

2-(12-*N*-Carbazolyldodecyl)-4,7-diphenylbenzotriazole (Ph—BTz(C12—CBz)—Ph). To a mixture of toluene (20 mL) solution of **Br$_2$BTz(C12—CBz)** (0.62 g, 1.0 mmol) and Pd(PPh$_3$)$_4$ (1.0 mg) and an aqueous solution of potassium carbonate (4.0 mL, 2.0 M) was added an methanol (10 mL) solution of phenylboronic acid (0.26 g, 2.1 mmol). After the reaction mixture was stirred at 80 °C for 16 h, hydrogen chloride (30%) was added slowly. The mixture was stirred for 4 h and extracted with $CHCl_3$. The $CHCl_3$ solution was dried over $MgSO_4$ and the solvent was removed. Purification by column chromatography on a SiO_2 column (eluent = $CHCl_3$) yielded **Ph—BTz(C12$-$CBz)—Ph** as a white solid. Yield: 40%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.98 (d, 2H, J = 8.3 Hz, Ph), 8.06 (m, 4H, CBz), 7.62 (s, 2H), 7.51 (t, 4H), 7.45 (m, 2H), 7.40 (m, 4H), 7.21 (m, 2H), 4.78 (t, 2H, J = 7.3 Hz, CH$_2^{\alpha}$ of BTz), 4.28 (m, 2H, CH$_2^{\alpha}$ of CBz), 2.15 (m, 2H, CH$_2^{\beta}$ of BTz), 1.85 (m, 2H, CH$_2^{\beta}$ of CBz), 1.40$-$1.20 (br, 16H, (CH$_2$)$_8$). Anal. Calcd for $C_{42}H_{44}N_4$: C, 83.40; H, 7.33; N, 9.26. Found: C, 83.10; H, 7.63; N, 9.23.

Synthesis of Polymers. Under N$_2$, to a toluene solution containing Ni(cod)$_2$ (1.32 g, 4.8 mmol), 1,5-cyclooctadiene (0.58 g, 4.8 mmol), and 2,2′-bipyridyl (0.75 g, 4.8 mmol), was added **Br$_2$BTz(C12—CBz)** (0.78 g, 1.3 mmol). The reaction mixture was stirred at 60 °C for 96 h to give a black precipitate. The precipitate was washed with methanol, aqueous ammonia, an aqueous solution of disodium ethylenediaminetetraacetic acid (Na$_2$-EDTA), distilled water, a methanol solution of dimethylglyoxime, diluted hydrochloric acid, and methanol, and it was dried under vacuum at 100 °C for 3 days to give **P[BTz(C12—CBz)]** as a red solid. Yield: 90%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.90 (br, 2H, CBz), 8.06 (br, 6H, CBz, BTz), 7.4$-$7.1 (br, 2H), 4.84 (br, 2H, BTz-CH$_2^{\alpha}$), 4.18 (br, 2H, CBz-CH$_2^{\beta}$), 2.17 (br, 2H, BTz-CH$_2^{\beta}$), 1.78 (br, 2H, CBz-CH$_2^{\beta}$), 1.25 (br, 16H, (CH$_2$)$_8$). Anal. Calcd for $H(C_{30}H_{34}N_4)_{10.5}H$: C, 79.93; H, 7.64; N, 12.43. Found: C, 78.80; H, 7.09; N, 12.11; Br, 0.

P[BTz(C6—CBz)] was prepared analogously, to give a red powder. Yield: 52%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.8 (br, 2H, CBz), 8.0 (br, 6H, CBz, BTz), 7.4$-$7.1 (br, 2H,CBz), 4.73 (br, 2H, BTz-CH$_2^{\alpha}$), 4.22 (br, 2H,CBz-CH$_2^{\alpha}$), 2.10 (br, 2H, BTz-CH$_2^{\beta}$), 1,83 (br, 2H, BTz-CH$_2^{\beta}$), 1.39 (br, 4H, (CH$_2$)$_2$). Anal. Calcd for $H(C_{24}H_{22}N_4)_{7.5}H$: C, 78.60; H, 6.12; N, 15.28. Found: C, 77.50; H, 6.15; N, 15.07; Br, 0.

P[BTz(C12—CBz)—Ph]. To a mixture of a toluene (20 mL) solution of **Br$_2$BTz(C12—CBz)** (0.61 g, 1.0 mmol), Pd(PPh$_3$)$_4$ (1.0 mg), and an aqueous solution of potassium carbonate (2.0 M, 4.0 mL) was added an methanol (10 mL) solution of 1,4-bis(1,3,2-dioxaborinane)benzene (0.25 g, 1.0 mmol). After the reaction mixture was stirred at 80 °C for 4 days, the reaction mixture was poured into methanol to obtain a precipitate. The crude product was separated by filtration and washed with water and methanol. The obtained polymer was dissolved in chloroform and reprecipitated in methanol to give an yellow powder of **P[BTz-(C12—CBz)—Ph]**. Yield: 62%.^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (m, 2H), 8.05 (m, 3H), 7.75 (br, 1H), 7.5$-$7.3 (br, 6H), 7.25 (m, 2H), 4.81 (s, 2H, BTz-CH$_2^{\alpha}$), 4.23 (s, 2H, CBz-CH$_2^{\alpha}$), 2.17 (br, 2H, BTz-CH$_2^{\beta}$), 1.80 (br, 2H, CBz-CH$_2^{\beta}$), 1.25 (br, 16H, (CH$_2$)$_8$. Anal. Calcd for $Br(C_{36}H_{38}N_4)_{51}H$: C, 81.84; H, 7.25; N, 10.60; Br, 0.30; M_n = 26 944. Calcd for $Br(C_{36}H_{38}N_4)_{51}Br$: C, 81.61; H, 7.23; N, 10.57; Br, 0.59; M_n = 27 023. Found: C, 81.01; H, 7.05; N, 9.91; Br, 0.36; M_n = 27 000. According to the ICP emission spectrometry, boron was not detected.

Instruments and Methods. ^{1}H NMR spectra were recorded on a JEOL JNM-EX-400 and JEOL Lambda 300. Elemental analyses of C, H, and N were carried out with a Leco CHNS-932 analyzer or a Yanaco CHN CORDER MT-5 microanalyzer. GPC traces were obtained with a Shimadzu LC-9A chromatograph equipped with a UV detector and Shodex 80M columns (eluent = $CHCl_3$; polystyrene standards). The cast films were prepared from chloroform solutions. UV$-$vis spectra were recorded on a Shimadzu UV-3100 PC spectrometer. PL spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer. Cyclic voltammograms and electrochemical polymerization of cast films of the polymers were performed in an acetonitrile solution of $[(C_2H_5)_4N]BF_4$ (0.10 M) or $[(n\text{-}C_4H_9)_4N]ClO_4$ (0.10 or 0.20 M) with a Pt counter electrode and an Ag^+/Ag reference electrode by using Hokuto Denko HSV-100. Thermogravimetric analysis (TGA) was performed on a Shimadzu TGA-50. ICP (inductively coupled plasma) emission spectrometry was applied for analysis of B in **P[BTz(C12—CBz)—Ph]** with Shimadzu ICPS-8100. HRMS was carried out with JEOL JMS-700.

Supporting Information Available: ^{1}H NMR spectra of **BTz(C12—Br)**, **Br$_2$BTz(C12—Br)**, **Br$_2$BTz(C12—CBz)**, and **Ph—BTz(C12—CBz)—Ph**, IR spectra of the polymers and electrochemically polymerized samples, XRD patterns of the polymers, and PL spectra of electrochemically polymerized **P[BTz(C12—CBz)—Ph]**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) *Handbook of Conducting Polymers*, 2nd ed.; Stokheim, T. A., Elsenbaumer, R. L., Reinolds, J. R., Eds.; Dekker: New York, 1997. (b) McCullough, R. D. *Handbook of Oligo- and polythiophene*; Ficher, D., Ed.; Wiley-VCH: Weinheim, Germany, 1999. (c) Yamamoto, T. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 621. (d) *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; Wiley: Chichester, U.K., 1997; Vol. 2.

(2) (a) Heywang, G.; Jonas, F. *Adv. Mater.* **1992**, *4*, 116. (b) Kudoh, Y.; Fukuyama, M.; Kojima, T.; Nanai, N.; Yoshimura, S. In *Intrinsically Conducting Polymers: An Emerging Technology*; Aldissi, M., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1992. (c) Patil, A. O.; Ikenoue, Y.; Wudl, F.; Heeger, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 1858. (d) Catalogue of Achilles Corporation; 22 Daikyo-cho, Shinjuku-ku, Tokyo, Japan.

(3) (a) Freudenmann, R.; Behnisch, B.; Hanack, M. *J. Mater. Chem.* **2001**, *11*, 1618. (b) Thomas, K. R. J.; Velusamy, M.; Lin, J. T.; Tao, Y.-T.; Chuen, C.-H. *Adv. Funct. Mater.* **2004**, *14*, 387. (c) Li, Z. H.; Wong, M. S.; Fukutani, H.; Tao, Y. *Chem. Mater.* **2005**, *17*, 5032. (d) Cea, P.; Hua, Y.; Pearson, C.; Wang, C.; Bryce, M. R.; Royo, F. M.; Petty, M. C. *Thin Solid Films* **2002**, *408*, 275. (e) Karabunarliev, S.; Bittner, E. R. *J. Phys. Chem. B* **2004**, *108*, 10219. (f) Morteani, A. C.; Dhoot, A. S.; Kim, J.-S.; Silva, C.; Greenham, N. C.; Murphy, C.; Moons, E.; Ciná, S.; Burroughes, J. H.; Friend, R. H. *Adv. Mater.* **2003**, *15*, 1708. (g) Lee, S. K.; Hwang, D.-H.; Jung, B.-J.; Cho, N. S.; Lee, J.; Lee, J.-D.; Shin, H.-K. *Adv. Funct. Mater.* **2005**, *15*, 1647.

(4) (a) Babel, A.; Wind, J. D.; Jenekhe, S. A. *Adv. Funct. Mater.* **2004**, *14*, 891. (b) Meijer, E. J.; deLeeuw, D. M.; Setayesh, S.; van-Veenendaal, E.; Huisman, B.-H.; Blom, P. W. M.; Hummelen, J. C.; Scherf, U.; Klapwijk, T. M. *Nat. Mater.* **2003**, *2*, 678. (c) Dodabalapur, A.; Katz, H. E.; Torsi, L.; Haddon, R. C. *Science* **1995**, *269*, 1560. (d) Chesterfield, R. J.; Newman, C. R.; Pappenfus, T. M.; Ewbank, P. C.; Haukaas, M. H.; Mann, K. R.; Miller, L. L.; Frisbie, C. D. *Adv. Mater.* **2003**, *15*, 1278. (e) Yamamoto, T.; Yasuda, T.; Sakai, Y.; Aramaki, S. *Macromol. Rapid Commun.* **2005**, *26*, 1214.

(5) (a) Chung, S.-J.; Kwon, K.-Y.; Lee, S.-W.; Jin, J.-I.; Lee, C. H.; Lee, C. E.; Park, Y. *Adv. Mater.* **1998**, *10*, 1112. (b) Sung, H.-H.; Lin, H.-C. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 2700. (c) Sanda, F.; Kawaguchi, T.; Masuda, T.; Kobayashi, N. *Macromolecules* **2003**, *36*, 2224. (d) Lee, G. J.; Kim, K.; Jin, J.-I. *Opt. Commun.* **2000**, *203*, 151. (e) An, B.-K.; Kim, Y.-H.; Shin, D.-C.; Park, S. Y.; Yu, H.-S.; Kwon, S.-K. *Macromolecules* **2001**, *34*, 3993. (f) Lu, S.; Liu, T.; Ke, L.; Ma, G.-G.; Chua, S.-J.; Huang, W. *Macromolecules* **2005**, *38*, 8494. (g) Liang, F.; Kurata, T.; Nishide, H.; Kido, J. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5765.

(6) (a) Meerhold, K.; Gregorius, H.; Müller, K.; Heinze, J. *Adv. Mater.* **1994**, *6*. 671. (b) Yamamoto, T.; Xu, Y.; Inoue, T.; Yamaguchi, I. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1493.

(7) (a) Yamamoto, T.; Sugiyama, K.; Kanbara, T.; Hayashi, H.; Etori, H. *Macromol. Chem. Phys.* **1998**, *199*, 1807. (b) Tanimoto, A.; Shiraishi, K.; Yamamoto, T. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 597.

(8) (a) Kanbara, T.; Yamamoto, T. *Chem. Lett.* **1993**, 583. (b) Bernius, M. T.; Inbasekaran, M.; O'brien, J.; Wu, W. *Adv. Mater.* **2000**, *12*, 1737 and references therein. (c) Tessler, N,; Medvedev, V.; Kazes, M.; Kan, S.; Banin, U. *Science* **2002**, *295*, 1506. (d) Huang, J.; Xu, Y.; Hou, Q.; Yang, W.; Yuan, M.; Cao, Y. *Macromol. Rapid Commun.* **2002**, *23*, 709. (e) Witker, D.; Reinolds, J. R. *Macromolecules* **2005**, *38*, 7636. (f) Yamamoto, T.; Fang, Q.; Morikita, T. *Macromolecules* **2003**, *36*, 4262.

(9) (a) Tanimoto, A.; Yamamoto, T. *Adv. Synth. Catal.* **2004**, *346*, 1818. (b) Ahn, S.-H.; Czae, M.-Z.; Kim, E.-R.; Lee, H.; Han, S.-H.; Noh, J.; Hara, M. *Macromolecules* **2001**, *34*, 2522.

(10) (a) Atta-ur-Rahman *Nuclear Magnetic Resonance. Basic Principles*; Springer-Verlag: New York, 1986. (b) Kamiya, M.; Katayama, S.; Akahori, Y. *Chem. Pharm. Bull.* **1969**, *17*, 1821.

(11) Xia, C.; Advincula, R. C. *Chem. Mater.* **2001**, *13*, 1682.

(12) Melhuish, W. H. *J. Phys. Chem.* **1962**, *65*, 229.

(13) (a) Diamant, Y.; Furmanovich, E.; Landau, A.; Lellouche, J.-P.; Zaban, A. *Electrochim. Acta* **2003**, *48*, 507. (b) Macit, H.; Sen, S.; Sacak, M. *J. Appl. Polym. Sci.* **2005**, *96*, 894. (c) Gracia-Melmonte, G.; Pomerantz, Z.; Bisquert, J.; Lellouche, J.-P.; Zaban, A. *Electrochim. Acta* **2004**, *49*, 3413. (d) Sarac, A. S.; Sezer, E.; Ustamehmetoglu, B. *Polym. Adv. Technol.* **1997**, *8*, 556.

(14) Yamamoto, T.; Sugiyama, K.; Kushida, T.; Inoue, T.; Kanbara, T. *J. Am. Chem. Soc.* **1996**, *118*, 3930.

(15) (a) Mazik, M.; Bläser, D.; Boese, R. *J. Org. Chem.* **2005**, *70*, 9115. (b) Pickering, A. L.; Seeber, G.; Long. D.-L.; Cronin, L. *Cryst. Eng. Commun.* **2005**, *7*, 504. (c) Aglifoglio, G.; Karam. A. R.; Catari, E. L.; Gronzalez, T.; Atencia, R. *Acta Crystallogr. Sect. E* **2005**, *61*, o2613.

(16) Jenekhe, S. A.; Lu, L.; Alam, M. M. *Macromolecules*, **2001**, *34*, 7315.

(17) Grochala, W.; Hoffman, R.; Edwards, P. P. *Chem.—Eur. J.* **2003**, *9*, 575.

(18) Ikeda, T.; Lee, B.; Kurihara, S.; Tazuke, S.; Ito, S.; Yamamoto, M. *J. Am. Chem. Soc.* **1988**, *110*, 8299.

(19) Bogdanovi, B.; Kroener, M.; Wilke, G.; Justus, L. *Ann. Chem.* **1966**, *699*, 1.

(20) Vahlenkamp, T.; Wegner, G. *Macromol. Chem. Phys.* **1994**, *195*, 1933.

MA052688B