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ORIGINAL ARTICLE

Synthesis and optical properties of poly(*p*-benzamide)s bearing oligothiophene on the amide nitrogen atom through an alkylene spacer

Koji Takagi, Katsuya Nobuke, Yuma Nishikawa and Ryohei Yamakado

Phenyl 4-((5′′-hexyl-2,2′-bithienyl)methyl)aminobenzoate (M1), phenyl 4-((5′′-hexyl-2,2′-bithienyl)propyl)aminobenzoate (M2) and phenyl 4-((5-hexyl-2,2′:5′,2′′-terthienyl)propyl)aminobenzoate (M3), each having oligothiophene on the nitrogen atom through the use of an alkylene spacer, were synthesized using a method in which the oligothiophene group was introduced by the reductive amination (M1) or the nucleophilic substitution (M2 and M3). The condensation polymerization was performed by adding the monomer and 4′-nitrophenyl 4-methylbenzoate to lithium bis(trimethylsilyl)amide and *N,N,N′,N′*-tetramethyl-ethylenediamine (Method A). Poly(*p*-benzamide)s with number-averaged molecular weights ranging from 4400–7300 were obtained in high yields (∼80%). From the gel permeation chromatography profiles and the ^{1}H-nuclear magnetic resonance spectra, the polymerization was found to proceed in a controlled manner. The C=O stretching vibration signal in the infrared spectra indicated the *cis* conformation of the amide group in the polymer backbone. However, the direct polycondensation of 4-((5′′-hexyl-2,2′-bithienyl)methyl)aminobenzoic acid using PPh₃ and hexachloroethane in pyridine produced a cyclic trimer, that is, *p*-calix[3]amide (Method B). In contrast to polyM2 and *p*-calix[3]amide, a broad emission peak at ∼480 nm was observed for polyM1, indicating the π-stacked interaction between the bithiophene chromophores. As polyM3 (having the terthiophene) also exhibited a redshift of the emission maxima, the wide conjugated system was found to be susceptible to the strong π-stacked interaction at the polymer side chain.

INTRODUCTION

π-Conjugated oligomers with well-defined shapes and a minimum amount of structural defects have a pivotal role in molecular devices, such as light-emitting diodes and field-effect transistors, because of the ability to easily fine-tune the optoelectronic properties. Not only the chemical structure but also the aggregation state of π-conjugated oligomers are well-known to influence the performance of materials. Thus, the programmable arrangement of π-conjugated oligomers in space and the understanding of the aggregation structure-properties relationship are of significant importance.[1] However, the three-dimensional aggregation state is strongly governed by the chemical structure of the π-conjugated oligomers, as represented by the herringbone packing of pentacene.

One possible strategy to adjust the aggregation state involves chemical modification at the periphery of the π-conjugated oligomers. Kobayashi *et al.*[2,3] succeeded in the cofacial packing of bis(methylthio)acenes by using S–S and S–π interactions. Another technique to control the aggregation state of π-conjugated oligomers is the utilization of a well-defined template unit. Morisaki *et al.*[4–6]

developed π-stacked oligomers and polymers, in which the xanthene skeleton was selected as the scaffold to align the π-conjugated oligomers in a cofacial fashion. Watanabe *et al.*[7] explored the H-aggregation of π-conjugated oligomers by the conformational control with a two-substituted trimethylene tether. In addition to these main chain π-stacked polymers, other polymers, such as poly(styrene),[8] poly(methacrylate),[9] poly(ureidophthalimide),[10] poly(dithienopyrrole)[11] and poly(dibenzofulvene),[12–14] were examined to finely align the π-conjugated oligomers at the side chain.

We have previously reported the synthesis and characterization of poly(*m*-benzamide)s and *m*-calix[3]amides bearing oligothiophene at the meta-position of the amide nitrogen atom.[15] Compared with the model compound corresponding to the repeating unit, the observed blueshift of the absorption spectra and the redshift of the emission spectra indicated an electronic interaction between the oligothiophenes. For poly(*p*-benzamide)s bearing bithiophene at the ortho-position of the amide nitrogen atom, a similar tendency was observed in the absorption and

emission spectra.[16] In the present study, the polymerization of phenyl 4-aminobenzoate derivatives and the optical properties of poly(*p*-benzamide)s having the oligothiophene chromophore on the amide nitrogen atom through the alkylene spacer are described. Tanatani *et al*.[17] revealed that poly(*p*-benzamide)s with a chiral side chain on the amide nitrogen atom adopt a helical conformationowing to the *cis* conformation of the amide bonds and the *syn* arrangement of the benzene rings.[18,19] As the substituents on the amide nitrogen atom are arrayed parallel to the poly(*p*-benzamide) main chain, the oligothiophene chromophores are expected to exhibit a regular arrangement that indicates the π-stacked interaction.

EXPERIMENTAL PROCEDURE

Materials
All reactions were performed under a dry nitrogen atmosphere. Dry tetrahydrofuran (THF), sodium triacetoxyborohydride (NaBH(OAc)$_3$), *n*-buthyllithium (*n*-BuLi, 1.6 M in hexane), ethyl 4-aminobenzoate, *p*-toluene-sulfonic acid monohydrate (*p*-TsOH•H$_2$O), 4-(dimethylamino)pyridine (DMAP) and triphenylphosphine (PPh$_3$) were purchased from Kanto Chemical (Tokyo, Japan). Dry hexamethylphosphoramide, lithium bis(trimethylsilyl)a-mide solution (1.0 M in THF) and tetrakis(triphenylphosphine)palladium(0) (Pd(PPh$_3$)$_4$) were purchased from Sigma-Aldrich (St Louis, MO, USA). 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC•HCl) and hexachloroethane were purchased from TCI (Tokyo, Japan). These reagents were used as received. *N*,*N*-dimethylformamide (DMF) and *N*,*N*,*N'*,*N'*-tetra-methylethylenediamine (TMEDA) were dried and distilled before use.

Characterization
^{1}H-nuclear magnetic resonance (NMR) and ^{13}C-NMR spectra were recorded on a Bruker Avance 200 FT-NMR spectrometer using either CDCl$_3$ or DMSO-d$_6$ as a solvent. IR spectra were recorded on a Jasco FT-IR 460 Plus spectrophotometer using the attenuated total reflection (ATR) method. The melting points (Mp) were determined using a Yanaco MP-500D micro melting point apparatus. Elemental analyses were performed on a Elementar Vario EL cube in the CHN mode. Gel permeation chromatography (GPC) analyses were performed on a Shodex GPC-104 system using tandem LF −404 columns (with THF as an eluent, flow rate = 1.0 ml min^{-1}, 40 °C) equipped with an ultraviolet (UV) detector (Shimadzu, Kyoto, Japan; SPP-20A). The number-averaged molecular weight (M_n) and molecular weight distribution (M_w/M_n) were determined on the basis of a calibration curve made from standard polystyrene samples. UV and photoluminescence (PL) spectra were recorded on a Shimadzu UV-1650PC spectrophotometer and a Shimadzu RF-5300PC spectrofluorom-eter, respectively, using a 1-cm quartz cell. Fluorescence quantum yields (QYs) in solution were determined relative to quinine sulfate in 0.1 M H$_2$SO$_4$ with a QY of 0.55.

Monomer synthesis
M1 (See, Supplementary Scheme S1 and Supplementary Figures S1–S6): (Step 1) A toluene solution (20 ml) of ethyl 4-aminobenzoate (1.1 g, 6.8 mmol), 5-hexyl-2,2'-bithiophene-5'-carboxyaldehyde (see, supporting information for the preparation.) (1.3 g, 4.5 mmol) and *p*-TsOH•H$_2$O (0.51 g, 2.7 mmol) was heated to reflux in a Dean-Stark apparatus to perform the dehydration condensation for 6 h. After cooling to room temperature, NaBH(OAc)$_3$ (1.4 g, 6.8 mmol) was added and the mixture was stirred overnight. Next, saturated aqueous Na$_2$CO$_3$ was added, and an aqueous phase was extracted with ethyl acetate. The combined organic phase was then dried over MgSO$_4$, and the solvents were removed using a rotary evaporator. The resulting crude product was purified by recrystallization from hexane/ethyl acetate to obtain ethyl 4-((5''-hexyl-2,2'-bithienyl)methyl)aminobenzoate as a pale yellow solid (1.4 g, 71% yield). (Step 2) A solution of ethyl 4-((5''-hexyl-2,2'-bithienyl)methyl)a-minobenzoate (0.70 g, 1.6 mmol) and 2 M aqueous NaOH (7 ml) in both methanol (13 ml) and THF (13 ml) was heated to 50 °C for 6 h. After cooling to room temperature, 1 M aqueous HCl was added to acidify the system, and the product was extracted with ethyl acetate. The organic phase was dried

over MgSO$_4$, and the solvents were removed using a rotary evaporator to obtain 4-((5''-hexyl-2,2'-bithienyl)methyl)aminobenzoic acid as a yellow solid (0.62 g, 95% yield), which was used for the next reaction without further purification. (Step 3) To a DMF solution (1.8 ml) of 4-((5''-hexyl-2,2'-bithienyl)methyl)aminobenzoic acid (0.26 g, 0.61 mmol) was added a DMF solution (1.8 ml) of phenol (70 mg, 0.75 mmol), DMAP (96 mg, 0.78 mmol) and *p*-TsOH•H$_2$O (118 mg, 0.62 mmol) at 0 °C. After stirring for 10 min, a DMF solution (3.0 ml) of EDC•HCl (160 mg, 0.81 mmol) was added, and the mixture was heated to 50 °C overnight. Water was then added, and the aqueous phase was extracted with CH$_2$Cl$_2$. The combined organic phase was washed with 1 M aqueous HCl and saturated aqueous NaHCO$_3$, then dried over MgSO$_4$. The solvents were removed using a rotary evaporator to yield the crude product, which was purified by SiO$_2$ chromatography (CH$_2$Cl$_2$/ethyl acetate = 9/1, Rf = 0.7) to obtain a pale yellow solid (0.21 g, 71% yield). Mp: 168–170 °C. Analytically calculated for C$_{29}$H$_{31}$NO$_2$S$_2$: C, 71.13%; H, 6.38%; N, 2.86%; S, 13.10%. Found: C, 70.58%; H, 6.36%; N, 2.64%; and S, 13.50%. ^{1}H-NMR (δ, CDCl$_3$) 8.04 (d, 2H, *J* = 8.4 Hz), 7.40 (t, 2H, *J* = 7.9 Hz), 7.20 (3H), 6.67 (3H), 4.55 (3H), 2.78 (t, 2H, *J* = 7.3 Hz), 1.67 (m, 2H), 1.50∼1.21 (6H), 0.89 (t, 3H, *J* = 6.3 Hz). ^{13}C-NMR (δ, CDCl$_3$) 165.2, 151.3, 150.1, 138.4, 137.9, 137.0, 133.2, 132.5, 129.4, 127.9, 127.3, 125.5, 124.7, 124.2, 124.0, 121.9, 118.5, 116.7, 110.9, 43.5, 31.8, 29.3, 29.2, 29.0, 27.1, 22.7, 14.1. IR (cm^{-1}, ATR) 3354, 2926, 2853, 1695, 1594, 1525, 1285, 1169.

M2 (See, Supplementary Scheme S2 and Supplementary Figures S7–S12): (Step1) A hexamethylphosphoramide solution (3 ml) of 5-hexyl-5'-(3-bromo-propyl)-2,2'-bithiophene (see, supporting information for the preparation.) (0.75 g, 2.0 mmol) and ethyl 4-aminobenzoate (0.67 g, 4.0 mmol) was heated to 125 °C overnight. Ice-water was then added, and the mixture was stirred at 0 °C for 3 h. The precipitate was collected and subsequently washed with 50% aqueous EtOH to obtain ethyl 4-((5''-hexyl-2,2'-bithienyl)propyl)amino-benzoate as a yellow solid (0.88 g, 96% yield). (Step 2) A solution of ethyl 4-((5''-hexyl-2,2'-bithienyl)propyl)aminobenzoate (0.83 g, 1.8 mmol) and 2 M aqueous NaOH (8 ml) in both methanol (14 ml) and THF (14 ml) was heated to 50 °C for 6 h. After cooling to room temperature, 1 M aqueous HCl was added to acidify the system, and the product was extracted with ethyl acetate. The organic phase was dried over MgSO$_4$, and the solvents were removed using a rotary evaporator to obtain 4-((5''-hexyl-2,2'-bithienyl)propyl)amino-benzoic acid as a yellow solid (0.76 g, 97% yield), which was used for the next reaction without further purification. (Step 3) To a DMF solution (6 ml) of 4-((5''-hexyl-2,2'-bithienyl)propyl)aminobenzoic acid (0.76 g, 1.8 mmol) was added a DMF solution (6 ml) of phenol (0.19 g, 2.1 mmol), DMAP (0.26 g, 2.1 mmol), and *p*-TsOH•H$_2$O (0.32 g, 1.7 mmol) at 0 °C. After stirring for 10 min, a DMF solution (9 ml) of EDC•HCl (0.43 g, 2.2 mmol) was added, and the mixture was heated to 50 °C overnight. Water was then added, and the aqueous phase was extracted with CH$_2$Cl$_2$. The combined organic phase was washed with 1 M aqueous HCl and saturated aqueous NaHCO$_3$, then dried over MgSO$_4$. The solvents were removed using a rotary evaporator to yield the crude product, which was purified by SiO$_2$ chromatography (CH$_2$Cl$_2$/ethyl acetate = 9/1, Rf = 0.7) to obtain a pale yellow solid (0.88 g, 60% yield). Mp: 133–135 °C. Analytically calculated for C$_{28}$H$_{29}$NO$_2$S$_2$: C, 71.53%; H, 6.60%; N, 2.78%; S, 12.73%. Found: C, 71.44%; H, 6.57%; N, 2.69%; S, 13.03%. ^{1}H-NMR (δ, CDCl$_3$) 8.01 (d, 2H, *J* = 8.3 Hz), 7.40 (t, 2H, *J* = 7.6 Hz), 7.20 (3H), 6.91 (2H), 6.73∼6.52 (4H), 4.21 (s, 1H), 3.29 (t, 2H, *J* = 6.3 Hz), 2.93 (t, 2H, *J* = 6.9 Hz), 2.78 (t, 2H, *J* = 7.6 Hz), 2.03 (m, 2H), 1.67 (m, 2H), 1.46∼1.22 (m, 6H), 0.89 (t, 3H, -CH$_3$, *J* = 6.9 Hz). ^{13}C-NMR (δ, CDCl$_3$) 165.4, 152.5, 151.4, 145.1, 142.6, 136.1, 135.0, 132.3, 129.4, 125.5, 125.3, 124.7, 122.9, 122.7, 122.0, 117.3, 111.6, 42.5, 31.6, 30.9, 30.2, 28.8, 27.6, 22.6, 14.1. IR (cm^{-1}, ATR) 3354, 2925, 1684, 1595, 1524, 1284, 1168, 1079, 794.

M3 (See, Supplementary Scheme S3 and Supplementary Figures S13–S18): this monomer was prepared in a similar method for **M2** (See supporting information for details). Mp: 145–146 °C. Analytically calculated for C$_{34}$H$_{35}$NO$_2$S$_3$: C, 69.71%; H, 6.02%; N, 2.39%; S, 16.42%. Found: C, 69.23%; H, 5.75%; N, 2.32%; S, 17.09%. ^{1}H-NMR (δ, CDCl$_3$) 8.02 (d, 2H, *J* = 8.7 Hz), 7.41 (t, 2H, *J* = 7.2 Hz), 7.20 (3H), 6.98 (4H), 6.72 (d, 1H, *J* = 3.7 Hz), 6.67 (d, 1H, *J* = 3.5 Hz), 6.59 (d, 2H, *J* = 8.3 Hz), 4.22 (s, 1H), 3.30 (m, 2H), 2.94 (t, 2H, *J* = 7.5 Hz), 2.79 (t, 2H, *J* = 6.5 Hz), 2.04 (m, 2H), 1.68 (m, 2H), 1.48–1.21 (6H), 0.89 (t, 3H, *J* = 5.6 Hz). ^{13}C-NMR (δ, CDCl$_3$) 165.4, 152.4, 151.4, 145.6, 143.3, 136.5, 135.7, 135.4, 134.5, 132.3, 129.4, 125.5, 124.9,

123.8, 123.5, 123.4, 123.3, 122.0, 117.4, 111.6, 42.5, 31.6, 30.9, 30.2, 28.8, 27.6, 22.6, 14.1. IR (cm^{-1}, ATR) 3371, 2926, 1685, 1595, 1521, 1194, 1167, 1078.

Polymerization (typical procedure)

To a THF solution (0.10 ml) of lithium bis(trimethylsilyl)amide solution (0.10 ml, 0.10 mmol) and TMEDA (76 µl, 0.50 mmol) was added a THF solution (0.5 ml) of **M1** (50 mg, 0.10 mmol) and 4′-nitrophenyl 4-methylbenzoate (3.0 mg, 10 µmol) via microsyringe at 0 °C, and the mixture was heated to 50 °C for 24 h. After the mixture was poured into saturated aqueous NH$_4$Cl, the aqueous phase was extracted with CH$_2$Cl$_2$. The combined organic phase was washed with water and dried over MgSO$_4$. The solution was concentrated and poured into hexane to obtain poly**M1** as a brown solid (26 mg, 85% yield). ^{1}H-NMR (200 MHz, CDCl$_3$) 7.19–6.40 (br, 8H), 5.06 (br, 2H), 2.75 (br, 2H), 2.18 (br, small), 1.62 (br, 2H), 1.47–1.13 (br, 6H), 0.88 (br, 3H).

Poly**M2**: ^{1}H-NMR (200 MHz, CDCl$_3$) 7.19–6.40 (br, 8H), 3.84 (br, 2H), 2.74 (br, 2H), 2.25 (br, small), 1.86 (br, 2H), 1.62 (br, 2H), 1.47–1.13 (br, 6H), 0.88 (br, 3H).

poly**M3**: ^{1}H-NMR (200 MHz, CDCl$_3$) 7.26–6.45 (br, 10H), 3.92 (br, 2H), 2.81 (br, 2H), 2.31 (br, small), 1.93 (br, 2H), 1.71 (br, 2H), 1.54–1.15 (br, 6H), 0.95 (br, 3H).

RESULTS AND DISCUSSION

Synthesis

The synthetic routes for obtaining the monomers are shown in schemes S1–S3. In the case of **M1** using the methylene spacer, the bithiophene group was introduced by the reductive amination between 5-hexyl-2,2′-bithiophene-5′-carboxyaldehyde and ethyl 4-aminobenzoate using NaBH(OAc)$_3$. However, in the case of **M2** and **M3** using the trimethylene spacer, the bithiophene and terthiophene groups were introduced by the nucleophilic substitution of 5-hexyl-5′-(3-bromopropyl)-2,2′-bithiophene and 5-hexyl-5″-(3-bromopropyl)-2,2′:5′,2″-terthiophene with ethyl 4-aminobenzoate in hexamethylphosphoramide.[20] The ethyl esters were converted to the phenyl esters to increase the monomer reactivity in the condensation polymerization. The structure and purity of the monomers were confirmed by NMR spectra and elemental analyses.

The condensation polymerization was performed by adding a THF solution of **M1** and 4′-nitrophenyl 4-methylbenzoate (initiator, 10 mol% relative to **M1**) to a THF solution of lithium bis(trimethylsilyl)amide solution (base) and TMEDA (activator), and the mixture was heated to 50 °C for 24 h (Scheme 1, method A).[21] The addition of TMEDA and the reaction at the elevated temperature were necessary for ensuring the higher monomer conversion (90%), as confirmed by the crude ^{1}H-NMR spectrum. The bulky substituent on the nitrogen atom might block the nucleophilic attack of the aminyl anion formed by the deprotonation of **M1**. In contrast to **M1** carrying the phenyl ester group, the monomer with the ethyl ester group could not
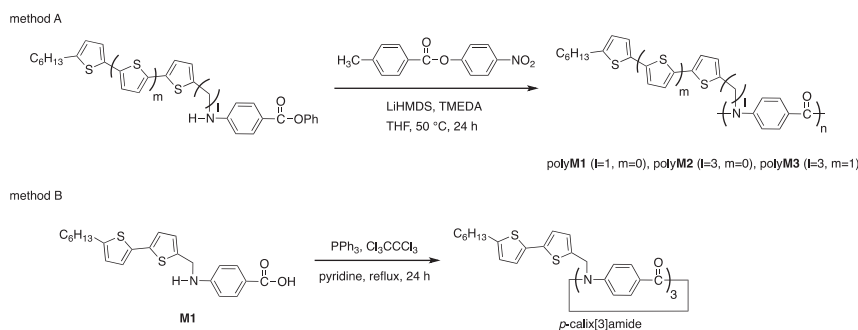
polymerize. By comparing the integral ratio of the methyl proton signal at the initiating group (2.2 p.p.m.) with that of the methyl proton signal at the hexyl chain end included in the repeating unit (0.9 p.p.m.), the molecular weight of the isolated poly**M1** was calculated to be 4700, which was in good agreement with the theoretical value (4000). The molecular weight distribution (M_w/M_n) determined by the GPC profile was narrow (1.10).

These results indicate that the condensation polymerization of **M1** starts from the initiator and proceeds in a controlled manner. The C=O stretching vibration signal was detected at 1637 cm^{-1} in the IR spectrum, which was close to the value of *N*-methylbenzanilide (1640 cm^{-1}), suggesting that the amide group in poly**M1** preferentially adopts the *cis* conformation.[17] The direct polycondensation of 4-((5″-hexyl-2,2′-bithienyl)methyl)aminobenzoic acid using PPh$_3$ and hexachloroethane was also examined in pyridine at reflux temperature for 24 h (Scheme 1, Method B); however, the polymer molecular weight could not be increased. In the ^{1}H-NMR spectrum of the isolated product, neither the initiating *p*-tolyl group nor the propagating phenyl ester group were detected.

The MALDI-TOF-MS of the product purified by the preparative GPC exhibited a signal at $m/z = 1166.36$ that agreed well with the theoretical mass number of the sodium cation adduct ($m/z = 1166.37$) of *p*-calix[3]amide (cyclic trimer). Accordingly, method A was found to be suitable for the preparation of poly**M1**. The condensation polymerization of **M2** and **M3** were likewise performed using method A, and the corresponding polymers exhibiting narrow molecular weight distributions were obtained after precipitation into hexane. When the concentration of the initiator was decreased to 5 mol% relative to **M2**, the molecular weight of poly**M2** became larger (7300 estimated by GPC) while maintaining the narrow molecular weight distribution (1.13). The C=O stretching vibration signal in poly**M2** and poly**M3** (1644 cm^{-1}) likely indicates the *cis* amide conformation similar to that in poly**M1**. All the polymers were soluble in THF, CHCl$_3$ and toluene, while poly**M2** and poly**M3** exhibited better solubilities than poly**M1**. The polymerization results are summarized in Table 1, and the typical ^{1}H-NMR spectrum of poly**M2** is shown in Figure 1.

Optical Properties

The UV and PL spectra of poly**M1** and poly**M2** carrying the bithiophene chromophore were measured in THF solution, and the data were compared with a reference sample **X**, consisting of a mixture of 5,5′-dimethyl-2,2′-bithiophene and poly(*N*-octyl-*p*-benzamide) having a number-averaged molecular weight of 4200 (Figure 2). The concentration of bithiophene was adjusted to 10^{-5} M. As the degree of polymerization was ~10, the concentration of the polymer chain was calculated to be ~10^{-6} M. (The concentration of 10^{-6} M may be

Scheme 1 Condensation polymerization of phenyl 4-aminobenzoate derivatives with oligothiophene attached to the nitrogen atom.

insufficient to completely exclude the possibility of 'intermolecular interaction' of polymer chains. However, the measurement at the lower concentration (10^{-7} M) included substantial experimental errors due to the small molar absorption coefficient and the low fluorescence QY of oligothiophene chromophores.) The absorption maximum of poly**M2** with the trimethylene spacer exhibited a small redshift (5 nm) from that of **X**, and the spectra did not depend on the polymer molecular weight. However, for poly**M1** with the methylene spacer, the absorption maximum exhibited a larger redshift (8 nm) and a shoulder peak was observed at ∼380 nm (Figure 3a). The emission spectrum of poly**M1** exhibited a broad peak at ∼480 nm, which is likely due to the electronic interaction between the bithiophene chromophores (Figure 3b).[15,16] When the emission

Table 1 Polymerization results of M1, M2 and M3

	M_n			M_w/M_n[a]	Conv/%[b]	Yield/%[c]
	Theoretical	GPC[a]	NMR[d]			
Poly**M1**	4000	4400	4700	1.10	90	85
Poly**M2**	4200[e]	4600	4200	1.17	Quant	76
	8400[f]	7300	6800	1.13	Quant	76
Poly**M3**	5100	4700	5100	1.18	91	76

Abbreviations: GPC, gel permeation chromatography; NMR, nuclear magnetic resonance.
[a]Estimated from GPC (THF as eluent) based on polystyrene standard samples.
[b]Calculated from the integral ratio of methylene proton signal on the amide nitrogen of monomer and polymer.
[c]Purified by precipitation into hexane.
[d]Calculated from the integral ratio of methyl proton signal at the initiating group with that of methyl proton signal at the hexyl chain end included in the repeating unit.
[e][**M2**]/[Initiator] = 10.
[f][**M2**]/[Initiator] = 20.

Figure 1 ^{1}H-nuclear magnetic resonance (NMR) spectrum of poly**M2** (M_n = 4200) in CDCl$_3$.

Figure 3 (**a**) Ultraviolet (UV) and (**b**) photoluminescence (PL) spectra of poly**M1** (solid line), poly**M2** (broken line), and the reference sample **X** (dotted line) in tetrahydrofuran (THF) (10^{-5} M relative to bithiophene) (The excitation wavelengths were those of the absorption maxima).

poly**M1** (l=1,m=0), poly**M2** (l=3, m=0), poly**M3** (l=3, m=1)

Reference sample
X (m=0) and **Y** (m=1)

Figure 2 Chemical structure of the samples used for the measurement of the Ultraviolet (UV) and photoluminescence (PL) spectra.

spectrum of poly**M1** in CH_2Cl_2 solution was collected, the corresponding peak became smaller.

Based on the circular dichroism spectra of polymers in solution and the X-ray crystallographic analyses of oligomers, Tanatani *et al.*[17] determined that poly(*p*-benzamide)s with a chiral side chain on the amide nitrogen atom adapt a helical conformation with three monomer units per turn. Although the circular dichroism spectra could not be collected for poly**M1** and poly**M2** without a chiral side chain, they might have a similar helical conformation, which would lead the bithiophene chromophores to have a regular arrangement along the polymer main chain, as depicted in Figure 4. The obtained results suggest that the short spacer of poly**M1** forces the bithiophene chromophores to be π-stacked to each other, particularly in the excited state and in THF solution (Figure 4a).(The fluorescence QYs of poly**M1** and poly**M2** were 0.75% and 1.1%, respectively.) When the UV and PL spectra of poly**M1** were measured at a higher

concentration (10^{-5} M relative to polymer chain), the absorption shoulder peak at ∼380 nm and the broad emission peak at ∼480 nm were slightly enhanced, suggesting the increased intermolecular interaction of the polymer chains (Supplementary Figure S19). Conversely, the bithiophenes included in poly**M2** with the long spacer are rather flexible, and the π-stacked interaction is impossible, not only in the ground state but also in the excited state (Figure 4b). (The fluorescence QYs of poly**M1** and poly**M2** were 0.75% and 1.1%, respectively.)

The UV and PL spectra of the cyclic trimer of **M1** (*p*-calix[3]amide) were also measured in THF solution (Supplementary Figure S20). In contrast to poly**M1**, the emission band at ∼480 nm was not observed, suggesting that the multiple assembly of bithiophene in the *p*-calix[3]amide scaffold is insufficient for the π-stacked interaction of the bithiophene chromophores. The UV and PL spectra of poly**M3** were likewise measured in THF solution (Supplementary Figure S21). A small shoulder was observed in the absorption spectrum of poly**M3,** and the emission spectrum of poly**M3** exhibited an unambiguous redshift compared with sample **Y**, which consists of a mixture of 5,5″-dihexyl-2,2′:5′,2″-terthiophene with poly(*N*-octyl-*p*-benzamide). The choice of solvent had a small influence on the emission spectra of poly**M3**. As both poly**M2** and poly**M3** have same trimethylene spacer between the oligothiophene and the amide nitrogen atom, the wide conjugated system of terthiophene is susceptible to the strong π-stacked interaction at the polymer side chain.

CONCLUSIONS

Three phenyl 4-aminobenzoate derivatives with oligothiophene connected to the amide nitrogen atom through an alkylene spacer were prepared. The condensation polymerization of the monomers was performed using an initiator and a base in the presence of a chelating reagent. Poly(*p*-benzamide)s with narrow molecular weight distributions were obtained, as confirmed by the GPC profile, and the ^{1}H-NMR spectra suggested that the polymerization starts from the initiator and proceeds in a controlled manner. From the IR spectra, the amide group in the polymer backbone was found to preferentially adopt the *cis* conformation. By measuring the UV and PL spectra in solution, the π-stacked interaction between the oligothiophene chromophores was found to depend on the length of both the alkylene spacer and the conjugated system.

Supporting Information Available: The complete synthetic procedure for producing the monomers and the UV and PL spectra of poly**M1**, the cyclic trimer of **M1**, and poly**M3** are available free of charge via the Internet at http://www.nature.com/pj.

CONFLICT OF INTEREST

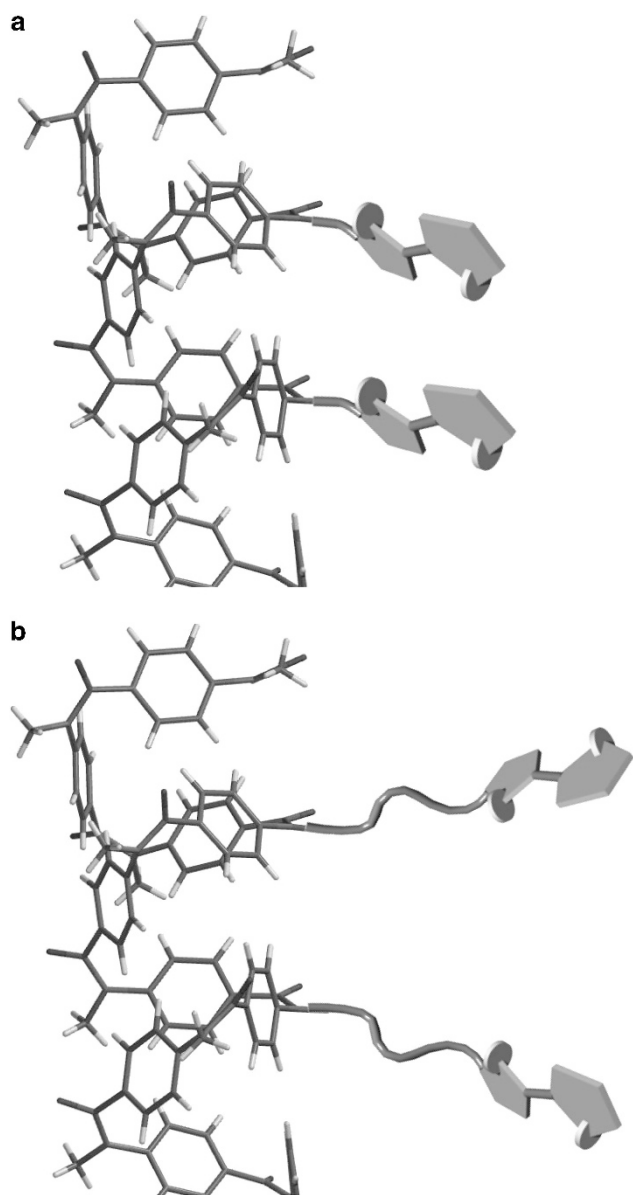The authors declare no conflict of interest.

Figure 4 Schematic illustration of (**a**) poly**M1** and (**b**) poly**M2** with a methylene and trimethylene spacer, respectively.

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