

ORIGINAL ARTICLE

Polymer reaction of poly(*p*-phenylene–ethynylene) by addition of decaborane: modulation of luminescence and heat resistance

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Polymer reactions of poly(*p*-phenylene–ethynylene) (PPE) based on the addition reaction of decaborane to the carbon–carbon triple bond were successfully carried out. The platform polymer was synthesized through Sonogashira–Hagihara coupling polymerization. The effective introduction of the boron cluster, and thus the subsequent formation of *o*-carborane, was supported by ^1H and ^{11}B nuclear magnetic resonance spectroscopies. The introduction rate of decaborane to the polymer main chain was proportional to the feed ratio of decaborane. Ultraviolet–visible absorption and photoluminescence studies illustrate the shortening of the effective π -conjugation length caused by the introduction of carborane clusters. Furthermore, the introduction of the boron cluster by the polymer reaction efficiently enhanced the heat resistance of PPE.

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Keywords: addition reaction; carborane; π -conjugated polymer; heat resistance; luminescence

INTRODUCTION

π -Conjugated polymers have attracted considerable attention for photonic and electronic applications, such as organic light-emitting diodes, photo-voltaics, organic lasers and organic field-effect transistors, as well as other organic devices.^{1–6} Among various π -conjugated polymers, poly(*p*-phenylene–ethynylene)s (PPEs) are a class of the most promising polymers because of their high fluorescence quantum yield, stimuli-responsive emission and highly planarized structure.^{7–10} A large number of studies have demonstrated the synthesis and device fabrication of PPEs; however, it still remains a matter of research to enhance various properties.

An expedient way to improve the properties of π -conjugated polymers, for example, large molar absorption coefficient, highly efficient emission and nonlinear optical properties, is by hybridizing π -conjugated polymers with inorganic materials.^{11–17} For example, π -conjugated polymers containing polyhedral oligomeric silsesquioxanes or polyoxometalate have shown high thermal, mechanical, oxidation-resistance and electrochemical properties, as well as heat resistance.^{18–24} Recently, we reported the synthesis of novel π -conjugated polymers with an icosahedral carborane cluster in their main chain, their great thermal durability and surprising optical properties, that is, aggregation-induced emission based on the molecular orbital of *o*-carborane.^{25–32} Although the hybridization of π -conjugated polymers with inorganic clusters has given prominent results, the multistep synthesis of monomers containing inorganic clusters would have obstructed a thorough investigation in this field. One methodology to lessen the burden on synthesis is the polymer reaction of π -conjugated polymers. Several reports have described the polymer reaction of π -conjugated polymers and drastic modification of

optical and/or thermal properties,^{33–36} while the variation is still limited. From this viewpoint, we focused attention on the addition reaction of decaborane to the carbon–carbon triple bond, known as a facile synthetic method, to obtain an *o*-carborane cluster. In this article, we present the efficient polymer reaction of PPEs by the addition reaction of decaborane and consequent changes in luminescent and thermal properties.

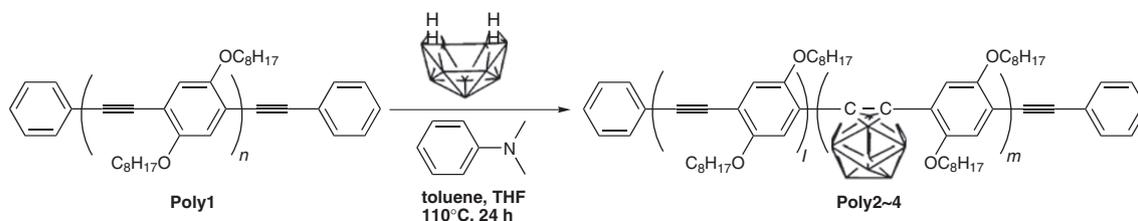
EXPERIMENTAL PROCEDURE

Instruments

^1H (400 MHz) and ^{11}B (128 MHz) nuclear magnetic resonance (NMR) measurements were recorded on a JEOL JNM-EX400 instrument (JEOL Ltd., Tokyo, Japan). ^1H NMR spectra used 0.05% tetramethylsilane as an internal standard, and ^{11}B NMR spectra were externally referenced to $\text{BF}_3\cdot\text{Et}_2\text{O}$ at room temperature. Number-average molecular weight and molecular-weight distribution values were estimated on a TOSOH size exclusion chromatography system (TOSOH Corp., Tokyo, Japan) equipped with a polystyrene gel column (TOSOH TSKgel G3000HXL) using an ultraviolet detector (UV-8020) and refractive-index (RI-8020) detector at 40 °C. Thermogravimetric analysis was performed using a TG/DTA 6200 (SEIKO Instruments Inc., Chiba, Japan) with a heating rate of 10 °C min⁻¹ under dry air. Ultraviolet–visible spectra were recorded on a Shimadzu UV-3600 spectrophotometer (SHIMADZU Corp., Kyoto, Japan) at room temperature. Fluorescence emission spectra and absolute quantum yield by the integrating sphere method were recorded on a HORIBA Jobin Yvon Fluoromax-4 spectrofluorometer (HORIBA Jobin Yvon Inc., Edison, NJ, USA).

Materials

All synthetic procedures were performed under an argon atmosphere. Unless stated otherwise, all reagents were obtained from commercial



Scheme 1 Polymer reaction of a PPE with decaborane.

sources and used without further purification. Tetrahydrofuran (THF) and triethylamine were purified using a two-column solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA, USA). 2,5-Bis(octyloxy)-1,4-diiodobenzene and 2,5-bis(octyloxy)-1,4-diethynylbenzene were synthesized and characterized according to literature.³⁷

Synthesis of Poly1

2,5-Bis(octyloxy)-1,4-diiodobenzene (1.47 g, 2.50 mmol), 2,5-bis(octyloxy)-1,4-diethynylbenzene (0.66 g, 2.25 mmol), Pd(PPh₃)₄ (146 mg, 125 μmol) and CuI (16 mg, 125 μmol) were combined in anhydrous THF (30 ml) and triethylamine (15 ml). Ethynylbenzene (110 μl, 0.50 mmol) was added to the reaction mixture, which was then refluxed for 24 h. After polymerization, the reaction mixture was diluted with CHCl₃ and washed with aqueous NH₃ solution (10 wt%), water and brine. The organic layer was dried over MgSO₄ and concentrated. The residue was dissolved in a small amount of CHCl₃ and reprecipitated from a large amount of methanol. The polymer was dried *in vacuo* to obtain **Poly1** as an orange powder. ¹H NMR (CDCl₃): δ (p.p.m.) 7.57–7.51 (trace (2H), end capping Ar-H), 7.37–7.31 (trace (3H), end capping Ar-H), 7.06–6.96 (2H, Ar-H), 4.12–3.93 (4H, -O-CH₂-), 1.93–1.78 (4H, -OCH₂-CH₂-), 1.55–1.44 (4H, -OCH₂CH₂-CH₂-), 1.44–1.07 (16H, -(CH₂)₆-), 0.95–0.77 (6H, -CH₃).

General procedure of polymer reaction

To **Poly1** (35.7 mg, 100 μmol; poly1, $M_n=4900$, $M_w/M_n=2.40$) placed in a dry glass ampule equipped with a magnetic stir bar were added decaborane (610 μg, 5 μmol) and *N,N*-dimethylaniline (1200 μg, 10 μmol) dissolved in toluene (2.5 ml) and THF (2.5 ml), and then the solution was degassed by three freeze-evacuate-thaw cycles. The ampule was subsequently immersed in an oil bath preheated to 110 °C, and it was held for 24 h before being quenched by rapid cooling with liquid nitrogen. The reaction mixture was diluted in chloroform, and the insoluble product was filtered off. The filtrate was concentrated with a rotary evaporator and reprecipitated from a large excess of methanol. The resulting product isolated by filtration was dried under vacuum at room temperature to yield the corresponding polymer **Poly2** as a brown powder with a 90% yield.

RESULTS AND DISCUSSION

Synthesis and characterization

PPE as a platform for the polymer reaction was synthesized by Sonogashira–Hagihara coupling polycondensation between 2,5-bis(octyloxy)-1,4-diiodobenzene and 2,5-bis(octyloxy)-1,4-diethynylbenzene in the mixed solvent of THF–triethylamine. For the end group estimation of molecular weight in ¹H NMR spectroscopy, the feed ratio of the diiodo monomer, diethynyl monomer and ethynylbenzene (end group) was 10/9/2. From ¹H NMR spectroscopy, the number-average molecular weight was resolved as 5200 ($n \sim 14$), and this result was in good agreement with that obtained by gel-permeation chromatography ($M_n=4900$), indicating that diiodo and diethynyl

Table 1 The results of the polymer reaction

Polymer	Decaborane/monomer unit (mol mol ⁻¹)		M_n^a	M_w^a	M_w/M_n^a	Yield (%) ^b
	Calculated	Observed ^c				
Poly1	0	0	4900	12000	2.40	—
Poly2	0.05	0.05	4600	10700	2.33	90
Poly3	0.10	0.08	4500	12400	2.75	84
Poly4	0.20	0.14	3200	4200	2.56	76
Poly5	0.40	—	—	—	—	—

^aCalculated by ¹H nuclear magnetic resonance spectra.

^bEstimated by size exclusion chromatography on the basis of polystyrene standards in CHCl₃.

^cIsolated yields after reprecipitation into MeOH.

monomers underwent an effective palladium-catalyzed polymerization, that is, the expected polymer structure was obtained.

The polymer reaction of **Poly1** was carried out with decaborane(14) in the mixed solvent of toluene–THF at 110 °C for 24 h (Scheme 1). During the reaction, a small amount of dark brown precipitate was formed, which was practically insoluble in chloroform, and the amount of insoluble parts increased with increasing amounts of decaborane. The formation of insoluble parts is presumably responsible for the decrease in yield of the polymer reaction.^{38–40}

Table 1 summarizes the results of the corresponding polymer reaction. The feed ratio of decaborane per triple bond was 0.05, 0.10, 0.20 and 0.40 for **Poly2**, **Poly3**, **Poly4** and **Poly5**, respectively. Unfortunately, an excess production of insoluble parts prevented us from obtaining **Poly5**. The number-average molecular weight of **Poly1–4** decreased with increasing feed ratio. The highly bent nature of the resulting *o*-carborane moieties in the polymer backbone and insoluble product more easily formed from higher molecular weight fragments is presumably responsible for the decrease in the number-average molecular weights of the polymers obtained. This notion is also supported by the decrease in yield with an increase in the feed ratio of decaborane.

The introduction of decaborane to the PPE main chain was confirmed by the ¹H NMR spectra of **Poly1–4** normalized by the signal at 4.05 p.p.m. (-O-CH₂-, Figure 1). **Poly1** exhibited no signal in the area between 3.80 and 2.50 p.p.m., which is attributed to B-H signals in *o*-carborane. As a result of the polymer reaction, a signal increase was observed at around 3.5 p.p.m. (**Poly2**), and broadened peaks were finally observed at 3.70–2.60 p.p.m. (**Poly4**). Furthermore, ¹¹B NMR spectra also showed broad peaks at ~0 to 10 p.p.m. These peaks are assigned to the presence of the *o*-carborane structure, indicating that the polymer reaction successfully introduced decaborane into the PPE main chain. The observed ratios of decaborane per monomer unit were slightly lower than the feed ratios, and the estimated reaction rates were more than 70%, which is consistent with previous reports.^{38,39}

Optical properties

To investigate the optical properties of polymers **Poly1–4**, ultraviolet-visible absorption and fluorescence experiments were carried out in THF (Figure 2). **Poly1** exhibited an absorption maxima at 431 nm, similar to the reported value.^{37,41–43} The introduction of decaborane into the PPE main chain resulted in the hypsochromic shift of the absorption maxima (**Poly2**: 428 nm, **Poly3**: 425 nm, **Poly4**: 419 nm, Figure 2a), probably due to the shortening of the effective π -conjugation length caused by the conversion of triple bonds. **Poly1–4** showed a light-blue emission in the solution state (Figure 2b), and the emission maxima stayed at around 470 nm with shoulder peaks at 497 nm (Table 2). The emission maxima of **Poly1–4** gave 40–50 nm Stokes shift values consistent with the reported PPEs. The contribution of the shoulder peak and Stokes shift value in the fluorescence spectra gradually increased with the increase in the feed ratio of decaborane, indicating the existence of the intramolecular charge transfer state.

In the mixed solvent of THF–H₂O (1:99), the absorption maxima of **Poly1–4** showed a slightly bathochromic shift compared with those in THF solution (**Poly1**: 446 nm, **Poly2**: 439 nm, **Poly3**: 436 nm, **Poly4**: 433 nm), and more importantly, a new shoulder in the

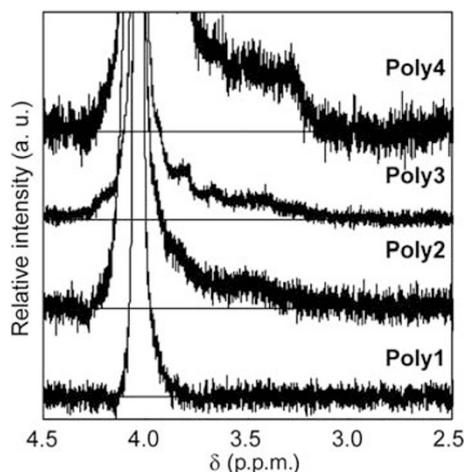


Figure 1 ¹H NMR spectra of **Poly1–4** in CDCl₃. Heights were normalized by the signal at 4.05 p.p.m. (–O–CH₂–).

absorption spectra appeared at around 475 nm (Figure 3a). The contribution of the new shoulder peaks diminished with increasing feed ratio. One possible reason for the appearance of the shoulder peak is the formation of an aggregate structure in the mixed solvent of THF–H₂O (1:99). This explanation was also supported by the fluorescence spectra of **Poly1–4** in the mixed solvent of THF–H₂O (1:99, Figure 3b). The emission maxima of these polymers appeared at longer wavelengths with lower feed ratios (**Poly1**: 568 nm, **Poly2**: 542 nm, **Poly3**: 536 nm, **Poly4**: 529 nm). These observations indicate that the introduction of carborane clusters resulted in the shortening of the effective π -conjugation length of **Poly1–4**.

Poly4 exhibited the broadest fluorescence spectrum in a range of 450–750 nm in the poor solvent, probably due to the contribution of the intramolecular charge-transfer state derived from *o*-carborane moieties. The fluorescence spectra of **Poly1–4** in the film state demonstrated the same tendency as those in the poor solvent (Figure 4). The contribution of emission at longer wavelengths (\sim 750 nm) in the fluorescence spectra increased with an increasing feed ratio of decaborane, whereas the emission maxima appeared at around the same position as those measured in the poor solvent (**Poly1**: 538 nm with shoulder band at 563 nm, **Poly2**: 534 nm with shoulder band at 549 nm, **Poly3**: 534 nm, **Poly4**: 516 nm). These data support the introduction of decaborane as a possible cause of the intramolecular charge-transfer state in the fluorescence spectra and show the applicability of this polymer reaction to tune the optical properties of PPE.

Thermal properties

Boron-containing compounds are typically known as cheap and low-toxic flame retardants because a surface layer of protective char

Table 2 Ultraviolet-visible absorption and photoluminescence properties of **Poly1–4**^a

Polymer	λ_{max} (nm)	$\epsilon\lambda_{max}$ (M ⁻¹ cm ⁻¹)	PL (nm)	Stokes shift (nm)
Poly1	431	36 000	471, 496	40
Poly2	428	22 000	471, 497	43
Poly3	425	69 000	471, 497	46
Poly4	419	56 400	469, 497	50

^aMeasured in tetrahydrofuran solution (1.0 \times 10⁻⁵ M) at room temperature.

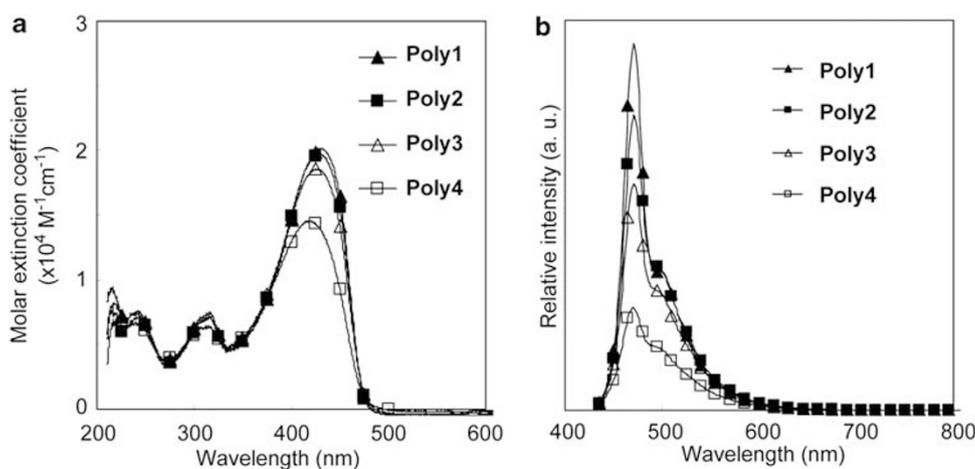


Figure 2 (a) Ultraviolet-visible absorption and (b) fluorescence spectra of **Poly1–4** THF solution (1.0 \times 10⁻⁵ M).

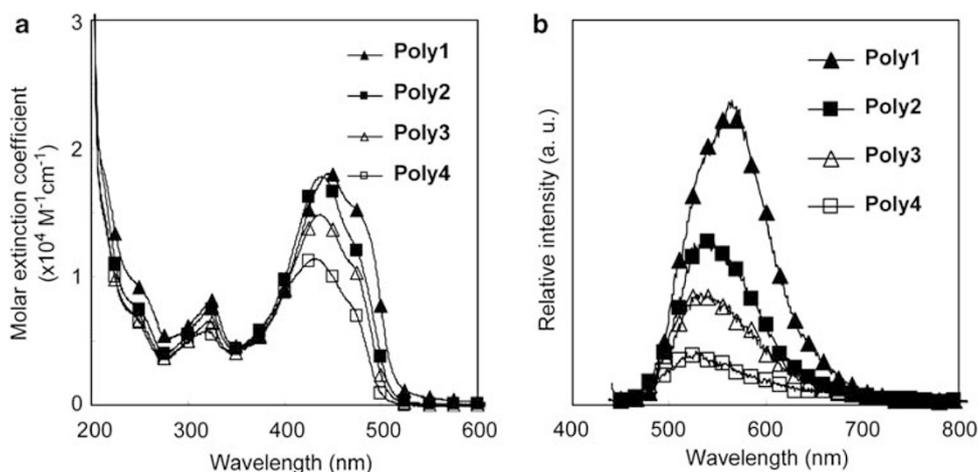


Figure 3 (a) Ultraviolet-visible absorption and (b) fluorescence spectra of Poly1–4 in the mixed solvent of THF–H₂O (1:99, 1.0 × 10⁻⁵ M).

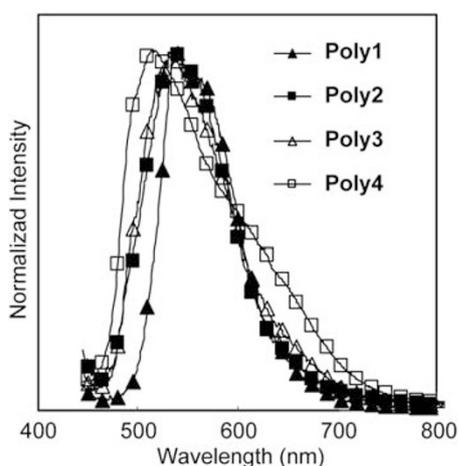


Figure 4 Fluorescence spectra of Poly1–4 in the film state.

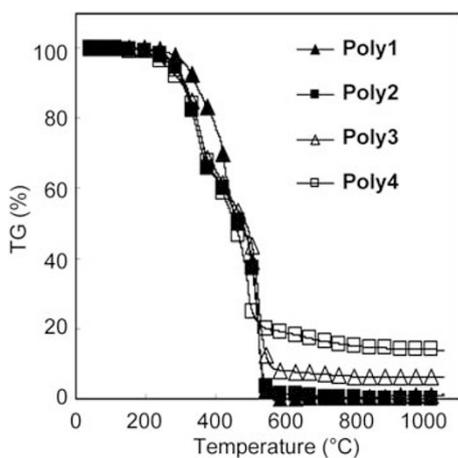


Figure 5 Thermogravimetric analysis thermograms of Poly1–4 under dry air.

formed on heating acts as a barrier against oxygen and prevents the oxidation of carbon.^{44–47} Information on the thermal properties of the obtained polymers was obtained by thermogravimetric analysis, as

Table 3 Thermal properties of Poly1–4

Polymer	Ceramic yield (%)		T_{d5} (°C) ^c	T_{d50} (°C) ^d
	Calculated ^a	Observed ^b		
Poly1	0	0	316.9	466.8
Poly2	4.8	1.11	283.6	468.5
Poly3	7.59	6.30	282.1	485.5
Poly4	12.71	13.92	258.1	453.7

^aDetermined by ¹H nuclear magnetic resonance.

^bDetermined by TGA under dry air after heating to 1050 °C: heating rate=10 °C min⁻¹.

^c5% Degradation temperature given by thermogravimetric analysis (TGA).

^d50% Degradation temperature given by TGA.

shown in Figure 5. The introduction of *o*-carborane moieties into the polymer main chain led to an extreme resistance to heat and an improvement in ceramic yields on thermolysis to 1050 °C (Table 3) because of the excellent char-forming property of compounds containing carborane. The 5% degradation temperature decreased with increasing *o*-carborane content, probably due to the promotion of carbonization and dehydration caused by boron. These findings suggest that the polymer reaction efficiently enhanced the heat resistance of PPE.

CONCLUSION

In summary, we synthesized PPE through Sonogashira–Hagihara coupling polymerization as a platform and successfully carried out subsequent polymer reactions by the addition of decaborane. The effective introduction of boron clusters, and thus the formation of *o*-carborane, was confirmed by ¹H and ¹¹B NMR spectroscopies, and the introduction rate was proportional to the feed ratio of decaborane. Ultraviolet-visible absorption and photoluminescence studies reveal the shortening of the effective π -conjugation length caused by the introduction of carborane clusters; however, the polymer with the highest *o*-carborane content showed indications of an intramolecular charge-transfer state. Moreover, the polymer reaction efficiently improved the heat resistance of PPE. Further work is currently underway to design the polymer reaction with greater amounts of decaborane.

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