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Enzyme and Transition-Metal-Complex Catalyzed Synthesis of Polyphenols with Pendant Oligo(*p*-phenylene) and Their Optical, Electrochemical, and Thermal Properties

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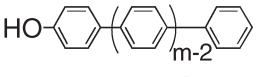
ABSTRACT: Horseradish peroxidaze (HRP)-catalyzed polymerization of 4-hydroxy[1,1′;4′,1″]terphenyl (**MonoPh(3)OH**), 4-bromo-4′-hydroxybiphenyl (**MonoBrPh(2)OH**), and 4-bromo-4″-hydroxy[1,1′;4′,1″]-terphenyl (**MonoBrPh(3)OH**) caused oxidative coupling at the hydroxyphenyl group to yield polyphenols with a pendant oligo-*p*-phenylene (OPP): **PolyPh(3)OH** and **PolyBrPh(*m*)OH** ($m = 2$ and 3; $m - 1$ denotes the number of pendant benzene rings). Polyphenols with a longer OPP chains (**PolyPh(*m*)OH**; $m = 4$ and 5) were obtained through the Pd-complex catalyzed reaction of **PolyBrPh(*m*)OH** ($m = 2$ and 3) with 4-biphenylboronic acid. The Pd-complex-catalyzed polymerization of 3,5-dibromo-4-methoxy[1,1′;4′,1″]-terphenyl or 3,5-dibromo-4-octyloxy[1,1′;4′,1″;4″,1‴]quaterphenyl with 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester or 2,5-dioctyloxybenzene-1,4-diboronic acid yielded polyphenylenes **PolyPh(*m*)OMeFlu** ($m = 3$ and 4) and **PolyPh(3)OMePh**, respectively, and hydrolysis of the methyl group provided polyphenylenes with the phenolic OH groups **PolyPh(3)OHFlu** and **PolyPh(3)OHPh**, respectively. Deprotonation of the OH group of the polyphenols with the pendant OPP obtained by the treatment with NaH caused a bathochromic shift of absorption maxima (λ_{max}'s) of the polymers. The bathochromic shift of the deprotonated species **PolyPh(*m*)ONa** ($m = 3$, 4, and 5), **PolyPh(3)ONaFlu**, and **PolyPh(3)ONaPh** increased with an increase in the donor numbers (DNs) of the solvents. **PolyPh(*m*)OH** ($m = 3$, 4, and 5), **PolyPh(3)OHFlu**, and **PolyPh(3)OHPh** were photoluminescent (PL) in solution. The emission peak positions of **PolyPh(*m*)OH** and **PolyPh(*m*)ONa** depended on the DNs of the solvents; that is, the emission colors could be tuned by changing the solvent. The polymers were electrochemically active in film.

Introduction

Oligo(*p*-phenylene)s (OPPs) have attracted much attention due to their usability as luminophores for light-emitting materials,[1] as semiconductors for field-effect transistors,[2] as rigid-rod cores for liquid crystalline materials,[3] and as amphiphilic materials for biological applications.[4] Recently, OPPs have been converted into planarized ladder-type materials,[5] relatively large polycyclic aromatic hydrocarbons,[6] novel macrocycles,[7] and star-shaped compounds.[8] Polymers containing OPP units are used as optical functional materials because they show photoluminescence with a high quantum yield.[9] The introduction of long alkyl side chains in the OPP unit and *m*-phenylene linkage in the polymer backbone can improve the solubility of the polymers.[10,11] Recently, soluble polyphenylenes comprising of *p*- and *m*-phenylenes have been reported.[12] On the basis of these reports, polyphenylenes with the OPP unit linked by the *m*-phenylene group may show photoluminescence and enhanced solubility.

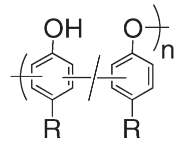
Recently, we reported the synthesis of OPPs with a hydroxyl group **MonoPh(*m*)OH** ($m = 3$, 4, and 5; *m* denotes the number of benzene rings) and their unique optical properties.[13]



MonoPh(*m*)OH

MonoPh(*m*)OH moieties exhibit significant solvatochromism after deprotonation of the OH group with NaH; that is, the absorption maxima (λ_{max}'s) of **MonoPh(*m*)ONa** in solution shift to longer wavelengths with an increase in the donor numbers (DNs) of the solvents. Moreover, the emission colors of the solutions of **MonoOPP(*m*)ONa** can be tuned by changing the solvent. On the basis of these results, poly(phenol)s with the pendant OPP and their deprotonated products should show interesting optical properties suitable for emitting materials. However, to the best of our knowledge, there have been no studies on poly(phenol)s with the pendant OPP. This appears to be due to the difficulty associated with synthesizing poly(phenol)s with the pendant OPP.

Horseradish-peroxidaze (HRP)-catalyzed polymerization of 4-substituted phenols has been applied to obtain functional poly(phenol)s under mild reaction conditions.[14] For example, poly(phenol)s with metal complexes, amino acids, and sugars have been synthesized.[15−17] In this study, poly(phenol)s with the pendant OPP unit were synthesized by HRP-catalyzed polymerization of **MonoPh(*m*)OH**. HRP-catalyzed polymerization of phenol derivatives is known to yield polymers comprised of the hydroxyphenylene (unit A) and oxyphenylene (unit B) units, as shown below.[14]



unit A unit B

In order to obtain well-defined poly(phenol)s with the pendant OPP, we carried out transition-metal-complex catalyzed

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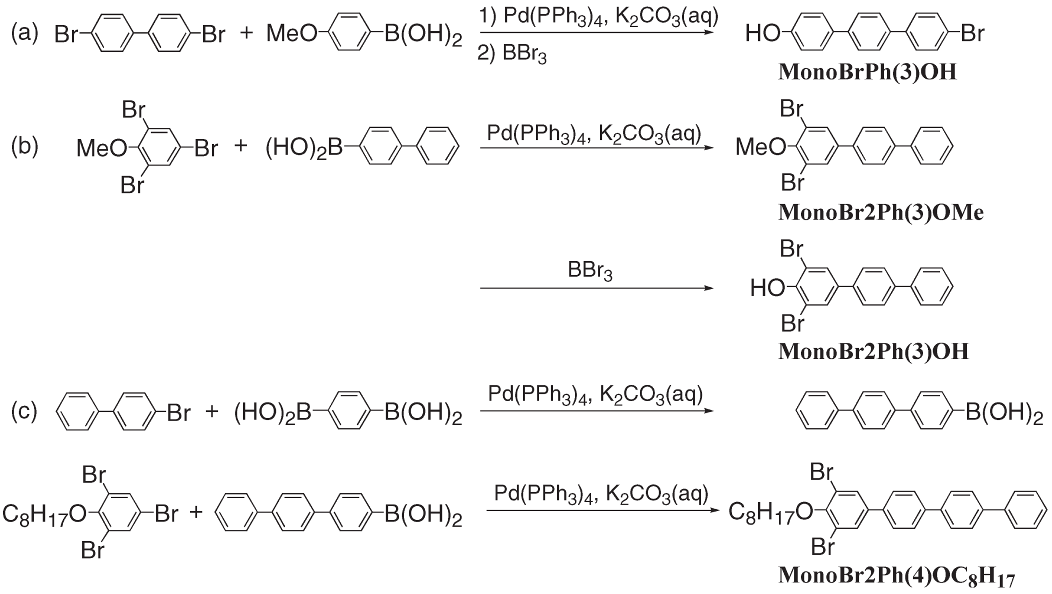
Scheme 1. Synthesis of Monomers



polymerization of 3,5-dibromo-4-methoxy[1,1′;4′,1″]terphenyl and 3,5-dibromo-4-octyloxy[1,1′;4′,1″;4″,1‴]quaterphenyl with aromatic diboronic acids and hydrolysis of the OMe group for the obtained polymers. Investigating the chemical properties of poly(phenol)s with the pendant OPP would provide fundamental information for the development of new emitting materials.

We herein report the synthesis of poly(phenol)s with the pendant OPP unit by enzymatic and transition-metal-complex catalyzed polymerization and their optical, electrochemical, and thermal properties.

Results and Discussion

Synthesis. A monomer with a 4-bromophenyl group (**MonoBrPh(3)OH**) was synthesized through the 1:1 Suzuki coupling reaction of 4,4′-dibromobiphenyl with 1-methoxyphenyl-4-boronic acid and hydrolysis of the methoxy group (Scheme 1a). Using an excess amount of 4,4′-bromobiphenyl prevented the 2:1 side reaction for 1-methoxyphenyl-4-boronic acid and yielded the expected product as a precipitate from the reaction mixture. The 1:1 Suzuki coupling reaction of 2,4,6-tribromoanisole with 4-biphenylboronic acid or [1,1′;4′,1″]terphenyl-4″-boronic acid, which was synthesized by the 1:1 Suzuki coupling reaction of 4-bromobiphenyl with benzene-1,4-diboronic acid, yielded 3,5-dibromo-4-methoxy-[1,1′;4′,1″]terphenyl (**MonoBr2Ph(3)OMe**) and 3,5-dibromo-4-methoxy[1,1′;4′,1″;4″,1‴]quaterphenyl (**MonoBr2Ph(4)OMe**), respectively (Scheme 1b). The hydrolysis of **MonoBr2Ph(3)OMe** with BBr_3 yielded **MonoBr2Ph(3)OH**. **MonoBr2Ph(4)OMe** showed poor solubility in organic solvents, which prevented its use as a monomer. In order to enhance the solubility, a long alkyl chain was introduced in the monomer; the reaction of 2,4,6-tribromooctyloxybenzene with [1,1′;4′,1″]terphenyl-4″-boronic acid yielded the soluble product **MonoBr2Ph(4)OC_8H_{17}** (Scheme 1c).

The structures of obtained compounds were determined by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. The ^{1}H NMR spectrum of **MonoBr2Ph(3)OMe** showed two singlet peaks due to the methoxy and phenyl protons of the 1-methoxy-2,6-dibromobenzene ring with a peak integral ratio of 3:2; this result confirmed the proposed structures.

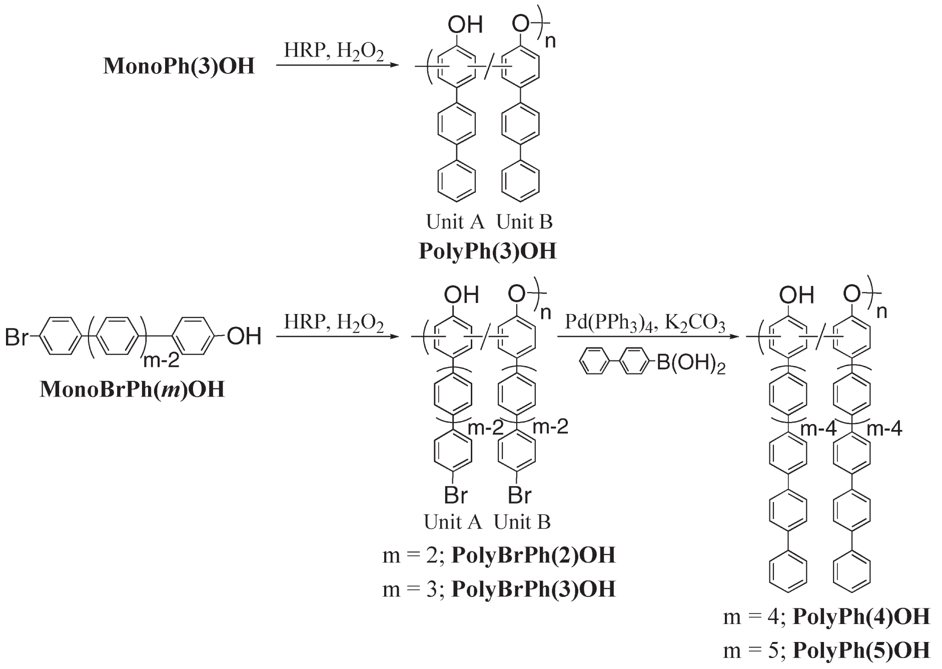
Methods for synthesizing polyphenols having the pendant OPP unit (**PolyPh(*m*)OHs**; $m = 3$, 4, and 5) are shown in Scheme 2.

The HRP-catalyzed polymerization of **MonoPh(3)OH** and **MonoBrPh(*m*)OH** ($m = 2$ and 3) by using hydrogen peroxide as an oxidizing reagent in a mixture of 1,4-dioxane and phosphate buffer (pH = 7.4) resulted in 90%, 94%, and 94% yields of **PolyPh(3)OH** and **PolyBrPh(*m*)OH** ($m = 2$ and 3), respectively (Scheme 2). Polyphenols with a prolonged OPP **PolyPh(*m*)OH** ($m = 4$ and 5) were obtained by the Pd-complex-catalyzed reaction of **PolyBrPh(*m*)OH** ($m = 2$ and 3) with 4-biphenylboronic acid in 95% and 98% yields, respectively. Elemental analysis revealed that the reaction of **PolyBrPh(*m*)OH** ($m = 2$ and 3) with 4-biphenylboronic acid proceeded to completion. **PolyPh(*m*)OH** ($m = 4$ and 5) could not be obtained through the direct polymerization of **MonoPh(4)OH** and **MonoPh(5)OH** because the monomers showed low solubility in the mixture of 1,4-dioxane and phosphate buffer.

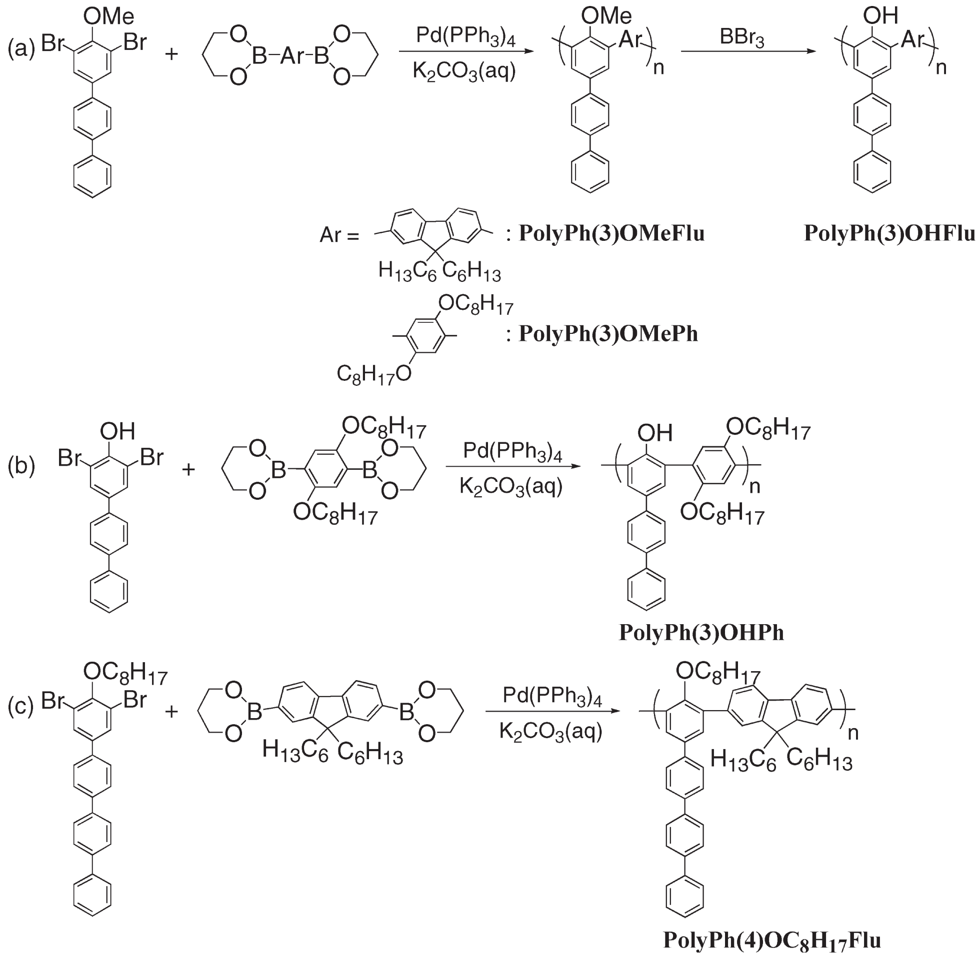
The molar ratio between the hydroxyphenylene (unit A) and oxyphenylene (unit B) units in the obtained polymers was determined by titration of the hydroxy group in unit A with KOH. The titration suggested that the molar ratios of units A and B in **PolyPh(3)OH** and **PolyBrPh(*m*)OH** ($m = 2$ and 3) were 74:26, 93:7, and 85:15, respectively. These values are in good agreement with the fact that HRP-catalyzed polymerization of phenol derivatives yields polymers with a high content of unit A.[14]

Well-defined polyphenylenes with the pendant OPP unit were obtained by transition-metal-complex catalyzed polymerization using **MonoBr2Ph(3)OMe** and **MonoBr2Ph(4)OC_8H_{17}** as starting materials. Pd-complex-catalyzed polymerization of **MonoBr2Ph(3)OMe** with 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester or 2,6-dioctyloxybenzene-1,4-diboronic acid resulted in 94% yields for both **PolyPh(3)OMeFlu** and **PolyPh(3)OMePh** (Scheme 3a). Hydrolysis of the OMe group of **PolyPh(3)OMeFlu** with BBr_3 yielded **PolyPh(3)OHFlu**. However, the treatment of **PolyPh(3)OMePh** with BBr_3 caused hydrolysis of the OMe and OC_8H_{17} groups and yielded a product with poor solubility. The Pd-complex-catalyzed polymerization of **MonoBr2Ph(3)OH** with 2,6-dioctyloxybenzene-1,4-diboronic acid resulted in a 46% yield of **PolyPh(3)OHPh** (Scheme 3b). The Pd-complex-catalyzed polymerization of **MonoBr2Ph(4)OC_8H_{17}** with 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester resulted in a 94%

Scheme 2. HRP-Catalyzed Synthesis of Poly(phenol)s Having a Pendant OPP Group



Scheme 3. Pd-Complex-Catalyzed Synthesis of Poly(phenol)s Having a Pendant Biphenyl Group



yield of **PolyPh(4)OC$_8$H$_{17}$Flu** (Scheme 3c). Hydrolysis of the OC$_8$H$_{17}$ group in **PolyPh(4)OC$_8$H$_{17}$Flu** with BBr$_3$ did not occur.

In contrast to **MonoPh(*m*)OH** (*m* = 3 and 4), which were insoluble in nonpolar organic solvents such as chloroform and dichloromethane, **PolyPh(*m*)OH** (*m* = 3 and 4) and

Table 1. Synthesis Results and Molecular Weights

	yield (%)	M_n[a]	M_w[a]
PolyPh(3)OH	90	5780[b]	7900[b]
PolyBrPh(2)OH	94	6210[b]	6390[b] (75700)[f]
PolyBrPh(3)OH	94	4590[b]	6130[b]
PolyPh(4)OH	95	8040[b]	9620
PolyPh(5)OH	98	c	c
PolyPh(3)OMeFlu	94	17230[d]	38440[d]
PolyPh(4)OMeFlu	94	5330[d,e]	8500[d,e]
PolyPh(3)OMePh	64	5100[d]	6800[d]
PolyPh(3)OHFlu	88	26660[d]	53370[d]
PolyPh(3)OHPh	46	3800[d]	4900[d]

[a] Determined by GPC (eluent = DMF containing 0.006 M LiBr[b] or $CHCl_3$[d]) vs polystyrene standards. [b] GPC eluent = DMF containing 0.006 M LiBr. [c] Not measured due to insolubility in the eluent. [d] GPC eluent = DMF containing $CHCl_3$. [e] Chloroform soluble part. [f] The M_w value determined by LS analysis was shown in parentheses.

PolyBrPh(*m*)OH ($m = 2$ and 3) were soluble in nonpolar and polar organic solvents such as 1,4-dioxane, *N*,*N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). However, **PolyPh(5)OH** showed a considerably lower solubility in the organic solvents. **PolyPh(3)OMeFlu**, **PolyPh(3)OMePh**, and their deprotonated products were soluble in chloroform and THF.

The M_n and M_w values of the obtained polymers determined by GPC measurements are summarized in Table 1. As shown in the table, **PolyPh(4)OH** showed higher M_n and M_w values than the starting material **PolyBrPh(2)OH** did. However, the molecular weights of **PolyPh(5)OH** were somewhat lower than those of **PolyBrPh(3)OH** due to the low solubility of **PolyPh(5)OH** in the eluent. The M_n and M_w values of **PolyPh(3)OMeFlu** were 17,230 and 38,440, respectively, while those of **PolyPh(3)OMePh** were 5,100 and 6,800, respectively. The higher M_n and M_w values of **PolyPh(3)OHFlu** and **PolyPh(3)OHPh** than those of **PolyPh(3)OMeFlu** and **PolyPh(3)OMePh** appears to be due to the strong interaction of **PolyPh(3)OHFlu** and **PolyPh(3)OHPh** with polystyrene gel in the GPC column. An absolute molecular weight (M_w = 75,700) of **PolyBrPh(2)OH** was determined by a light scattering (LS) method. The larger M_w value of **PolyBrPh(2)OH** estimated by the light scattering method as compared with that estimated by the GPC method suggests the presence of interaction of the polymer with the GPC column and/or partial aggregation of the polymer in the static solution used for the light scattering analysis. The light scattering analysis by the scattered light intensity gives an M_w of aggregated molecules in the solution.[18]

IR Spectra. Figure 1 depicts IR spectra of **PolyPh(*m*)OHs** ($m = 3$, 4, and 5). The main features of the three spectra are identical: the absorption peak at 3428 cm^{-1} is due to O−H stretching vibrations; the strong peak at 1484 cm^{-1} is due to phenyl ring vibrations; and the bands at approximately 820 and 760 cm^{-1} are due to the out-of-plane C−H bending of *p*-phenylene and phenyl rings, respectively. The intensities of absorptions due to the out-of-plane C−H bending of the *p*-phenylene and terminal phenyl rings were used to estimate the degree of polymerization of poly(*p*-phenylene).[19] The absorption ratios I_{820}/I_{760} of **PolyPh(*m*)OHs** ($n = 3$, 4, and 5) were 0.8, 1.7, and 2.7, respectively; they were largely consistent with the ratio of *p*-phenylene to phenyl rings in these polymers.

The absorptions due to the OMe group disappeared after hydrolysis of the OMe group, and new absorptions due to O−H stretching vibration were observed at 3536 and 3534 cm^{-1} in the IR spectra of **PolyPh(3)OHFlu** and **PolyPh(3)OHPh**, respectively.

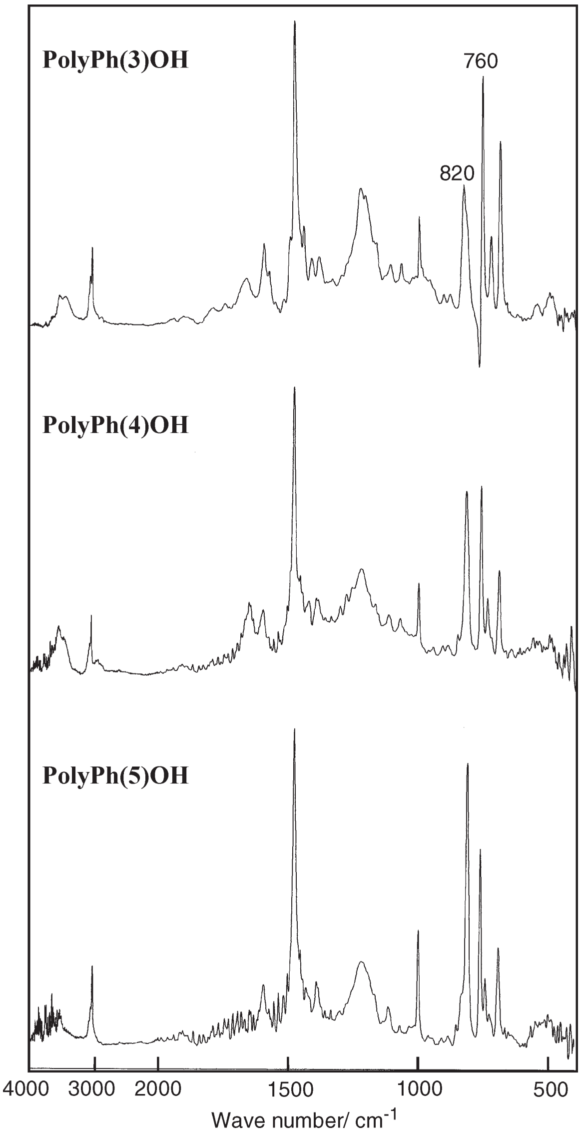


Figure 1. IR spectra of **PolyPh(*m*)OH** (m = 3, 4, and 5).

^{1}H NMR spectra. Figure 2 shows the ^{1}H NMR spectra of **MonoPh(3)OH**, **MonoBrPh(2)OH**, **PolyPh(3)OH**, and **PolyBrPh(2)OH** in $CDCl_3$. Peak assignments for **MonoPh(3)OH** and **MonoBrPh(2)OH** are shown in the figure. The disappearance of the peak assignable to protons (H^a and $H^{a\prime}$) at the *o*-positions of the phenol ring in the ^{1}H NMR spectra of the polymers suggests that the polymerization proceeded predominately at the *o*-positions. This assumption is consistent with the fact that HRP-catalyzed polymerization of phenol derivatives proceeds predominately at the *o*-positions.[14] **PolyPh(3)OH** and **PolyBrPh(2)OH** show the broadening ^{1}H NMR spectra, which is apparently due to the presence of Unit A, Unit B, and the unit bonded at the *m*-positions of the phenol ring to some extent in the polymers. It has been reported that polyphenols synthesized by the HRP-catalyzed polymerization often show broadening ^{1}H NMR spectra.[20]

Figure 3a shows the ^{1}H NMR spectrum of **PolyPh(3)OMeFlu** in $CDCl_3$. The peak at δ 3.28 is assigned to the methyl protons. Signals for aromatic (H^a−H^i) and aliphatic (H^j−H^o) protons were observed in the ranges δ 0.7−2.1 and δ 7.3−7.9, respectively. The relative peak integral ratio supports the structure shown in Scheme 3. As shown in Figure 3b, complete hydrolysis of the OMe group was

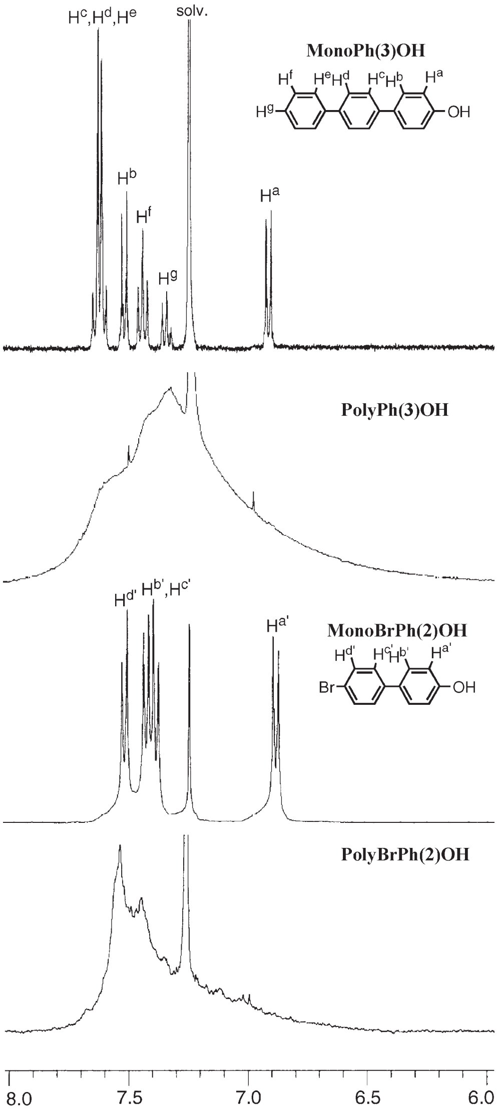


Figure 2. ^{1}H NMR spectra of ^{1}H NMR spectra of **MonoPh(3)OH**, **MonoBrPh(2)OH**, **PolyPh(3)OH**, and **PolyBrPh(2)OH** in $CDCl_3$.

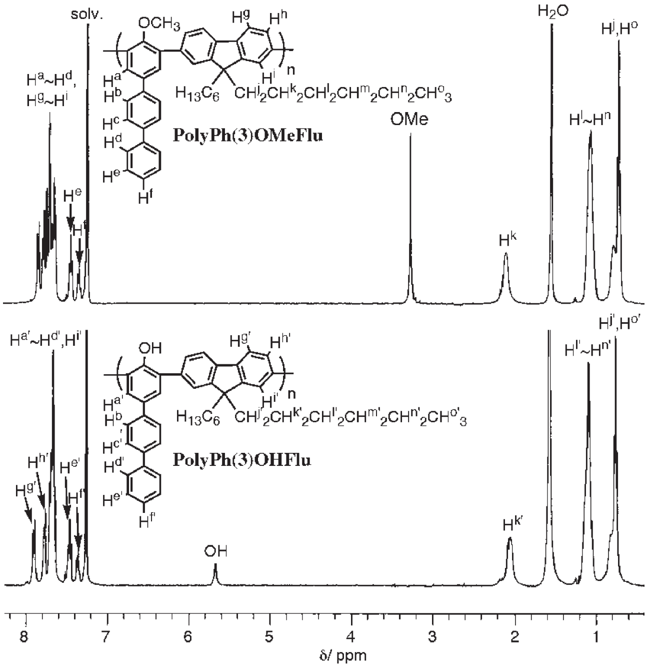


Figure 3. ^{1}H NMR spectra of **PolyPh(3)OMeFlu** and **PolyPh(3)OHFlu** in $CDCl_3$.

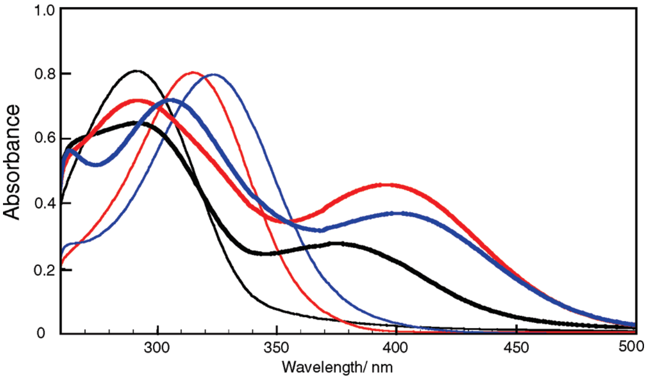


Figure 4. UV−vis spectra of **PolyPh(*m*)OH** (m = 3; black lines, 4; red lines, and 5; blue lines) in DMSO before (thin lines) and after (bold lines) the addition of an excess amount of NaH.

confirmed by the disappearance of the OMe group and appearance of a new peak assignable to the OH group at δ 5.66 in the ^{1}H NMR spectrum of **PolyPh(3)OHFlu**. The structures of **PolyPh(3)OMePh**, **PolyPh(3)OHPh**, and **PolyPh(4)OC$_8$H$_{17}$-Flu** were determined by the ^{1}H and ^{13}C NMR spectra (see Supporting Information) and elemental analysis.

UV−Vis Spectra. Figure 4 depicts UV−vis spectra of **PolyPh(*m*)OH** (m = 3, 4, and 5) in DMSO before and after the addition of an excess amount of NaH. The optical properties are summarized in Table 2. The absorption maxima (λ_{max}'s) of the **PolyPh(*m*)OH** shifted progressively toward longer wavelengths due to the expansion of the π-conjugation system as the number of benzene rings increased. New absorptions were appeared at longer wavelengths by the treatment of the DMSO solutions of **PolyPh(*m*)OH** with NaH. The appearance of the new absorptions was apparently due to the formation of phenoxy anion of the unit A; the charge shift from the sodium phenoxy group to the adjacent phenylene rings was mainly responsible for the appearance of the absorptions at longer wavelengths. The DMSO solutions of **MonoPh(*m*)OH** caused similar bathochromic shifts of λ_{max}'s by deprotonation with NaH.[13] The absorptions at shorter wavelengths in the UV−vis spectra of **PolyPh(*m*)ONa** were due to unit B. **PolyPh(*m*)OH** had a larger content of unit A than unit B; however, the absorption due to the deprotonated unit A was smaller than that due to unit B in the UV−vis spectra of **PolyPh(*m*)ONa**. This appeared to correspond to the fact that the molar absorption coefficients of **MonoPh(*m*)ONa** were smaller than those of **MonoPh(*m*)OH**.

The wavelength at which the absorptions due to the Unit A of **PolyPh(*m*)ONa** were observed depended on the donor number (DN) of the solvents. As shown in Figure 5, the absorptions due to **PolyPh(*m*)OH** (m = 3, 4, and 5) and unit A of **PolyPh(*m*)ONa** (m = 3, 4, and 5) shift to longer wavelengths as the DNs of the solvent increase. In contrast to the smaller bathochromic shift ($\Delta\lambda$) of **PolyPh(*m*)OH** (m = 3, 4, and 5) with an increase in DNs of the solvents, the $\Delta\lambda$ values of **PolyPh(4)ONa** increased from 313 nm in 1,4-dioxane (DN = 14.8) to 396 nm in DMSO (DN = 29.8) through to a values of 350 nm in THF (DN = 20.0). The larger $\Delta\lambda$ value obtained under the assumption that solvents with a high DN solvate effectively with Na^+ to stabilize the deprotonated species in the solutions. Similar solvatochromic behavior was observed in **MonoPh(*m*)ONa** (m = 3 and 4).[13]

Table 2. UV−Vis Data of Polymers

	absorption/nm					absorption/ nm			
	1,4-dioxane, DN^a = 14.8	THF, DN^a = 20.0	DMF, DN^a = 26.6	DMSO, DN^a = 29.8		1,4-dioxane, DN^a = 14.8	THF, DN^a = 20.0	DMF, DN^a = 26.6	DMSO, DN^a = 29.8
PolyPh(3)OH	288	287	290	291	**PolyPh(3)ONa**	290, 338^b	283, 352	280, 365	293, 374
PolyPh(4)OH	307	308	312	315	**PolyPh(4)ONa**	313, 339^b	300, 360^b	273, 386	292, 396
PolyPh(5)OH	307	315	322	323	**PolyPh(5)ONa**	316	315	308, 384	307, 396
PolyPh(3)OMeFlu	302, 322	302, 323	302, 324	c					
PolyPh(4)OMeFlu	308, 323	307, 321	308 322	318					
PolyPh(3)OMePh	295	294	298	c					
PolyPh(3)OHFlu	301, 317, 340	301, 318, 340	303, 319, 340	c	**PolyPh(3)ONaFlu**	308, 339, 416	306, 358, 415	305, 414, 464	305, 407, 466
PolyPh(3)OHPh	304	305	308	c	**PolyPh(3)ONaPh**	341	366	388	414

[a] DN = donor number of solvents. [b] Shoulder peak. [c] Not measured due to low solubility.

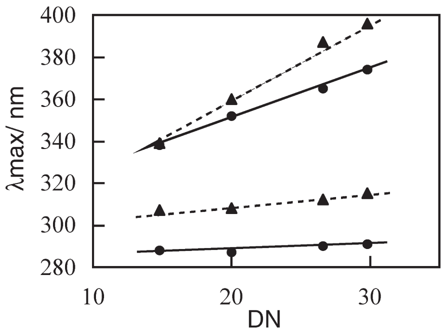


Figure 5. Dependence of absorption positions of **PolyPh(*m*)OH** (*m* = 3 and 4) (*m* = 3 (●) and 4 (▲); solid line) and deprotonated unit A of **PolyPh(*m*)OH** (dotted line) on the DNs of solvents.

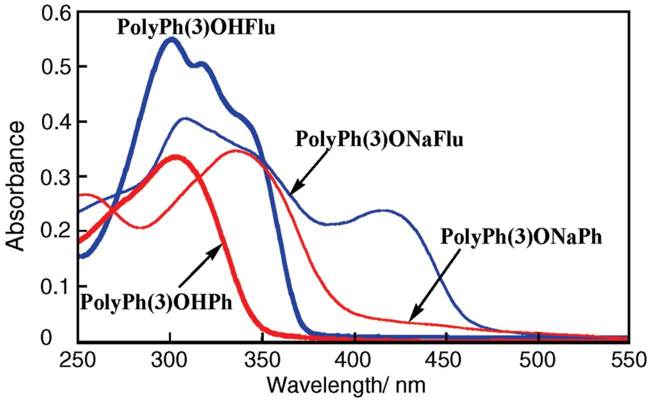


Figure 6. UV−vis spectra of **PolyPh(3)OHFlu** (blue bold line), **PolyPh(3)OHPh** (red bold line), **PolyPh(3)OnaFlu** (blue thin line), and **PolyPh(3)ONaPh** (red thin line) in 1,4-dioxane.

Figure 6 shows the UV−vis spectra of **PolyPh(3)OHFlu**, **PolyPh(3)OHPh**, **PolyPh(3)ONaFlu**, and **PolyPh(3)ONaPh** in 1,4-dioxane. The deprotonation of the OH group in **PolyPh(3)OHFlu** and **PolyPh(3)OHPh** caused a bathochromic shift of the absorptions, as shown in Figure 6. To prove that these observations are due to the deprotonation of the OH group after the treatment with NaH, we confirmed that there was no change in the absorption spectra of **PolyPh(3)OMeFlu** and **PolyPh(3)OMePh** on the addition of NaH. The absorption positions of **PolyPh(3)OHPh** were observed at shorter wavelengths than those of **PolyPh(3)OHFlu** because the octyloxy groups in **PolyPh(3)OHPh** resulted in bond twisting along the polymer backbone.

In 1,4-dioxane, both **PolyPh(3)OMeFlu** and **PolyPh(4)OC$_8$H$_{17}$Flu** showed two absorption peaks at 302, 322, 308, and 323 nm, respectively. These absorption positions are similar to those of **MonoPh(3)OMe**, **MonoPh(4)OMe**, and poly(9,9-dialkyl-2,7-fluorene-*co*-*m*-phenylene), respectively.[21] This observation can be explained by the assumption that **PolyPh(3)OMeFlu** and **PolyPh(4)OC$_8$H$_{17}$Flu** are regarded formally as combinations of 4-methoxy-*p*-terphenyl and poly(9,9-dihexyl-2,7-fluorene-*co*-*m*-phenylene) and 4-octyloxy-*p*-quaterphenyl and poly(9,9-dihexyl-2,7-fluorene-*co*-*m*-phenylene), respectively.

Photoluminescence. It has been reported that OPPs exhibit photoluminescence (PL) with a high quantum yield. **PolyPh(m)OH**, **PolyPh(3)OHFlu**, **PolyPh(3)OHPh**, and their deprotonated species are photoluminescent in solution. The PL data are summarized in Table 3. The PL peak positions of **PolyPh(m)OH** (*m* = 3, 4, and 5) shifted to longer wavelengths with an increase in the number of the pendant benzene rings. This behavior was comparable to the emission behavior of **MonoPh(m)OH** (*m* = 3, 4, and 5). The quantum yields of PL of the 1,4-dioxane solutions of **PolyPh(m)OH** (*m* = 3, 4, and 5) were 11%, 26%, and 39%, respectively; these values were lower than those of **MonoPh(m)OH** (*m* = 3, 4, and 5) reported earlier.[13]

The PL peak positions of **PolyPh(*m*)OH** (*m* = 3, 4, and 5) and their deprotonated species depended on the DNs of the solvents; that is, the emission color could be tuned by changing the solvent. As shown in Figure 7, **PolyPh(4)ONa** exhibited blue, green, and orange emissions after it was irradiated with UV light in 1,4-dioxane (DN = 14.8), THF (DN = 20.0), and DMSO (DN = 29.8), respectively. Deprotonated products **PolyPh(*m*)ONa** (*m* = 3, 4, and 5) showed PL peaks at longer wavelengths than those of **PolyPh(*m*)OH** (*m* = 3, 4, and 5).

Figure 8 exhibits the dependence of the emission peak positions of **PolyPh(*m*)OH** (*m* = 3, 4, and 5) on the DNs of the solvents. Thus, by alternating between the solvents such as CH_2Cl_2, which have a small DN value, and those such as DMF and DMSO, which have larger DN values, it is observed that the emission peak positions of **PolyPh(*m*)OH** shift by only approximately 20 nm. However, a relatively large shift in the emission peaks of **PolyPh(*m*)ONa** occurred as the DNs of the solvents increased. These observations are comparable to the result that the absorption due to unit A of **PolyPh(*m*)ONa** in solution shifts to a longer wavelength than that of **PolyPh(*m*)OH** with an increase in the DNs of the solvents. The remarkable solvatochromic shift of the PL of **PolyPh(*m*)ONa** appeared to be due to the charge shift from the sodium phenoxide group to the adjacent rings. In addition to the charge shift effect, a large amount of stabilization energy produced by the solvation of unit A of **PolyPh(*m*)ONa** may contribute to the solvatochromic red shift as the DNs of the solvents increased. These phenomena were significant in the case of organic solvents that had high DN values, such as DMF and DMSO, which was similar to the case of **MonoOPP(*m*)ONa**.

Table 3. PL Data of Polymers

	photoluminescence/nm^b					photoluminescence/nm			
	1,4-dioxane, DN^a = 14.8	THF, DN^a = 20.0	DMF, DN^a = 26.6	DMSO, DN^a = 29.8		1,4-dioxane, DN^a = 14.8	THF, DN^a = 20.0	DMF, DN^a = 26.6	DMSO, DN^a = 29.8
PolyPh(3)OH	364 (0.11)	369	378	386	**PolyPh(3)ONa**	433	465	511	513
PolyPh(4)OH	385 (0.26)	393	403	402	**PolyPh(4)ONa**	473	510	522	556
PolyPh(5)OH	397 (0.31)	404	410	412	**PolyPh(5)ONa**	484	526		
PolyPh(3)OMeFlu	365, 379 (0.48)	365, 379	368, 381	c					
PolyPh(4)OMeFlu	380 (0.51)	381	392	c					
PolyPh(3)OMePh	384 (0.21)	391	391	c					
PolyPh(3)OHFlu	387 (0.18)	393	412	c	**PolyPh(3)ONaFlu**	494	499	522	519
PolyPh(3)OHPh	384 (0.08)	385	389	c	**PolyPh(3)ONaPh**	437	476	503	547

[a] DN = donor number of solvents. [b] Quantum yields of photoluminescence were shown in parentheses. [c] Not measured due to low solubility.

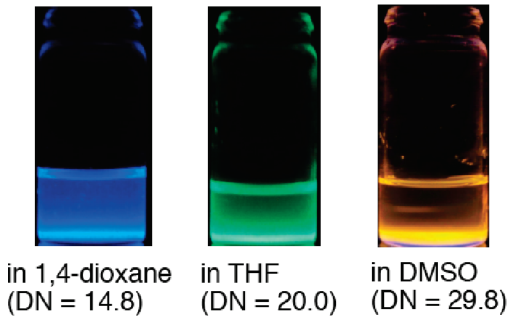


Figure 7. Photographs of **PolyPh(4)OH** in 1,4-dioxane (DN = 14.8), THF (DN = 20.0), and DMSO (DN = 29.8) when irradiated with UV light.

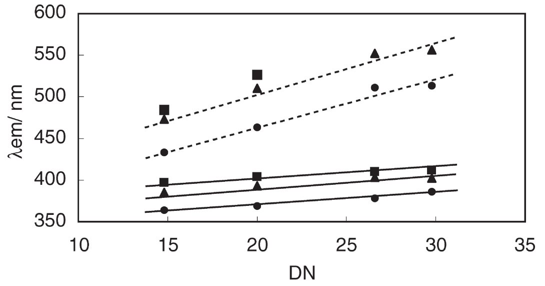


Figure 8. Dependence of λ_{em} of **PolyPh(*m*)OH** (m = 3, 4, and 5) (m = 3 (●), 4 (▲), and 5 (■); solid line) and their deprotonated species (dotted line) on the DNs of solvents.

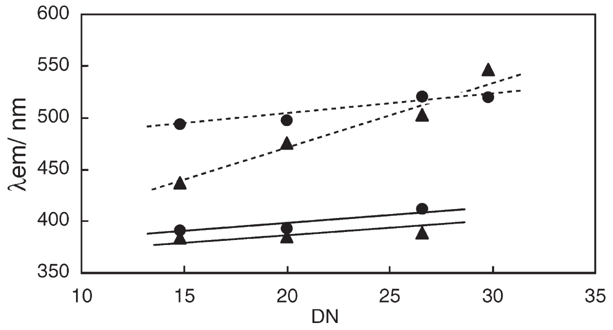


Figure 9. Dependence of λ_{em} of **PolyPh(3)OHFlu** (solid line with ●), PolyPh(3)OHPh (solid line with ▲), and their deprotonated species (dotted line) on the DNs of solvents.

As mentioned earlier, an increase in the DNs of the solvents caused the large bathochromic shift of the PL peaks of **PolyPh(*m*)ONa** (m = 3, 4, and 5). **PolyPh(3)OHPh** showed a similar bathochromic shift of the PL peaks with an increase in the DNs of the solvents. However, the DNs of the solvents had a small effect on the PL peak positions of **PolyPh(3)-OHFlu** and their deprotonated species, as shown in Figure 9.

Their PL peaks appeared at approximately 390 and 500 nm when they were dissolved in solvents with moderate DNs, such as 1,4-dioxane (DN = 14.8) and THF (DN = 20), respectively. The PL peak position of **PolyPh(3)ONaFlu** in 1,4-dioxane showed a PL peak at 494 nm; this position was comparable to that of **PolyPh(3)ONa** in DMSO (DN = 29.8). These observations can be attributed to the presence of 2,7-fluorene groups at the *m*-position of the sodium phenoxide ring. It was reported that OPP(*n*) adopted more planar configurations in the S^1-excitated state than in the S^0-grand state.[22] Hence, in the S^1-excitated state, the 2,7-fluorene units linked by the sodium phenoxide group of **PolyPh(3)ONaFlu** could adopt a more planar configuration with the phenoxy ring. Because of this configuration, the wavelength at which the PL peak of **PolyPh(3)ONaFlu** appeared was longer than that of **PolyPh(3)ONa**; however, the solution of **PolyPh(3)-ONaFlu** exhibited λ_{max} at a shorter wavelength than that of **PolyPh(3)ONa**. In contrast, the 2,5-dioctyloxyphenylene units linked by the sodium phenoxide group of **PolyPh(3)-ONaPh** could not adopt a planar configuration with the phenoxy ring in the S^1-excitated state due to the steric hindrance of the dioctyloxy groups. This assumption is consistent with the results that the PL peak positions of **PolyPh(3)ONaPh** shift to longer wavelengths with an increase in the DNs of the solvents, as shown in Table 3.

Cyclic Voltammograms. Figure 10 shows cyclic voltammograms of cast films of **PolyPh(3)OMeFlu**, **PolyPh-(3)OHFlu**, **PolyPh(3)OMePh**, and **PolyPh(3)OHPh**. The polymers showed two peaks corresponding to the electrochemical oxidation of the pendant group and main chain. The peak potentials due to the electrochemical oxidation of the main chain and pendant group of **PolyPh(3)OMeFlu**, **PolyPh(3)OHFlu**, and **PolyPh(4)OC$_8$H$_{17}$Flu** were 1.38, 1.56, 1.21, 1.51, 1.18, and 1.46 V, respectively, while those of **PolyPh(3)OMePh** and **PolyPh(3)OHPh** were 0.96, 1.27, 0.93, and 1.31 V, respectively.

The peak assignment is related to the fact that **PolyPh-(3)OH** showed a peak due to electrochemical oxidation at 1.57 V. However, the corresponding reduction (p-dedoping) peak does not appear in the cyclic voltammograms; this is likely because of the formation of a stable adduct between the electrochemically oxidized polymer and BF_4^-. Electrochemically oxidized π-conjugated polymers have been reported to form stable adducts with BF_4^- during cyclic voltammetry measurements.[23] The fact that **PolyPh(3)OMe-Ph** and **PolyPh(3)OHPh** have lower peak potentials than **PolyPh(3)OMeFlu** and **PolyPh(3)OHFlu** is due to the presence of the two electron-donating octyloxy groups in **Poly-Ph(3)OMePh** and **PolyPh(3)OHPh**. The electrochemical reaction is accompanied by electrochromism; the light brown cast films of the polymers changed to black after electrochemical oxidation.

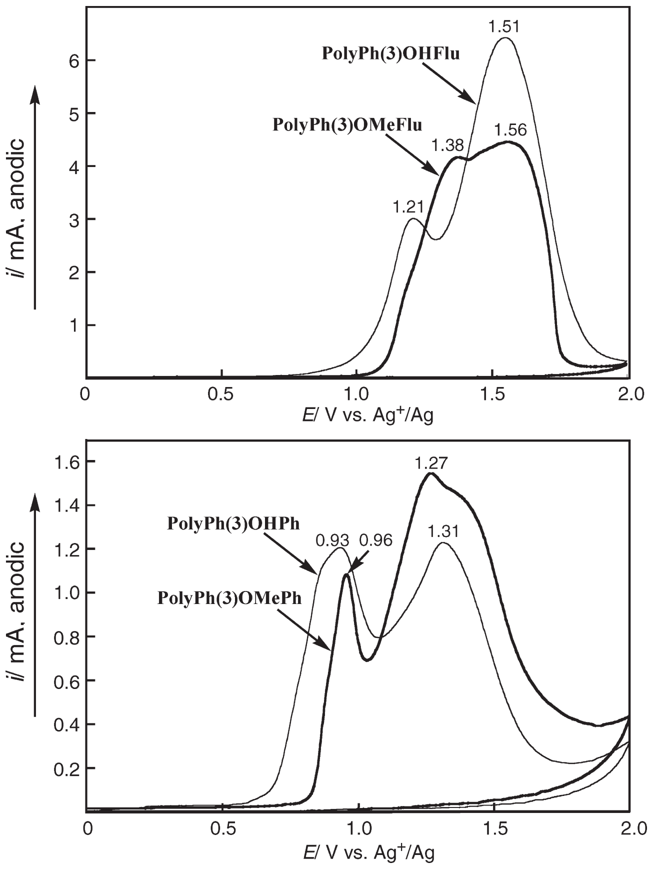


Figure 10. Cyclic voltammgrams of cast films of **PolyPh(3)OMeFlu**, **PolyPh(3)OHFlu**, **PolyPh(3)OMePh**, and **PolyPh(3)OHPh** on a Pt plate in an acetonitrile solution of $[Et_4N]BF_4$ (0.10 M). The scan rate was 50 mV s^{-1}.

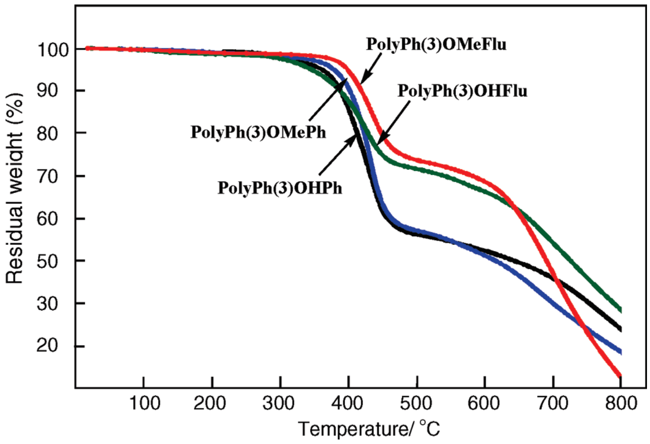


Figure 11. TGA curves of **PolyPh(3)OMeFlu** (red curve), **PolyPh(3)OHFlu** (green curve), **PolyPh(3)OMePh** (blue curve), and **PolyPh(3)OHPh** (black curve) under nitrogen. Heating rate was 10 °C min^{-1}.

Thermal Properties. Figure 11 shows TGA curves of **PolyPh(3)OMeFlu**, **PolyPh(3)OHFlu**, **PolyPh(3)OMePh**, and **PolyPh(3)OHPh**. The polymers showed good thermal stability up to 350 °C. The 5% weight-loss temperatures of **PolyPh(3)OMeFlu**, **PolyPh(3)OHFlu**, **PolyPh(3)OMePh**, and **PolyPh(3)OHPh** were 399, 346, 379, and 362 °C, respectively. The polymers exhibited a two-stage thermal decomposition process, with the first decomposition occurring in the range of 380−430 °C. In the first stage, **PFluBPyEt** and **PPhBPyEt** showed weight losses of 28 and 39 wt %, respectively. These values are largely consistent with the content of the alkyl groups in the polymers, suggesting that the first thermal decomposition can be attributed to alkyl loss of the polymers.

Conclusion

HRP-catalyzed polymerization of hydroxy-*p*-oligophenylenes yielded poly(phenol)s with the pendant OPP unit: **PolyPh(*m*)OH**. Pd-complex-catalyzed polymerization of 3,5-dibromo-4-methoxy[1,1′;4,1″]terphenyl with 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester and benzene-1,4-diboronic acid along with the hydrolysis of the methyl group provided polyphenylenes with phenolic OH groups: **PolyPh(3)OHFlu** and **PolyPh(3)OHPh**. The treatment of **PolyPh(*m*)OH** with NaH produced deprotonated species **PolyPh(*m*)ONa**, whose absorption and PL peak positions in solution shifted toward long wavelengths with an increase in the DNs of the solvents. The emission colors for the **PolyPh(*m*)ONa** solutions could be tuned by changing the solvent. The optical properties of the poly(phenol)s with the pendant OPP unit were considerably affected by the structure of the polymer backbone. The results obtained in this study indicate that new luminescent materials can be developed on the basis of the remarkable solvatochromic behavior of **PolyPh(*m*)ONa**.

Experimental Section

General Data. Solvents were dried, distilled, and stored under nitrogen. 2,6-Dioctyloxybenzene-1,4-diboronic acid was synthesized according to the literatures. Other reagents were purchased and used without further purification. Reactions were carried out with standard Schlenk techniques under nitrogen.

IR and NMR spectra were recorded on a JASCO FT/IR-660 PLUS spectrophotometer with a KBr pellet and a JEOL AL-400 spectrometer, respectively. Concentration of samples for the NMR analysis was approximately 2 mg/mL. Elemental analysis was conducted on a Yanagimoto MT-5 CHN corder. GPC analyses were carried out by a Toso HLC 8020 with polystyrene gel columns (TSKgel G2000H_{HR} and TSKgel GMH_{HR}-M) using a DMF solution of LiBr (0.006 M) as an eluent with RI and UV detectors and a Jasco 830 refractometer with polystyrene gel columns (K-803 and K-804) using chloroform as an eluent with a RI detector. Light scattering measurement was performed with a Otsuka Electronics DLS-7000 using He−Ne laser (632.8 nm) in a DMF solution of the polymer. UV−vis and PL spectra were obtained by a JASCO V-560 spectrometer and a JASCO FP-6200, respectively. Quantum yields were calculated by using a diluted ethanol solution of 7-dimethylamino-4-methylcoumarin as the standard. Cyclic voltammetry was performed in a DMSO solution containing 0.10 M $[Et_4N]BF_4$ with a BAS 100B. TGA curves were obtained by a Rigaku Thermo plus TG8120.

MonoBrPh(3)OMe and **MonoBrPh(3)OH** were synthesized according to the reported manner.[13]

Synthesis of MonoBr2Ph(3)OMe. 2,4,6-Tribromoanisole (1.0 g, 3.0 mmol) and 4-biphenylboronic acid (0.59 g, 3.0 mmol) were dissolved in 20 mL of dry THF under N_2. To the solution were added K_2CO_3(aq) (2.0 M, 10 mL; N_2 bubbled before use) and $Pd(PPh_3)_4$ (0.086 g, 0.045 mmol). After the mixture was refluxed for 48 h, the solvent was removed under vacuum. The resulting solid was washed with water and methanol and dried under vacuum to give a white solid, which was purified by silica gel column chromatography (eluent = a mixture of chloroform and hexane (*v*/*v* = 1/4)). The solvent was removed by evaporation and a resulting solid was dried in vacuo to give **MonoBrPh(3)OMe** as a white powder (0.40 g, 32%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.77 (s, 2H), 7.58−7.69 (m, 6H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 3.94 (s, 3H). $^{13}C\{^1H\}$ NMR

(100 MHz, $CDCl_3$): δ 153.4, 141.0, 140.3, 139.4, 136.8, 131.0, 128.9, 127.7, 127.6, 127.3, 127.0, 118.5, 60.7. Anal. Calcd for $C_{19}H_{14}Br_2O$: C, 54.58; H, 3.37. Found: C, 54.59; H, 3.48.

Synthesis of MonoBr2Ph(3)OH. To a CH_2Cl_2 solution (2.0 mL) of **MonoBrPh(3)OMe** (0.32 g, 0.80 mmol) was added dropwise a CH_2Cl_2 solution (3.0 mL) of BBr_3 (0.10 mL, 1.1 mmol). After the reaction solution was stirred at 25 °C for 8 h, water (10 mL) was added to the solution. The CH_2Cl_2 solution was dried over magnesium anhydride. The solvent was removed by evaporation and the resulting solid was dried under vacuum to give **MonoBr2Ph(3)OH** as a white powder (0.31 g, 99%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.73 (s, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 8.4 Hz, 2H), 7.47 (t, J = 8.0 Hz, 2H), 7.37 (t, J = 7.6 Hz, 1H), 5.90 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 148.7, 140.7, 140.3, 137.0, 135.7, 130.4, 128.9, 127.7, 127.5, 127.1, 127.0, 110.3. Anal. Calcd for $C_{18}H_{12}Br_2O$: C, 53.50; H, 2.99. Found: C, 53.22; H, 2.82.

Synthesis of [1,1′;4′,1″]terphenyl-4″-boronic acid was performed analogous to the reported manner.[13]

Data of [1,1′;4′,1″]Terphenyl-4″-boronic Acid. Yield = 40%. ^1H NMR (400 MHz, DMSO-d_6): δ 8.09 (s, 2H), 7.89 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.8 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.38 (t, J = 7.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 141.0, 139.6, 139.2, 139.1, 134.8, 129.0, 127.5, 127.20, 127.17, 126.6, 125.5.

Synthesis of 2,4,6-Tribromooctyloxybenzene. After a methanol solution (40 mL) of 2,4,6-tribromophenol (6.6 g, 20 mmol) and KOH (2.2 g, 40 mmol) was stirred at 50 °C for 1 h, *n*-octyl bromide (7.8 mL, 40 mmol) was added dropwise to the mixture. The mixture was refluxed for 24 h. After the solvent was removed by evaporation, the resulting solid was extracted with chloroform. Evaporation of the solvent gave a light yellow liquid, which was purified by silica gel column chromatography (eluent = hexane). The solvent was removed by evaporation and a resulting liquid was dried in vacuo to give 2,4,6-tribromooctyloxybenzene as a colorless liquid (4.4 g, 50%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.64 (s, 2H), 3.97 (t, J = 6.8 Hz, 2H), 1.85 (m, 2H), 1.49 (m, 2H), 1.30 (m, 8H), 0.89 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 153.1, 135.9, 119.1, 117.1, 73.8, 31.8, 30.0, 29.4, 29.3, 25.8, 22.7, 14.1.

MonoBr2Ph(4)OC$_8$H$_{17}$ was synthesized analogous to the reported manner.[13]

Data of MonoBr2Ph(4)OC$_8$H$_{17}$. ^1H NMR (400 MHz, $CDCl_3$): δ 7.78 (s, 2H), 7.60−7.73 (10H), 7.47 (t, J = 7.6 Hz, 2H), 7.37 (t, J = 7.2 Hz, 1H), 4.05 (t, J = 6.8 Hz, 2H), 1.91 (m, 2H), 1.56 (m, 2H), 1.31 (m, 8H), 0.90 (t, J = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.8, 140.6, 140.5, 140.4, 139.1, 139.0, 137.0, 131.0, 128.9, 127.6, 127.5, 127.44, 127.39, 127.35, 127.1, 118.8, 73.8, 31.9, 30.1, 29.4, 29.3, 25.9, 22.7, 14.1. Anal. Calcd for $C_{32}H_{32}Br_2O$: C, 64.88; H, 5.44. Found: C, 64.72; H, 5.44.

Synthesis of PolyPh(3)OH. MonoPh(3)OH. (0.37 g, 1.5 mmol) and HRP (3.5 mg, 1000 units) purchased from Sigma Chemical Co. in a mixture of 1,4-dioxane (30 mL) and an aqueous phosphate buffer solution (pH 6.9, 5 mL) were placed in a round bottle flask. To the mixture, 200 μL of 35% hydrogen peroxide (2.0 mmol) was added dropwise (less than 20 mM H_2O_2 at each time) over 3 h. After the reaction mixture was stirred at room temperature for 24 h, the precipitate was collected by filtration and washed with water. **PolyPh(3)OH** was collected by filtration and dried in vacuo (0.33 g, 90%). ^1H NMR (400 MHz, $CDCl_3$): δ 6.8−7.7 (br). Anal. Calcd for $(C_{18}H_{12}O \cdot 0.2H_2O)_n$: C, 87.50; H, 5.00. Found: C, 87.26; H, 4.96.

PolyBrPh(*m*)OHs (*m* = 2 and 3) were prepared analogously. Spectroscopic and analytical data of the polymers are shown below.

PolyBrPh(2)OH. ^1H NMR (400 MHz, $CDCl_3$): δ 6.9−7.5 (m). Anal. Calcd for $(C_{12}H_7BrO \cdot 0.5H_2O)_n$: C, 57.29; H, 3.00. Found: C, 57.43; H, 3.32.

PolyBrPh(3)OH. ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (br). Anal. Calcd for $(C_{18}H_{11}BrO \cdot 0.5H_2O)_n$: C, 65.98; H, 3.54. Found: C, 65.77; H, 3.65.

Synthesis of PolyPh(4)OH. PolyBrPh(2)OH (0.50 g, 2.0 mmol) and 4-biphenylboronic acid (0.67 g, 3.4 mmol) were dissolved in 25 mL of dry THF under N_2. To the solution were added K_2CO_3(aq) (2.0 M, 12.5 mL; N_2 bubbled before use) and Pd(PPh_3)$_4$ (0.034 g, 0.029 mmol). After the mixture was refluxed for 80 h, the solvent was removed under vacuum. The resulting solid was dissolved in a small amount of THF and reprecipitated in methanol. **PolyPh(4)OH** was collected by filtration, dried under vacuum, and obtained as a gray powder (0.67 g, 100%). ^1H NMR (400 MHz, DMSO-d_6): δ 7.65−7.72 (m, 11H), 7.41 (m, 2H), 7.30 (m, 1H). Anal. Calcd for $(C_{24}H_{16}O \cdot 0.5H_2O)_n$: C, 88.73; H, 5.12. Found: C, 88.75; H, 5.26; Br, 0.

PolyPh(5)OH was synthesized by the reaction of **PolyBrPh(3)OH** with 4-biphenylboronic acid in a similar manner. Yield = 98% (gray powder).

Synthesis of PolyPh(3)OMeFlu. MonoBrPh(3)OMe (0.084 g, 0.20 mmol) and 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (0.10 g, 0.20 mmol) were dissolved in 4 mL of dry toluene under N_2. To the solution were added K_2CO_3(aq) (2.0 M, 2 mL; N_2 bubbled before use), Pd(PPh_3)$_4$ (0.026 g, 0.022 mmol), and several drops of the phase transfer catalyst (Aliquat336). After the mixture was stirred for 72 h at 80 °C, the solvent was removed under vacuum. The resulting solid was washed with water and hexane, dissolved in a small amount of THF, and reprecipitated in acetone. **PolyPh(3)OMeFlu** was collected by filtration, dried under vacuum, and obtained as a gray powder (0.10 g, 86%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.65−7.87 (m, 14H), 7.47 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 5.6 Hz, 1H), 3.28 (s, 3H), 2.12 (br, 4H), 1.07−1.10 (m, 12H), 0.70−0.78 (m, 10H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 154.6, 150.7, 140.7, 140.2, 140.1, 139.6, 137.5, 136.8, 136.2, 128.8, 128.2, 127.6, 127.5, 127.4, 127.1, 124.1, 119.6, 60.1, 55.3, 40.6, 31.6, 29.8, 24.0, 22.5, 14.0. Anal. Calcd for $(C_{44}H_{46}O)_n$: C, 89.44; H, 7.85; O, 2.71. Found: C, 88.97; H, 7.47; O, 2.85.

Synthesis of PolyPh(3)OHFlu. To a $CHCl_3$ solution (2 mL) of **PolyPh(3)OMeFlu** (0.038 g, 0.090 mmol) was added dropwise a $CHCl_3$ solution (3 mL) of BBr_3 (0.1 mL, a.a mmol). After the reaction solution was stirred at 25 °C for 48 h, water was added to the solution. The mixture was extracted with $CHCl_3$ and the $CHCl_3$ solution was dried over $MgSO_4$. The solvent was removed under vacuum and the resulting solid was washed with acetone (200 mL). **PolyPh(3)OHFlu** was collected by filtration, dried under vacuum, and obtained as a light yellow powder (0.029 g, 79%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.4 Hz, 2H), 7.64−7.71 (m, 10H), 7.46 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 6.8 Hz, 1H), 5.67 (s, 1H), 2.06 (br, 4H), 1.10 (br, 12H), 0.75−0.83 (m, 10H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.9, 149.2, 140.7, 140.3, 139.8, 139.6, 136.4, 133.4, 129.7, 128.8, 128.6, 128.2, 127.6, 127.2, 127.0, 124.1, 120.3, 55.5, 40.2, 31.5, 29.7, 24.0, 22.6, 14.0. Anal. Calcd for $(C_{43}H_{44}O \cdot H_2O)_n$: C, 86.83; H, 7.79. Found: C, 87.39; H, 7.56.

PolyPh(3)OMePh, **PolyPh(4)OC$_8$H$_{17}$Flu**, and **PolyPh(3)OHPh** were prepared analogously. Spectroscopic and analytical data of the polymers are shown below.

PolyPh(3)OMePh. ^1H NMR (400 MHz, $CDCl_3$): δ 7.77−7.64 (8H), 7.46 (t, J = 7.6 Hz, 2H), 7.37 (t, J = 7.6 Hz, 1H), 7.16 (s, 2H), 3.98 (t, J = 6.4 Hz, 4H), 3.45 (s, 3H), 1.67 (s, 4H), 1.30 (s, 4H), 1.17 (s, 16H), 0.79 (t, J = 7.2 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 155.8, 150.3, 140.8, 139.7, 139.5, 134.4, 132.0, 129.7, 128.8, 128.5, 127.4, 127.3, 127.2, 127.0, 126.97, 116.8, 69.1, 60.7, 31.8, 29.7, 29.5, 29.3, 26.1, 22.6, 14.1. Anal. Calcd for $(C_{41}H_{50}O_3 \cdot 0.5H_2O)_n$: C, 82.10; H, 8.57. Found: C, 82.22; H, 8.24.

PolyPh(4)OC$_8$H$_{17}$Flu. ^1H NMR (400 MHz, $CDCl_3$): δ 7.66−7.85 (18H), 7.46 (t, J = 7.2 Hz, 2H), 7.37 (t, J = 7.2 Hz, 1H), 3.36 (s, 2H), 2.12 (s, 4H), 0.74−1.22 (27H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 154.6, 150.91, 150.88, 142.2, 140.7, 140.2, 140.1, 139.8, 139.6, 139.5, 138.0, 137.8, 137.1, 136.5, 133.8, 133.1, 128.8, 128.5, 124.15, 124.11, 63.6, 55.3, 20.6, 31.7, 31.6, 29.99, 29.93, 29.89, 29.7, 29.30, 29.27, 29.1, 25.8, 22.66, 22.63. Anal. Calcd for $(C_{57}H_{64}O\cdot 0.5H_2O)_n$: C, 88.44; H, 8.46. Found: C, 88.69; H, 7.82.

PolyPh(3)OHPh. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78−7.65 (8H), 7.46 (t, $J=7.6$ Hz, 2H), 7.36 (t, $J=7.2$ Hz, 1H), 7.20 (s, 2H), 4.03 (m, 4H), 1.71 (s, 4H), 1.29 (s, 4H), 1.16 (s, 16H), 0.79 (t, $J=6.8$ Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.2, 140.8, 139.7, 139.5, 132.4, 132.2, 128.8, 129.17, 129.13, 120.10, 128.29, 127.4, 127.1, 127.0, 118.1, 70.6, 31.8, 29.4, 29.3, 29.2, 25.9, 22.6, 14.1. Anal. Calcd for $(C_{40}H_{48}O_3\cdot 0.5H_2O)_n$: C, 82.01; H, 8.43. Found: C, 81.75; H, 8.47.

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Supporting Information Available: Figures showing ^{13}C NMR spectra of the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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