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Convenient synthesis of poly(2,6-dihydroxy-1,5-naphthylene) by Cu(II)-amine catalyzed oxidative coupling polymerization

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Abstract

A convenient synthesis of regiocontrolled poly(2,6-dihydroxy-1,5-naphthylene) (PDHN) with high molecular weights by oxidative coupling polymerization of 2,6-dihydroxynaphthalene (2,6-DHN) has been developed. Polymerizations were conducted in 2-methoxyethanol in the presence of di-μ-hydroxo-bis[(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)copper (II)] chloride (CuCl(OH)TMEDA) as the catalyst under air at 25 °C. To determine the optimum conditions, the effects of the amounts of the catalysts and the solvents were investigated. In the presence of 5 mol% of the catalyst to the monomer in 2-methoxyethanol, polymerization proceeded smoothly, giving PDHN with a number average molecular weight (M_n) of 52,000. PDHN was converted to poly(2,6-dibutoxy-1,5-naphthylene) (PDBN) to improve the solubility. The structure of PDBN was characterized by ^{1}H and ^{13}C NMR spectroscopy and was estimated to consist completely of the 1,5-linkage. The average refractive indices (n_{AV}) of the PDHN and PDBN films were 1.6003 and 1.5815, respectively, and the dielectric constants (ε) estimated from the refractive indices were 2.82 and 2.75, respectively.

Keywords: Low *k* materials; Regiocontrolled oxidative coupling polymerization; Refractive index

1. Introduction

Formation of C–C bonds between aromatic rings is an important step in the synthesis of many aromatic polymers such as polyphenylenes [1,2], polypyrroles [3,4], and polythiophenes [5,6]. These polymers can be prepared in two ways; by the oxidative coupling polymerization using an electrochemical or chemical method and by the transition-metal-catalyzed coupling polymerization of aryl dihalides. The former method is more practical because of the direct dehydrogenation coupling of aromatic rings.

As a part of the program on the synthesis of condensation polymers by oxidative coupling polymerization, we reported the syntheses of regiocontrolled poly(2,5-dibutoxy-1,4-phenylene) [7] and poly(dinaphthylene ether) [8] through oxovanadium catalyzed oxidative coupling polymerization. We also showed the synthesis of a regiocontrolled polymer having 2-naphthol units by Cu(II)-amine catalyzed oxidative coupling polymerization of bis(2-naphthol), which is in a few examples of the aromatic polymer syntheses having phenolic hydroxyl groups through C–C coupling reactions [9]. Phenolic hydroxyl groups are generally involved in the formation of C–O bonds in the oxidative coupling polymerization such as the polymerization of 2,6-dimethylphenol to give poly(phenylene ether) [10–12]. In addition to the interest in finding synthetic methods of these polymers, the hydroxy-modified polymer with high thermal stability are applicable to alkaline developable photosensitive polymers by blending with photosensitizer [13] and are required in semiconductor manufacturing as protection and insulation layers. Moreover, phenolic hydroxyl containing polymers can be converted into the polymers having several functional groups by chemical modification, so they must be very useful materials.

Solution and electrolytic polymerizations of 2,6-dihydroxynaphthalene (2,6-DHN) were investigated by several researchers, and produced only oligomer mainly because of the poor solubility of the resulting polymer [14–16]. Quite recently, we reported a simple synthetic method for regiocontrolled poly(2,6-dihydroxy-1,5-naphthylene) (PDHN) with a number-average molecular weight (M_n) of 13,000 by oxidative coupling polymerization of 2,6-DHN and benzylamine complex using iron (III) chloride ($FeCl_3$)

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hexahydrate in the solid state [17]. This method, however, requires excess amounts of $FeCl_3$ for 2,6-DHN and the formation of the 2,6-DHN-benzylamine complex beforehand. Therefore, it is noteworthy to establish a more efficient polymerization method of 2,6-DHN.

We here describe the successful synthesis of regiocontrolled PDHN by di-μ-hydroxo-bis[(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)copper (II)] chloride (CuCl(OH)TMEDA) catalyzed oxidative coupling polymerization of 2,6-DHN in solutions.

2. Experimental section

2.1. Materials

Ethyl lactate was purified by vacuum distillation from 4 Å molecular sieves. *N*,*N*-Dimethylformamide (DMF) was distilled from calcium hydride under vacuum. 2-Methoxyethanol was purified by distillation from 4 Å molecular sieves under atmospheric pressure. All solvents were stored over 4 Å molecular sieves. 2,6-DHN, *n*-butyl iodide, and CuCl(OH)TMEDA were purchased from Tokyo Kasei Kogyo Co., Ltd. and used as received. Potassium carbonate purchased from Kanto Chemical Kogyo Co., Inc. was crushed and baked at 200 °C for 12 h before use.

2.2. Synthesis of PDHN

A typical procedure of the polymerization of 2,6-DHN is as follows; Into a 10 ml round-bottomed flask fitted with a calcium chloride drying tube were placed CuCl(OH)TMEDA (4.6 mg, 0.01 mmol) and 2-methoxyethanol (3 ml). The light-bluish colored solution was kept stirring for 30 min, and then 2,6-DHN (0.16 g, 1.0 mmol) was added to initiate the polymerization under air. After 3 h, the resulting extremely viscous solution was poured into methanol containing 1 M hydrochloric acid (80 ml/20 ml). The precipitate was collected, washed with water, and dried in vacuo at 80 °C for 9 h. Yield: 0.16 g (>99%). IR (KBr): 3383 (OH), 1597 (Ar), 1508 (Ar), 822 cm^{-1} (CH in the 3, 4- and 7, 8-positions of β-substituted naphthalenes).

2.3. Synthesis of 2,6-dibutoxynaphthalene (2,6-DBN)

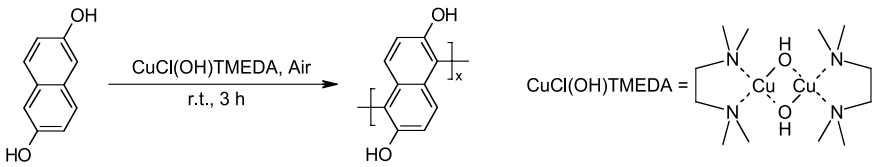
A mixture of 2,6-DHN (0.21 g, 1.3 mmol), *n*-butyl iodide (1.20 g, 6.5 mmol), potassium carbonate (0.90 g, 6.5 mmol), and DMF (3 ml) was stirred at 25 °C for 2 d. The reaction mixture was poured into water (100 ml), extracted with ethyl acetate (three times), and dried over anhydrous magnesium sulfate. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel eluted with hexane/dichloromethane = 3:1 (v/v) to give white platy crystals. Yield: 0.29 g (82%). Mp 98.0–100.3 °C. IR (KBr): 2962 (CH), 2920 (CH), 2870 (CH), 1604 (Ar), 1508 (Ar), 1230 (COC), 856 (CH at the 1, 5-positions of naphthalene), 806 cm^{-1} (CH at the 3, 4 and 7, 8-positions of β-substituted naphthalene). ^{1}H NMR (CD_2Cl_2): $\delta = 1.00$ (t, CH_3, 6H), 1.46–1.60 (m, CH_3–CH_2–, 4H), 1.75–1.86 (m, –O–CH_2–CH_2–, 4H), 4.04 (t, –O–CH_2–, 4H), 7.07–7.12 (m, Ar-H, 4H), 7.59–7.64 (m, Ar-H, 2H). ^{13}C NMR (CD_2Cl_2): $\delta = 13.3$, 19.0, 31.0, 67.4, 106.4, 118.7, 127.6, 129.3, 155.2. ^{13}C/DEPT45 NMR (CD_2Cl_2): $\delta = 13.1$, 18.8, 30.8, 67.2, 106.2, 118.5, 127.3. ^{13}C/DEPT90 NMR (CD_2Cl_2): $\delta = 13.1$, 18.8, 30.8, 67.2, 106.2, 118.5, 127.4. Anal. $C_{18}H_{24}O_2$: calcd C 79.37, H 8.88, O 11.75; Found C 79.17, H 8.85, O 11.66.

2.4. Synthesis of poly(2,6-dibutoxy-1,5-naphthylene) (PDBN)

To a solution of PDHN (0.21 g, 2.6 mmol as OH group) in DMF (6 ml) were added *n*-butyl iodide (1.20 g, 6.5 mmol) and potassium carbonate (0.90 g, 6.5 mmol). The mixture was stirred at 25 °C for 2 d and then poured into water (100 ml). The precipitate was collected, washed with water, and dried in vacuo at 80 °C for 9 h, giving a light-orange-colored solid. Yield: 0.30 g (85%). IR (NaCl): 2958 (CH), 2870 (CH), 1598 (Ar), 1500 (Ar), 1246 (COC), 1076 (COC), 810 cm^{-1} (CH in the 3, 4- and 7, 8-positions of β-substituted naphthalenes). ^{1}H NMR (CD_2Cl_2): $\delta = 0.82$ (s, CH_3, 6H), 1.18 (s, CH_3–CH_2–, 4H), 1.54 (s, –O–CH_2–CH_2–, 4H), 4.03 (s, –O–CH_2–, 4H), 7.10–7.60 (m, Ar, 4H). ^{13}C NMR (CD_2Cl_2): $\delta = 13.2$, 18.6, 31.3, 69.1, 115.9, 120.6, 126.3, 129.8, 152.7. ^{13}C/DEPT45 NMR (CD_2Cl_2): $\delta = 13.0$, 18.4, 31.0, 68.9, 115.6, 126.1. Anal. $C_{18}H_{22}O_2$ 0.55 H_2O: calcd C 77.09, H 8.30; Found C 77.09, H 7.61.

2.5. Measurements

The infrared spectra were recorded on a Horiba FT-720 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX300 (^{1}H: 300 MHz, ^{13}C: 75 MHz) spectrometer. The ultraviolet–visible (UV–Vis) spectra of the polymer films formed on quartz were recorded on a Jasco V-560 spectrophotometer. Molecular weights were determined by gel permeation chromatography (GPC) using standard polystyrenes on a Tosoh HLC-8120 GPC system equipped with polystyrene gel columns (TSK GELs, GMH_{HR}-M and GMH_{HR}-L) at 40 °C in DMF (containing 0.01 M of lithium bromide) at a flow rate of 1.0 ml/min. Refractive indices of polymer films on quartz substrates were measured at a wavelength of 1.320 μm at 25 °C with a Metricon model PC-2000 prism coupler. Using linearly-polarized laser light with parallel (transverse electric (TE)) and perpendicular (transverse magnetic (TM)) polarization to the film plane, the in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices and the film thickness of the samples were determined.



Scheme 1.

3. Results and discussion

3.1. Polymerization of 2,6-DHN

To conduct the solution polymerization, it is essential to find good solvents for PDHN. During the development of positive-type photosensitive polymers using PDHN as a matrix [18], PDHN was found to be soluble in ethyl lactate, DMF, and 2-methoxyethanol at 25 °C. Thus, the oxidative coupling polymerization of 2,6-DHN was conducted with 1.0 mol% of CuCl(OH)TMEDA to 2,6-DHN in these solvents under air at 25 °C (Scheme 1).

The results were summarized in Table 1. In the polymerization in ethyl lactate, a light-bluish catalyst solution immediately changed into dark brown. No precipitation, however, was obtained when the resulting solution was poured into 1 M hydrochloric acid containing 20 vol% of methanol (Run 1 in Table 1). On the other hand, the presence of 10 mol% of the catalyst produced PDHN with M_n of 24,000 (Run 2). Polymerizations in DMF also required 10 mol% of the catalyst to obtain the quantitative yield of PDHN with M_ns over 10,000 (Runs 3, 4). In 2-methoxyethanol, the polymerization efficiently proceeded even in the presence of 1 mol% of the catalyst in dark-browned solutions, producing PDHN with M_n of 27,000 for 3 h (Runs 5, 6).

Consequently, to obtain PDHN with higher molecular weights, the effect of the amounts of CuCl(OH)TMEDA on the polymerization was investigated in 2-methoxyethanol under air at 25 °C (Table 2). The highest molecular weight polymer was produced in the presence of 3.0–5.0 mol% of the catalyst (Runs 8, 9). Besides, to find the lower limit of the amounts of CuCl(OH)TMEDA, the polymerization was carried out with the less amount of the catalyst (0.7–0.3 mol%) (Runs 12–15). When the reaction time was extended to 17 h, PDHN with M_n of 26,000 could be quantitatively obtained even in the presence of 0.5 mol% of CuCl(OH)TMEDA (Run 13).

Then, the influence of the amounts of the solvent of 2-methoxyethanol was studied in the presence of 5.0 mol% of CuCl(OH)TMEDA (Table 3). The optimal monomer concentration was found to be 0.2 mol/l (Run 17). Lower monomer concentration slowed the reaction (Run 16), and higher one disturbed it due to the high viscosity of the reaction mixture (Runs 18–19).

Table 1
Preparation of PDHN in various solvents

Run	Catalyst[a] (mol%)	Solvent	Time (h)	Yield (%)	M_n[b] ($\times 10^{-4}$)	M_w/M_n[b]
1	1.0	Ethyl lactate	24	0	–	–
2	10.0	Ethyl lactate	7	100	2.4	2.1
3	1.0	DMF	24	45	0.5	2.1
4	10.0	DMF	24	94	1.9	2.8
5	1.0	2-Methoxyethanol	3	100	2.7	2.4
6	10.0	2-Methoxyethanol	3	98	3.1	2.3

The reaction was carried out with 1.0 mmol of monomer in 3 ml of the solvent at 25 °C under air.
[a] The amount of CuCl(OH)TMEDA for 2,6-DHN.
[b] Determined by GPC using polystyrene standards (DMF).

3.2. Polymer characterization

The polymer obtained was confirmed as the desired PDHN by IR and NMR spectroscopies.

Fig. 1 represents the IR spectra of 2,6-DHN and PDHN.

Table 2
Preparation of PDHN with various amounts of the catalyst

Run	Catalyst (mol%)[a]	Time (h)	Yield (%)	M_n ($\times 10^{-4}$)[b]	M_w/M_n[b]
7	1.0	3	100	2.7	2.4
8	3.0	3	96	4.3	1.9
9	5.0	3	100	4.3	1.8
10	7.0	3	99	3.7	2.2
11	10.0	3	98	3.1	2.3
12	0.7	12	100	2.7	2.3
13	0.5	17	100	2.6	2.4
14	0.4	24	87	2.1	2.4
15	0.3	24	76	1.1	2.5

The reaction was carried out with 1.0 mmol of 2,6-DHN in 3 ml of 2-methoxyethanol at 25 °C in air.
[a] The amount of CuCl(OH)TMEDA for 2,6-DHN.
[b] Determined by GPC using polystyrene standards (DMF).

Table 3
Effect of the monomer concentration on the polymerization

Run	Solvent (ml)	Monomer concentration (mol l^{-1})	Time (h)	M_n[a] ($\times 10^{-4}$)	M_w/M_n[a]
16	3.0	0.33	3	4.3	1.8
17	5.0	0.20	3	5.2	1.8
18	7.0	0.14	3	2.0	2.0
19	10.0	0.10	3	1.6	2.4

The reaction was carried out with 1.0 mmol of 2,6-DHN and 5.0 mol% of CuCl(OH)TMEDA to 2,6-DHN in 2-methoxyethanol at 25 °C under air, and PDHNs were obtained quantitatively in all cases.
[a] Determined by GPC using polystyrene standards (DMF).

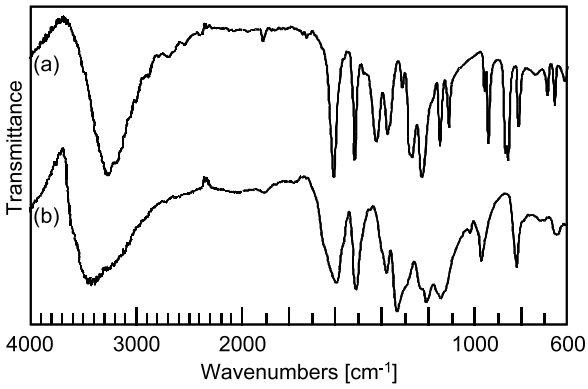


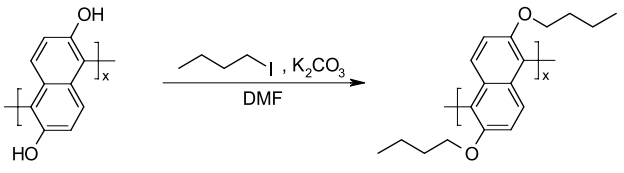
Fig. 1. IR spectra (KBr pellet): (a) 2,6-DHN and (b) PDHN.

The IR spectrum of PDHN showed characteristic absorptions at 3383 and 1597 cm^{-1} due to O–H and C=C stretching, respectively. The absorption at 810 cm^{-1} corresponding to a C–H out-of-plane bending vibration of 2,6-DHN that is characteristic of two adjacent hydrogens at the 3, 4- and 7, 8-positions of β-substituted naphthalenes was observed to shift to 818 cm^{-1} in PDHN. The absence of a characteristic absorption at 856 cm^{-1} attributed to the C1 and C5 hydrogens of the naphthalene ring of 2,6-DHN indicates the coupling reactions occurred on those carbons. No absorption due to the C=O stretching at 1745 cm^{-1} indicates that phenolic hydroxyl groups in 2,6-DHN were unchanged during the polymerization [18].

To increase the solubility of PDHN for NMR analysis, it was converted to PDBN by treating with butyl iodide in the presence of potassium carbonate at 25 °C for 24 h (Scheme 2).

Prior to the analysis of the polymer, 2,6-DBN was prepared as a standard compound from 2,6-DHN through the same procedure as described above. The ^{1}H NMR spectrum of 2,6-DBN consisted of two triplets at 1.00 (3H) and 4.04 ppm (2H), two multiplets at 1.46–1.60 (2H) and 1.75–1.86 ppm (2H) that were assigned to introduced *n*-butyl groups. Two multiplets at 7.07–7.12 (2H) and 7.59–7.64 ppm (2H) were assigned to the naphthalene ring. Fig. 2 shows the ^{13}C NMR spectrum of 2,6-DBN, where all signals were precisely assigned on the basis of the C–H COSY and ^{13}C/DEPT NMR analyses.

Next, the microstructure of PDBN was investigated by NMR spectroscopies (^{1}H, ^{13}C, ^{13}C/DEPT). The ^{1}H NMR spectrum of PDBN is shown in Fig. 3, where characteristic resonances for the methylene protons adjacent to the ether and aromatic protons were observed at 4.03 (4H) and 7.10–7.60 ppm (4H), respectively.



Scheme 2.

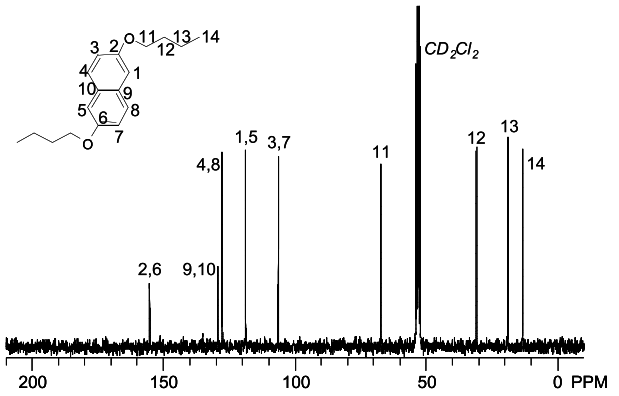


Fig. 2. ^{13}C NMR spectrum of 2,6-DBN in CD_2Cl_2 at 25 °C.

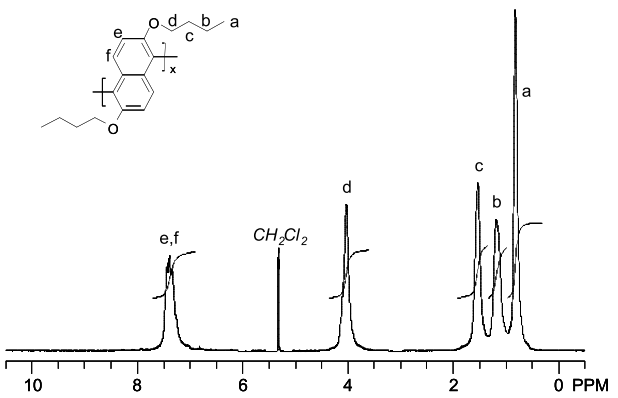


Fig. 3. ^{1}H NMR spectrum of PDBN in CD_2Cl_2 at 25 °C.

Further spectral evidence for the proposed structure of the polymer was provided by the ^{13}C NMR and DEPT spectroscopies. Aromatic regions of the ^{13}C NMR and DEPT spectra and assignment of the polymer were presented in Fig. 4. The DEPT spectrum indicates that the signals at 120.6, 129.8, and 152.7 ppm were due to the quaternary carbons. The C1 and C5 resonance of 118.7 ppm in 2,6-DBN shifted to 120.6 ppm in PDBN, and then this new signal disappeared in the DEPT spectrum of the polymer. This finding clearly indicates the coupling took

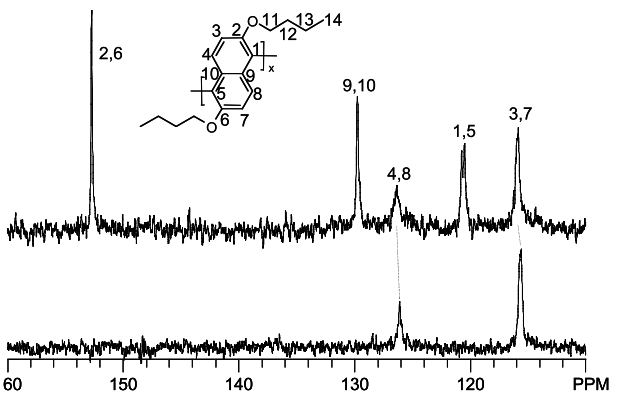


Fig. 4. NMR spectra of PDBN: (a) ^{13}C NMR and (b) ^{13}C/DEPT45 NMR in CD_2Cl_2 at 25 °C.

Table 4
Refractive indices and dielectric constants of the polymer films

Run	d (μm)[a]	n_{TE}[b]	n_{TM}[c]	n_{AV}[d]	ε[e]
PDHN	5.0	1.6225	1.5558	1.6003	2.82
PDBN	8.0	1.5887	1.5670	1.5815	2.75

[a] Film thickness.
[b] The in-plane refractive indices.
[c] The out-of-plane refractive indices.
[d] Average refractive indices; $n_{AV} = (2n_{TE} + n_{TM})/3$.
[e] Optically estimated dielectric constant; $\varepsilon = 1.10n_{AV}^2$.

place selectively at the C1 and C5 positions and gave PDHN having the expected regiocontrolled structure.

As described in Section 1, PDHN can be used as protection and insulation layers in the semiconductor field. Thus, it is important to measure the dielectric constant (ε) of it. The ε of PDBN was also estimated as a comparative example. The ε of the polymer film at around 1 MHz can be estimated from the refractive index (n) of the film according to modified Maxwell's equation, $\varepsilon \approx 1.10n^2$ [19]. The films of PDHN and PDBN on quartz were prepared by spin-casting from the ethyl lactate and *N*,*N*-dimethylacetoamide/dichloromethane solutions, respectively, and then these films were dried at 200 °C for 4 h under nitrogen.

Table 4 summarizes the refractive indices and the dielectric constants of the films. The average refractive indices (n_{AV}) of the PDHN and PDBN films were determined as 1.6003 and 1.5815, respectively, which were translated into dielectric constants of 2.82 and 2.75, respectively. These values are relatively low compared to other thermally stable polymers such as poly(arylene-ether)s [20,21] ($\varepsilon \approx 3.0$) or aromatic poly(imide)s [22] ($\varepsilon \approx 3.5$).

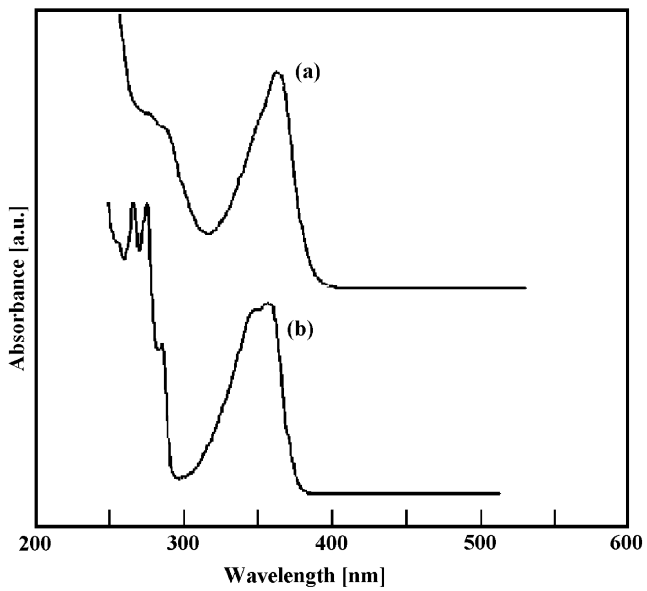


Fig. 5. UV–Vis spectrum of (a) the PDHN film with 1 μm thickness and (b) 2,6-DHN in methanol.

To disclose the reason why these polymers containing many hydroxyl groups and double bonds possess so low ε values, the UV–Vis spectra of (a) PDHN and (b) the starting monomer of 2,6-DHN were measured (Fig. 5). Both spectra are quite similar and the onset positions of both compounds are 380 and 400 nm, respectively, indicating a low extended π-conjugation in PDHN. This suggests the dihedral angle between the neighboring naphthalene rings may be very large because of the steric repulsion of the bulky naphthalenes, which reduces the density and lowers the dielectric constants of the resulting polymers.

4. Conclusion

Regiocontrolled PDHN was prepared by the oxidative coupling polymerization of 2,6-DHN. Polymerizations were conducted in 2-methoxyethanol in the presence of CuCl(OH)TMEDA as the catalyst under air at 25 °C, producing polymers with M_ns up to 52,000. The structure of PDBN derived from PDHN was characterized by ^{1}H and ^{13}C NMR spectroscopies and was estimated to consist completely of the 1,5-linkage. The average refractive indices of the PDHN and PDBN films were 1.6003 and 1.5815, respectively, and the dielectric constants estimated from the refractive indices were 2.82 and 2.75, respectively. These results indicate that this solution polymerization is a simple and effective method for the preparation of PDHN with high molecular weights.

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