Oxidative Coupling Polymerization of 2,6-Dihydroxynaphthalene in Basic Water

Yosuke TSUTSUI, Naoko NUMAO, and Masato SUZUKI^{†,††}

Department of Organic and Polymeric Materials, and International Research Center of Macromolecular Science, Tokyo Institute of Technology, O-okayama, Meguro-ku 152-8552, Japan

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ABSTRACT: The oxidative coupling polymerization of 2,6-dihydroxynaphthalene was found to take place in basic water. Alkaline metal bases such as NaOH and K₂CO₃ with the catalyst of copper(II) disodium ethylenediaminetetraacetate tetrahydrate resulted in promoting the over-oxidation to form the quinone unit and the C–O coupling to form the ether unit. When amines were employed as the base, their structures affected the polymerization results. HOCH₂CH₂-NH₂, and (HOCH₂)₃CNH₂ produced poly(2,6-dihydroxy-1,5-naphthylene) without the quinone and the ether units, however, which were formed in the presence of Me₂NH, Me₃N, and BnNH₂. Surprisingly, it was found that the catalyst was dispensable for amines to promote this polymerization. [DOI 10.1295/polymj.38.234]

KEY WORDS Oxidative Coupling Polymerization / 2,6-Dihydroxynaphthalene / Water / Base / Copper Catalyst / Noncatalytic Polymerization /

Oxidative coupling polymerization is attractive methodology for the preparation of aromatic polymers since non-functionalized aromatic carbons participate the polymerization forming C–C or C–O bonds.¹ Especially, the catalytic system with aerobic oxidation is valuable from the standpoint of green chemistry, atom-economically giving H₂O as the byproduct. Poly(2,6-dimethyl-1,4-phenylene oxide) is commercially produced by using such a system.

We have been studying the synthesis of novel polymers using oxidative coupling polymerization. In our recent articles, 2,6-dihydroxynaphthalene (2,6-DHN) was found to undergo the regio-selective C–C bond forming polymerization (Scheme 1).^{2,3} Poly(2,6-dihydroxy-1,5-naphthylene) (PDHN) was obtained by the solvent-free polymerization in the presence of the stoichiometric amount of FeCl₃·6H₂O² and also by the solution polymerization catalyzed with CuCl(OH)-TMEDA (TMEDA: *N,N,N',N'*-tetramethylethylenediamine).³ In the former case, the polymerization took place at r.t. to yield PDHN (*M*_n = 9800 after the *O*-acetylation) when the 2,6-DHN-benzyl amine complex was used as the monomer. In the later case, high molecular weight PDHN (*M*_n = 52000) was obtained by the reaction at r.t. for 3 h under air. Prior to our works, Marin and Horak synthesized PDHN oligomer by the electrochemical oxidation coupling.⁴

Interestingly, PDHN is composed of the BINOL (1,1'-bi(2-naphthol)) type repeating unit. It is well-known that BINOL has atropisomerism due to no free rotation between two naphthalene rings at r.t., so that

there is tacticity in PDHN. Figures 1 and 2 show the diad tacticity, meso and racemo, of the PDHN units and the schematic models of isotactic and syndiotactic PDHN, respectively. The PDHN prepared in the above-mentioned articles had the stereoregularity a little.

The allied stereoregular polymer from 2,3-dihydroxynaphthalene (2,3-DHN) derivatives has been investigated. Fuji *et al.* successfully isolated the uniform oligomers, which have the perfect stereoregularity, by repeating the oxidative coupling and the optical resolution.⁵ Habaue and Okamoto performed the oxidative coupling polymerization of optically active 2,3-DHN dimer derivatives in the presence of chiral catalysts, producing the chiral binaphthalene polymers (the highest chirality *R:S* = 84:16).⁶ Habaue *et al.* recently prepared also the non chiral polymer by the direct oxidative coupling of 2,3-DHN.⁷

On the course of exploring the polymerization system to prepare stereoregular PDHN, we noticed the recent articles by Nishide *et al.* about the oxidative coupling polymerization of 2,6-dimethylphenol in water.⁸ We have already found that PDHN, as well as 2,6-DHN, is soluble in basic water and can be used as alkaline-developable photo-resist.⁹ Therefore, basic water would be expected to work as a good solvent for the polymerization of 2,6-DHN, possibly giving a significant influence on the stereoregularity of the product polymer. In this context, we report herein the oxidative coupling polymerization of 2,6-DHN in basic water.

[†]To whom correspondence should be addressed (Tel/Fax: +81-52-735-5260, E-mail: suzuki.masahito@nitech.ac.jp).

^{††}Present address: Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya Institute of Technology, Gokisocho, Showa-ku, Nagoya 466-8555, Japan

Scheme 1. Oxidative coupling polymerization of 2,6-DHN and acetylation of the polymer.

Figure 1. The diad tacticity, meso (a) and racemo (b), of PDHN.

Figure 2. The schematic models of 12 mer of 2,6-DHN (isotactic (a) and syndiotactic (b)).

EXPERIMENTAL

Materials and Measurement

The monomer, 2,6-dihydroxynaphthalene (2,6-DHN), and the catalyst, copper(II) disodium ethylenediaminetetraacetate tetrahydrate ($\text{Cu}(\text{edta}) \cdot 4\text{H}_2\text{O}$),

were used as received from Tokyo Kasei Kogyo Co., Ltd. and Nacalai Tesque, Inc., respectively. Other materials such as acetic anhydride, dry pyridine, metal salts, and amines (Kanto Kagaku Co., Ltd.) were also used as received. Water was deionized through ion-exchange resin (an ORGANO G-20B system) and then used as the polymerization solvent. The IR spectra

Table I. Oxidative coupling polymerization of 2,6-DHN in water with alkaline metal bases^a

Run	Base (Mol ratio) ^b	PDHN ^c		CHCl ₃ -soluble part: insoluble part ^d	PDAcN			
		Quinone	Ether		CHCl ₃ -soluble and Et ₂ O-insoluble part			
					Yield (%)	<i>M</i> _w ^e	<i>M</i> _n ^e	<i>M</i> _w / <i>M</i> _n ^e
1	NaOH (2)	+	+	31:69	21	2700	1600	1.74
2	KOH (2)	+	+	25:75	16	1600	1400	1.25
3	Na ₂ CO ₃ (1.5)	+	+	10:90	6	3100	1500	2.05
4	Cs ₂ CO ₃ (1.5)	+	+	32:68	16	4200	2200	1.86

^aThe polymerizations were performed with the catalyst of Cu(edta)·4H₂O (10 mol % for 2,6-DHN) at r.t. for 24 h. At every run, 2,6-DHN was completely dissolved in the basic water. [2,6-DHN] = 0.1 M. ^bThe mol ratio for 2,6-DHN.

^cThe symbol of + means that the peaks of the quinone and the ether groups were detected in the IR spectrum of the polymer before acetylation. ^dThe weight ratio. ^eGPC (solvent: CHCl₃, standard: polystyrene).

were recorded on a JASCO FT/IR-460plus spectrophotometer equipped with an attenuated total reflection (ATR) apparatus, JASCO ATR PRO400-S (prism: ZnSe). ¹H NMR spectra were measured at 300 MHz on a Bruker DPX 300 spectrometer. Molecular weights were evaluated by gel permeation chromatography (GPC) calibrated with polystyrene standards; a Shodex K-804L column with CHCl₃ as the eluent (a flow rate of 1 mL/min) was used on a JASCO system of a PU-1580 pump and a UV-1570 detector. Thin-layer chromatography (TLC) was performed on a Merck silica gel 60 F₂₅₄ aluminum plate.

The Typical Procedure for the Polymerization

Into water (2.0 mL) were successively added ethanolamine (78 μL, 1.3 mmol) and 2,6-dihydroxynaphthalene (34.1 mg, 0.21 mmol). The pink mixture was stirred at r.t. so as to become a homogenous and red-purple solution, then, to which Cu(edta)·4H₂O (10.0 mg, 0.021 mmol) was added. Stirring at r.t. for 2 h under air was followed by the addition of 1 M HCl aq. The precipitated material was collected by centrifugation and successively washed with 1 M HCl aq. and water. Drying *in vacuo* gave poly(2,6-dihydroxy-1,5-naphthylene) as dark brown powder (29.6 mg).

When other bases were used, the monomer concentration was arranged to be 0.1 M by adjusting the amount of water.

Acetylation of Poly(2,6-dihydroxy-1,5-naphthylene)

Poly(2,6-dihydroxy-1,5-naphthylene) (17.8 mg) was stirred with acetic anhydride (0.6 mL) in pyridine (0.55 mL) at r.t. for 24 h; the reddish solution became yellowish. The reaction mixture was poured into water, giving brown precipitate, which was washed with water several times and dried *in vacuo*. The brown powder of poly(2,6-diacetoxy-1,5-naphthylene) was obtained (23.3 mg, 86% yield).

RESULTS AND DISCUSSION

Tables I–III summarize the polymerization results of 2,6-DHN in basic water. Consequently, the molecular weights of the product polymers were found to be much lower than that produced in 2-methoxyethanol (*M_n* = 17000 after the *O*-acetylation). This is ascribable to the precipitation of the product polymer. In addition, the IR analysis of the product polymers suggested that side reactions were involved in many cases. The representative IR spectra are shown in Figure 3. The polymer prepared in the presence of KOH shows the IR absorption bands due to ν_{C=O} (1700 and 1650 cm⁻¹), suggesting the formation of 2,6-naphthoquinone-1,5-diyl unit by the over-oxidation (Figure 3a). Additionally, there are observed the different absorption bands in the area of 1200–1400 cm⁻¹ from those of the authentic sample of PDHN, most likely suggesting the formation of the naphthylene ether unit by the C–O coupling instead of the C–C coupling. In the corresponding columns of Tables I–III, the symbols of + and – inform whether the quinone and the ether units are detected or not, respectively. The further characterization of the product polymers was performed for poly(2,6-diacetoxy-1,5-naphthylene) (PDAcN) that was prepared by the acetylation of the hydroxyl groups. The quinone and the ether units could reduce the solubility of the polymer, giving a CHCl₃-insoluble part of PDAcN. The CHCl₃-soluble PDAcN was characterized by GPC measurement and NMR spectroscopy, which informed the diad tacticity ratio of meso and racemo (*vide infra*) of the polymer unit.

Table I shows the reaction results in the presence of alkaline metal bases such as NaOH, KOH, Na₂CO₃, and Cs₂CO₃. The polymerization took place in the homogenous solution of 2,6-DHN with Cu(edta)·

Table II. Oxidative coupling polymerization of 2,6-DHN in water with amine^a

Run	Base (Mol ratio) ^b	Solubility ^c	Temp. (Time)	PDHN ^d		PDAcN					
				Quinone	Ether	CHCl ₃ -soluble part: insoluble part ^e	CHCl ₃ -soluble and Et ₂ O-insoluble part				
							Yield (%)	<i>M</i> _w ^f	<i>M</i> _n ^f	<i>M</i> _w / <i>M</i> _n ^f	Meso:Racemo ^g
5	MeNH ₂ (2)	+	r.t. (1.5 h)	—	+—	100:0	41	6600	3400	1.93	35:65
6	MeNH ₂ (2)	+	60 °C (1 d)	+—	+	62:38	35	2200	1200	1.82	45:55
7	Me ₂ NH (2)	+	r.t. (1 d)	+	+	51:49	33	3600	1700	2.16	32:68
8	Me ₃ N (6)	—	r.t. (1 d)	+	+	62:38	42	3100	1300	2.43	43:57
9	HOCH ₂ CH ₂ NH ₂ (6)	+	r.t. (2 h)	—	—	100:0	73	18600	6400	2.92	46:54
10	(HOCH ₂) ₃ CNH ₂ (14)	—	r.t. (1 d)	—	—	100:0	71	22200	5300	4.19	37:63
11	BnNH ₂ (20)	—	r.t. (1 d)	+	—	100:0	50	7500	3600	2.07	64:36
12	H ₂ NCH ₂ CH ₂ NH ₂ (2)	—	r.t. (1 d)	+—	+—	100:0	89	1800	1300	1.37	46:54
13	—	—	r.t. (5 d)	<i>No reaction</i>							
14	—	—	50 °C (12 h) 80 °C (16 h)	+—	+—	100:0	89	<i>M</i> _p = 1500, 650 ^h			— ⁱ

^aThe polymerizations were performed with the catalyst of Cu(edta)•4H₂O (10 mol % for 2,6-DHN). [2,6-DHN] = 0.1 M. ^bThe mol ratio for 2,6-DHN. ^cSolubility of 2,6-DHN in the amine aq. (+: soluble; —: insoluble). ^dRemarks about the peaks of the quinone and the ether groups in the IR spectrum of the polymer before the acetylation (+: the clear peak was observed; +—: the peak was observed but not clear; —: the peak was not observed). ^eThe weight ratio. ^fGPC (solvent: CHCl₃, standard: polystyrene). ^gThe diad tacticity ratio, evaluated by ¹H NMR (CDCl₃). ^hMolecular weight at the peak tops, measured by GPC. ⁱNot determined.

Table III. No catalyst oxidative-coupling polymerization of 2,6-DHN in water with amine^a

Run	Base (Mol ratio) ^b	Solubility ^c	Time	PDHN ^d		CHCl ₃ -soluble part: insoluble part ^e	PDAcN				
				Quinone	Ether		CHCl ₃ -soluble and Et ₂ O-insoluble part				
							Yield (%)	<i>M</i> _w ^f	<i>M</i> _n ^f	<i>M</i> _w / <i>M</i> _n ^f	Meso:Racemo ^g
15	MeNH ₂ (2)	+	3.5 h	+−	+−	100:0	46	3400	2100	1.65	26:74
16	Et ₃ N (4)	−	3 d	+	+	39:61	28	4700	2700	1.71	35:65
17	HOCH ₂ CH ₂ NH ₂ (2)	−	2 d	−	−	100:0	83	2600	2000	1.34	37:63
18	HOCH ₂ CH ₂ NH ₂ (6)	+	4 h	−	−	100:0	71	5000	3400	1.45	37:63
19	(HOCH ₂ CH ₂) ₃ N (4)	−	2 d	+	−	100:0	61	3800	2900	1.62	42:58
20	H ₂ NCH ₂ CH ₂ NH ₂ (2)	−	2 d	−	−	100:0	77	2400	1800	1.32	44:56

^aThe polymerizations were performed without the catalyst at r.t. [2,6-DHN] = 0.1 M. ^bThe mol ratio for 2,6-DHN. ^cSolubility of 2,6-DHN in amine aq. (+: soluble; —: insoluble). ^dRemarks about the peaks of the quinone and the ether groups in the IR spectrum of the polymer before the acetylation (+: the clear peak was observed; +—: the peak was observed but not clear; —: the peak was not observed). ^eThe weight ratio. ^fGPC (solvent: CHCl₃, standard: polystyrene). ^gThe diad tacticity ratio, evaluated by ¹H NMR (CDCl₃).

4H₂O (10 mol %) at r.t. for 24 h. As described above, the product polymers were found to contain the quinone and the ether units, and a large amount of the CHCl₃-insoluble part for PDAcN, giving low yields of the CHCl₃-soluble part. Usage of Cs₂CO₃ as the base afforded a little higher molecular weight polymer for the CHCl₃-soluble part.

The polymerizations by use of several amines were also performed in the presence of Cu(edta)•4H₂O (10 mol %) (Table II). MeNH₂, Me₂NH, and HOCH₂CH₂NH₂ gave the homogenous solution of 2,6-DHN in water, while Me₃N, (HOCH₂)₃CNH₂, BnNH₂, and H₂NCH₂CH₂NH₂ did not even in the presence of excess amounts of them; these findings are shown by the sym-

Figure 3. IR spectra of the product polymers (solid lines) at runs 2 (a), 9 (b), 20 (c). The broken line in each of (a)–(c) is the IR spectrum of PDHN prepared in 2-methoxyethanol.³

bols + and – in the column of solubility. Independently of the solubility of the monomer, the polymerization was greatly promoted by the amines (runs 5–12). In the absence of amine (runs 13 and 14), no polymerization took place at room temperature and heating at 80 °C resulted in the formation of oligomeric materials. Interestingly, whether the side reactions are involved or not is dependent on the amine employed. When HOCH₂CH₂NH₂, and (HOCH₂)₃CNH₂ (runs 9 and 10) were used, the product polymers contained no quinone and ether units, and were fully soluble in CHCl₃. As shown in Figure 3b, the IR spectrum of the product polymer at run 9 is wholly identical with that of the authentic sample prepared in 2-methoxyethanol. Additionally, runs 9 and 10 produced the relatively higher molecular weight polymers in satisfactory yields. The

heterogeneous reaction at run 10 brought the broad polydispersity to the product polymer. As shown in run 6, heating tends to promote the undesirable reactions, forming the CHCl₃-insoluble part. In contrast, the quinone and/or the ether units were apparently formed even in the reaction at room temperature when Me₂NH, Me₃N, and BnNH₂ were employed (runs 7, 8, and 11). The above findings that the polymerization results are dependent on the amine structure could be ascribable to the coordination property of amine to the copper catalyst to affect the activity.

Surprisingly, the blank experiment without the copper catalyst was found to conduct the aerobic oxidative coupling polymerization in the presence of amine (Table III). The IR spectrum of the polymer produced in the presence of H₂NCH₂CH₂NH₂ (run 20), as is

Figure 4. ^1H NMR spectrum of PDAcN (run 9) (solvent: CDCl_3).

representatively shown in Figure 3c, is completely identical with the authentic sample, suggesting the formation of PDHN. Even the quinone unit was detected when Et_3N or $(\text{HOCH}_2\text{CH}_2)_3\text{N}$ was used (runs 16 and 19). The reaction rate is obviously larger under the condition that the monomer is soluble in the aqueous amine solution (runs 15 and 18). Comparing runs 5 and 9 (Table II) with runs 15 and 18 (Table III), respectively, suggests that the copper catalyst works to accelerate the polymerization. The monomer was consumed faster in the presence of the catalyst, giving the higher molecular weight polymer.

The diad tacticity of the parent PDHN is computable from the ^1H NMR spectra of PDAcN (Figure 4). Against our expectations, the aqueous media consequently brought only some diad selectivity (meso:racemo = 64:36–32:68) to the product polymers. These values are comparable with those of PDHN prepared under the solvent-free conditions with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (meso:racemo = 54:46–37:63)² and in 2-methoxyethanol with the catalyst of $\text{CuCl}(\text{OH})\text{TMEDA}$ (meso:racemo = 42:58).

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REFERENCES

1. M. B. Jones and P. Kovacic, in "Encyclopedia of Polymer Science and Engineering," 2nd ed., H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges, and J. I. Kroschwitz, Ed., Wiley-Interscience, New York, 1987, vol. 10, p 670.
2. M. Suzuki and Y. Yatsugi, *Chem. Commun.*, 162 (2002).
3. Y. Sasada, Y. Shibasaki, M. Suzuki, and M. Ueda, *Polymer*, **44**, 355 (2002).
4. G. H. Marin and V. Horak, *J. Org. Chem.*, **59**, 4267 (1994).
5. a) K. Tanaka, T. Furuta, K. Fuji, Y. Miwa, and T. Taga, *Tetrahedron: Asymmetry*, **7**, 2199 (1996).
b) K. Fuji, T. Furuta, and K. Tanaka, *Org. Lett.*, **3**, 169 (2001).
6. a) S. Habaue, T. Seko, M. Isonaga, H. Ajiro, and Y. Okamoto, *Polym. J.*, **35**, 592 (2003).
b) S. Habaue, H. Ajiro, Y. Yoshii, and T. Hirasa, *J. Polym. Sci., Part A: Polym. Chem.*, **42**, 4528 (2004).
7. S. Habaue, R. Muraoka, A. Akikawa, S. Murakami, and H. Higashimura, *J. Polym. Sci., Part A: Polym. Chem.*, **43**, 1635 (2005).
8. a) K. Saito, T. Masuyama, and H. Nishide, *Green Chem.*, **5**, 535 (2003).
b) K. Saito, T. Tago, T. Masuyama, and H. Nishide, *Angew. Chem., Int. Ed.*, **43**, 730 (2004).
9. a) Y. Sasada, Y. Shibasaki, M. Suzuki, and M. Ueda, *J. Polym. Sci., Part A: Polym. Chem.*, **40**, 393 (2002).
b) K. Tsuchiya, Y. Shibasaki, M. Suzuki, and M. Ueda, *J. Polym. Sci., Part A: Polym. Chem.*, **42**, 2235 (2004).