Polymer Bulletin 50, 55–60 (2003)

Polymer Bulletin
© Springer-Verlag 2003

Enzymatic Synthesis of Poly(quinolinol) and Its Fluorescent Aluminum Complex

Takakazu Yamamoto (✉), Isao Yamaguchi (✉)

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan
e-mail: tyamamot@res.titech.ac.jp, Fax: +81-45-924-5276

Received: 27 February 2003 / Accepted: 5 March 2003

Summary

Horseradish peroxidaze (HRP)-catalyzed polymerization of 8-quinolinol proceeded regioselectively to give a soluble poly(quinolinol) (**1**). Reaction of **1** with Alq'$_2$(Et) (q' = 2-methy-8-quinolinolato) provided a polymer-aluminum complex (**2**). **2** was photoluminescent both in solutions and in the solid state. Quantum yield (Φ) of the photoluminescence in the chloroform solution was 23%.

Introduction

Polymer materials for organic light-emitting diodes (LEDs) have been the subject of recent many papers [1]. Incorporation of luminescent metal complex into the polymers has been carried out for improvement of LED performance [2]. Tri(8-quinolinolato)aluminum (Alq$_3$) is one of the most widely used complexes for LEDs, because of not only its desired green emitting but also highly efficient electron transporting properties of Alq$_3$ [3]. Recently, we reported preparation of an aluminum complex, Alq'$_2$(Et) (q' = 2-methyl-8-quinolinolato), and its reaction with 8-quinolinol to provide Alq'$_2$q [4]. Extension of this work, reaction of poly(quinolinol) with Alq'$_2$(Et), will lead to a polymer having the Alq$_3$ type structure that may be an useful material for LEDs.

There is a report on synthesis of poly(quinolinol) by using electrochemical oxidative polymerization of 8-quinolinol, however, structure of the polymer has not been identified [5]. On the other hand, horseradish peroxidaze (HRP) catalyzed polymerization is of use for preparation of functional poly(phenol)s [6,7]. The HRP-catalyzed polymerization has been applied for synthesis of poly(quinolinol) with sulfonic acid groups which are not suitable for reaction with Alq'$_2$(Et) [8]. Enzymatic preparation of well-defined poly(quinolinol) has no precedent to our knowledge. In this work we report synthesis and structure of poly(quinolinol) by using the HRP-catalyzed polymerization as well as reaction of the polymer with Alq'$_2$(Et). Optical properties of the polymers are also reported.

Experimental

Measurements

IR and NMR spectra were recorded on a JASCO-IR 460 spectrophotometer and a

JEOL EX-400 spectrometer, respectively. Elemental analyses were carried out with a Yanagimoto Type MT-2 CHN autocorder. UV-vis and photoluminescence spectra were obtained by Shimadzu UV-vis 3100PC and Hitachi F4010 spectrometers, respectively. Quantum yields were calculated by using a diluted sulfuric acid (0.50 M) solution of quinine as the standard. GPC analyses were performed by a Toso HLC 8020 equipped with polystyrene gel columns (TSK gel G2500, G4000, and G5000), using a DMF solution of LiBr (0.010 M) as an eluent with a flow rate of 1.0 mL min^{-1} and with RI and UV detectors.

*Synthesis of **1***

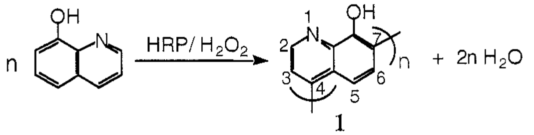
8-Quinolinol (0.72 g, 5.0 mmol) and HRP (7.5 mg, 1000 units) purchased from Sigma Chemical Co. in a mixture of 1,4-dioxane (35 mL) and an aqueous acetate buffer solution (pH 4.7, 15 mL) were placed in a round bottle flask. To the mixture, 500 μL of 35% hydrogen peroxide (5.1 mmol) was added dropwise (less than 0.5 mmol H_2O_2 at each time) over 3 h. After the reaction mixture was stirred at room temperature for 6 h, the solvent was removed under vacuum. The resulting solid was washed with water and dissolved in DMSO. Reprecipitation in methanol and drying in vacuo gave **1** as a light brown solid (0.25 g, 35%). Element anal. $(C_9H_5NO$□$0.75H_2O)_n$: Calcd. C 69.00, H 4.18, N 8.94; Found C 69.09, H 4.73, N 9.10. ^1H NMR (400 MHz, $CDCl_3$): δ about 8.85 (OH), 8.80 (position 2 of the quinolinol ring), 7.76 (position 3 of the quinolinol ring), 7.46 (position 5 of the quinolinol ring), 7.28 (position 6 of the quinolinol ring). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.0, 147.8, 147.7, 138.2, 136.0, 134.8, 129.9, 121.9, 109.4.

*Synthesis of **2***

To a THF (5 mL) solution of Alq'$_2$(Et) (72 mg, 0.21 mmol) was added THF (10 mL) solution of **1** (28 mg, 0.2 mmol). After the reaction mixture was stirred at 20 • C for 6 h, the solvent was removed by evaporation. Resulting solid was washed with toluene and dried under reduced pressure to give **2** as a yellow solid (48 mg, 49%). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.24 (d, H at the position 2 of the quinolinol ring in the polymer main chain, 1H, *J* = 8 Hz), 8.03 (d, 1H, *J* = 8 Hz), 7.86 (d, H at the position 3 of the quinolinol ring in the polymer main chain, 1H, *J* = 8 Hz), 7.47 (d, H at the position 5 of the quinolinol ring in the polymer main chain, 1H, *J* = 8 Hz), 7.43 (d, H at the position 6 of the quinolinol ring in the polymer main chain, 1H, *J* = 8 Hz), 7.40-7.35 (2H, m), 7.31 (d, 1H, *J* = 8 Hz), 7.18-7.13 (2H, m), 7.03 (d, 1H, *J* = 8 Hz), 6.92 (d, 1H, *J* = 8 Hz), 6.65 (d, 1H, *J* = 8 Hz), 3.15 (1.5H, Me), 2.73 (1.5H, Me), 2.42 (1.5H, Me), 2.36 (1.5H, Me).

Results and discussion

HRP-catalyzed oxidative polymerization of 8-quinolinol was carried out by using hydrogen peroxide as an oxidizing reagent in a mixture of 1,4-dioxane and acetate buffer (pH = 4.7) to give poly(quinolinol), **1**, in 35% yield (eq. 1).



(1)

1

Polymer **1** is soluble in chloroform, THF, DMF, and DMSO. GPC measurement revealed that M_n and M_w values of **1** were 2,500 and 3,400, respectively. Intrinsic viscosity, $[\eta]$, of **1** was 0.09 dLg^{-1} in DMF at 30 °C.

Figure 1 shows ^1H and ^{13}C NMR spectra of **1**. ^1H NMR peaks of hydrogens at 2, 5, and 6 positions of the quinolinol ring showed signals at positions similar to those of 8-quinolinol. A peak due to hydrogen at 3 position of the quinolinol ring was observed at lower magnetic field (δ 7.76) than that of 8-quinilinol (δ 7.46). A broad peak at about δ 8.85 was assigned to OH group. This peak disappeared on addition of a small amount of D_2O in the NMR sample tube, supporting the assignment. Peaks of hydrogens at 4 and 7 positions of the quinolinol ring were disappeared in the ^1H NMR spectrum. ^{13}C NMR spectrum showed nine peaks whose assignments were depicted in Figure 1b. These NMR data revealed that HRP-catalyzed polymerization of 8-quinolinol proceeded predominantly by coupling at the 4 and 7 positions of the quinolinol ring.

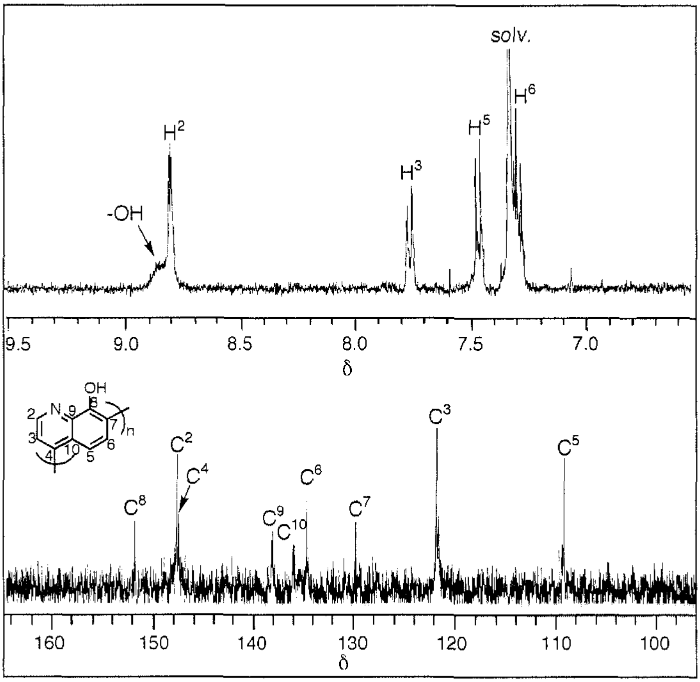
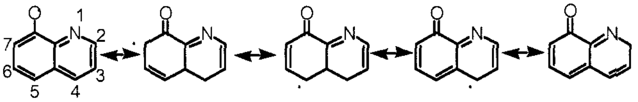


Figure 1. ^1H and ^{13}C NMR spectra of **1** in $CDCl_3$.

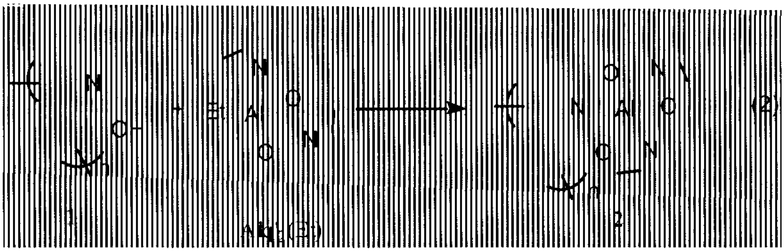
HRP-catalyzed polymerization of phenols has been reported to proceed by free radical coupling, and the bonding positions between the monomeric units have been correlated to the positions where the radical can be delocalized in the oxidized phenols [6,8]. Scheme 1 depicts resonance structures of oxidized 8-quinolinol.



Scheme 1. Possible resonance structures of oxidized 8-quinolinol.

From scheme 1, the coupling at 4 and 7 positions of the quinolinol ring in the present polymerization is conceivable. Although a coupling at the oxygen may also be possible to form quinolinolene oxide unit (like the phenylene oxide unit in poly(phenylene oxide)), absence of absorption peaks due to ν(C-O-C) vibration in the IR spectrum of **1** and the simple ^{1}H and ^{13}C NMR patterns exclude formation of the quinolinolene oxide unit.

Reaction of **1** with Alq'$_2$(Et) gave a polymer complex, **2**, in 49% yield (eq. 2).



The polymer complex **2** showed solubility similar to that of **1**. Disappearance of absorption due to the OH group in the IR spectrum of **2** indicated formation of the new Al-O bond. ^{1}H NMR spectrum of **2** showed four peaks, in almost equal intensities, assignable to methyl hydrogens bonded to the quinolinol ring at positions, similar to the case of Alq'$_2$q [4]. The four CH_3 peaks suggest existence of both facial and meridional isomers concerning the aluminum complex part. Peaks due to hydrogens at 3, 5, and 6 positions of the quinolinol ring in the polymer main chain were observed at similar positions to those in **1**. Whereas the peak of H at the 2 position of the quinolinol ring in the polymer main chain was shifted to a higher magnetic field compared with that in **1** (see *synthesis of* ***2*** in Experimental), similar to the case of Alq'$_2$q [4]. Hydrogens of the 2-methyl-8-quinolinol rings showed signals in the range of δ 6.65 to δ 8.03. Relative peak intensity between the methyl hydrogens and the quinolinol hydrogens revealed that essentially all of the quinolinol unit in **1** reacted with the aluminum complex.

UV-vis spectra of **1** and **2** showed an absorption maximum (λmax) at 350 and 359 nm, respectively. It has been reported that introduction of an electron-withdrawing group at position 7 of the quinolinol ring of Alq_3 caused a blue-shift of λmax in organic solvent [9]. The shorter λmax of chloroform solution of **2** than that of Alq'$_2$q (λmax = 375 nm) may be ascribed to the structure of the macromolecular ligand which has electron-withdrawing polyquinoline [10] chain bonded at the 4,7-positions.

Although **1** did not show photoluminescence (PL), **2** was photoluminescent both in solutions and in the solid state. Figure 2 depicts PL and excitation spectra of **2** in $CHCl_3$ and in a thin film cast on a quartz glass plate. In the chloroform solution of **2**, a PL peak was observed at 489 nm and its excitation spectrum showed a peak (360 nm) near its absorption peak. Quantum yield (Φ) of the photoluminescence was 23%, whose value was higher than that of Alq'$_2$q (Φ = 7%). PL spectrum of the film of **2** showed a peak at a longer wavelength (564 nm) than that of $CHCl_3$ solution of **2**.

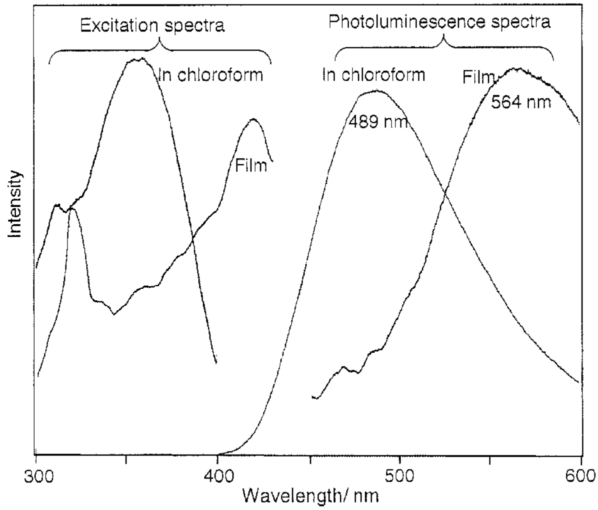


Figure 2. Photoluminescence and excitation spectra of **2** in $CHCl_3$ and in film of **2** cast on a quartz glass plate.

Conclusion

HRP-catalyzed polymerization of 8-quinolinol proceeded regioselectively to give a soluble poly(quinolinol) (**1**). Reaction of **1** with $Alq'_2(Et)$ provided a photoluminescent polymer-aluminum complex (**2**). The polymer-aluminum complex may be a candidate for a useful material of LEDs.

Acknowledgements. This work was partly supported by a Grant-in-Aid for Scientific Research from Ministry of Education, Science, Culture, and Sports Japan.

References

1. Friend RH, Gymer RW, Holmes AB, Burroughes JH, Marks RN, Taliani C, Bradley DDC, Dos Santos DA, Bredas JL, Logdlund M, Salaneck WR (1999) Nature 397:121
2. (a) McGehee MD, Bergstedt T, Zhang C, Saab AP, O'Regan MB, Bazan GC, Srdanov VI, Heeger AJ (1999) Adv Mater 11:1349 (b) Chen FC, Yang Y, Thompson ME, Kido J Appl Phys Lett (2002) 80:2308
3. (a) Adachi C, Tokio S, Tsutsui T, Saito S (1988) Jpn J Appl Phys 27:L713 (b) Tang CW, VanSlyke SA, Chen CH (1989) J Appl Phys 65:3611 (c) Hamada Y, Sano T, Fujita M, Fujii T, Nishio Y, Shibata K (1993) Jpn J Appl Phys 32: L514 (d) Bulovic V, Gu G, Burrows PE, Forrest SR (1996) Nature 380:29 (e) Shen Z, Burrows PE, Bulovis V, Borrest SR, Thompson ME (1997) Science 276:2009 (f) Aziz H, Popovic ZD, Hu NX, Hor AM, Xu S (1999) Science 283:1900 (g) Wu Q, Esteghamatian M, Hu NH, Popovic Z, Enright G, Tao Y, D'Iorio M, Wang S (2000) Chem Mater 12:79
4. Yamaguchi I, Iijima T, Yamamoto T (2002) J Organomet Chem 654:229
5. Pham MC, Dubois JE, Lacaze PC (1983) J Electrochem Soc: Electrochem Sci Tech 130:346
6. (a) Kobayashi S, Uyama H, Ohmae M (2001) Bull Chem Soc Jpn 74:613 (b) Kobayashi S, Uyama H, Kimura S (2001) Chem Rev 101:3793

7. Yamaguchi I, Yamamoto T Inorg Chim Acta in press
8. Alva KS, Marx KA, Kumar J, Tripathy SK (1997) Macromol Rapid Commun 18:133
9. Van Slyke SA, Bryan PS, Lovecchio FV (1992) US. 5150006; (1992) Chem Abstr 119:105561
10. Kanbara T, Saito N, Yamamoto T (1991) Macromolecules 24:5883