



## Efficient oxidation of hydroquinone and alcohols by tailor-made solid polyaniline catalyst

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### ABSTRACT

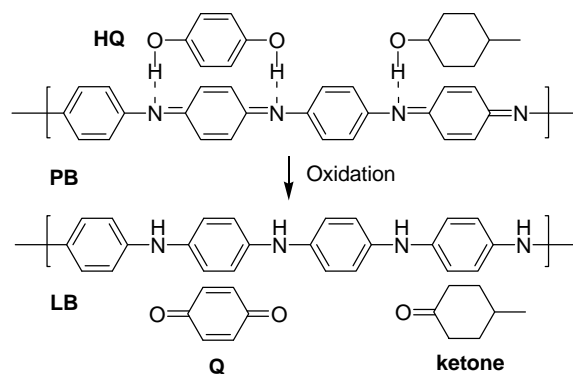
We described the efficient and convenient catalytic oxidation of hydroquinone and primary/secondary alcohol compounds into benzoquinone and aldehyde/ketone using various oxidation states of polyaniline. We analyzed the oxidation catalyzing capabilities of the pernigraniline base polymer by designing a tailor-made catalyst to be used as a powerful oxidant, and it was easily recovered and regenerated for recycling.

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The catalyzed oxidation of hydroquinone (HQ)/phenol is being extensively investigated with the dual objectives of removing phenolic waste from industrial effluent and achieving regio-selective oxidation of useful products. The latter process often involves a milder reaction condition. The oxidation of hydroquinone to benzoquinone (Q) is a very important physiological reaction and copper metal is found to be the most efficient catalyst for this reaction.<sup>1,2</sup> A general method for the preparation of quinones is the oxidation of HQ and its derivatives.<sup>3</sup> A number of oxidants, for example, mineral acids,<sup>4</sup> Femy's salt,<sup>5</sup> lead tetraacetate,<sup>6</sup> cerium ammonium nitrate,<sup>7</sup> and other transition metal ions,<sup>8</sup> have been employed, but most of these suffer from drawbacks such as homogenous reaction conditions and the generation of toxic wastes. Thus, new catalytic protocols need to be developed to fulfill the demands of green chemistry. For the 1:1 HQ–Q complex, in the presence of light, an electron can be donated from the HQ to the Q, forming a charge-transfer complex with a characteristic purple color.<sup>9</sup>

Among polymers, polyaniline (PANI) is well known to have various oxidation states such as leucoemeraldine base (LB, fully reduced form), emeraldine base (EB, half reduced form), pernigraniline base (PB, fully oxidized form), which permits the construction of a reversible redox cycle for the potential catalytic reactions.<sup>10–12</sup> Recently, we demonstrated that the synthesis of nano-porous PANI emeraldine salt (ES) by self-stabilized disper-

sion polymerization (SSDP) method results in an insoluble solid catalyst for the dehydrogenative oxidation of primary amines and primary alcohols.<sup>13–16</sup> The structure of PANI consists of a repeating unit of benzenoid and quinoid, which is similar to the structure of quinone derivatives. Accordingly, if the quinoid moiety of PANI was introduced into a hydroquinone or alcohol system, it is expected that HQ and primary/secondary alcohol compounds would be readily oxidized by suitable attractions such as a hydrogen bond and  $\pi$ – $\pi$  interaction between the PANI and these compounds. In a continuation of our ongoing work, we focused on the simple and efficient oxidation using tailor-made solid PANI



**Scheme 1.** Design for the oxidation of HQ or secondary alcohol using a tailor-made solid PANI catalyst.

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catalyst, which had never been used for the oxidation of HQ or primary/secondary alcohols (Scheme 1). These reactions are, to the best of our knowledge, the first example of the direct redox reactions system being catalyzed by the various oxidation states of PANI. In addition, the key strengths of solid-phase organic synthesis include the relatively easy work-up, purification, and recycling: simple filtration that separates the reagents, starting materials, and solvents from the desired products.

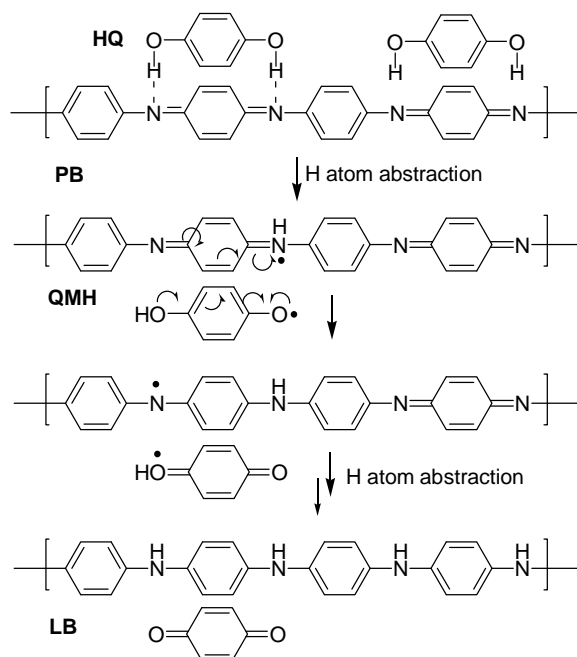
The PANI was prepared by the SSDP method with a honey-comb like nano-structure. The PB, ES, EB, and LB were prepared according to previous studies.<sup>13,14</sup> Initially, we attempted the oxidation of HQ (0.11 g, 1 mmol) with the PB (0.2 g) in the presence of dioxane (20 mL) at room temperature for 30 min after sonication for 5 min to produce the desired Q product as shown in Table 1 (entry 1). The colorless solution changed to purple due to the charge-transfer complexes associated with the formation of Q. The resultant product was exclusively and rapidly obtained by a simple filtration and then confirmed by comparison with an authentic sample. To obtain further information regarding the redox behavior, we characterized the oxidation state of PANI after transition into the LB structure by IR spectroscopy. Thus, the characteristic reduced peak at  $1495\text{ cm}^{-1}$  of the resulting PANI was identical to that of the synthesized LB form.<sup>15</sup> From the oxygen bubbling and catalytic amount of PB (50 mg) at  $80\text{ }^{\circ}\text{C}$  for 6 h, the reaction rate was slowly progressed and the yield of Q was still retained (entry 2). This finding means that the oxidation process was activated by the catalytic pathway. We think that the amount of HQ in the early stage of oxidation was in kinetically predominant competition with the reduction process of PB to give the LB form, which was retarded by the oxidation process of HQ. With the oxygen bubbling, the LB polymer was readily oxidized to the PB form for the catalytic pathway. The choice of a solvent is also important. The reaction in a polar aprotic solvent such as dioxane gave an exclusive yield, while the reaction in a polar protic solvent such as ethanol resulted in lower yield (compare the entries 1 and 3). This shows that the hydrogen bonding between HQ and PANI is hindered by a protic solvent.

To investigate another potential catalyst, the ES, EB doped with HCl was used for the oxidation of HQ. The reaction result (entry 4) shows that HQ can be oxidized by ES, but the efficiency was inferior to that of the PB (compare the entry 1). The efficiency was improved under the combinations of oxygen bubbling and at high temperature conditions (entries 5 and 6). These results show that not only the PB but also the ES polymer which have radical cation structure referred to as the polaron band that can be used as an oxidant because this radical species can participate in oxidation process by hydrogen atom abstraction pathway. As expected, the LB and EB forms under dioxane solvent did not oxidize to HQ (entry 7). These results imply that PANI should be in oxidized form in order to oxidize HQ; the fully oxidized form, PB can oxidize effectively, however reduced form such as LB and EB does not. In addition, we think, quinoid moiety of PB is designed to oxidize HQ as a tailor-made catalyst by hydrogen bonding donor-acceptor interaction.

Accordingly, the PB polymer is a powerful oxidant than ES polymer, which does not have a quinoid structure.

To study the dehydrogenative oxidation mechanism of HQ, we proposed a hydrogen atom abstraction mechanism by hydrogen bonding interaction (Scheme 2). Initially, hydrogen atom abstraction from HQ to the quinoid moiety (QM) of PB occurs to give the protonated quinoid moiety (QMH) radicals and phenoxy radical species. The QMH changes into the corresponding resonance structure by a single electron transfer to neighboring nitrogen. Finally, the resulting nitrogen radical of QMH abstracts another H atom of HQ to give Q.

Punniyamurthy and co-workers reported about EB-supported metal complex-catalyzed aerobic oxidation of alcohols to aldehydes and ketones.<sup>17</sup> In a previous study, we also reported that primary alcohols are successfully oxidized by ES catalyst.<sup>15</sup> However, secondary alcohols did not oxidize to the corresponding ketone compounds. To improve the synthetic method for the oxidation



Scheme 2. The proposed oxidation mechanism of HQ.

Table 2  
Oxidation of alcohols by various oxidation states of PANI<sup>a</sup>

Entry	Substrate	PANI	Yield (%)
1		PB	82
2		ES	38
3	Cinnamyl alcohol	PB	78
4		ES	–
5		PB	71
6		PB	54
7	2-Butanol	PB	61

<sup>a</sup> The alcohol (1 mmol) and oxidant (50 mg) were heated at  $80\text{ }^{\circ}\text{C}$  for 6 h under oxygen bubbling in dioxane.

Table 1  
Oxidation of HQ according to the various oxidation states of PANI

Entry	Catalyst	O <sub>2</sub>	Time (h)	Solvent	Temp. ( $^{\circ}\text{C}$ )	Yield (%)
1	PB <sup>a</sup>	×	0.5	Dioxane	rt	≥95
2	PB <sup>b</sup>	o	6	Dioxane	80	≥90
3	PB <sup>a</sup>	×	0.5	EtOH	rt	63
4	ES <sup>a</sup>	×	1	Dioxane	rt	47
5	ES <sup>a</sup>	o	2	Dioxane	80	68
6	ES <sup>b</sup>	o	6	Dioxane	80	56
7	EB or LB	×	12	Dioxane	80	–

<sup>a</sup> The reactant (1 mmol) and catalyst (200 mg) were used.

<sup>b</sup> The reactant (1 mmol) and catalyst (50 mg) were used.

**Table 3**  
Recycling of the PB for the oxidation of HQ<sup>a</sup>

Cycle	PB	Conversion (%)	Yield (%)
1	Fresh	93	87
2	Recovered <sup>b</sup>	5	Trace
3	Regenerated <sup>b</sup>	95	92

<sup>a</sup> Reaction condition: HQ (1 mmol), dioxane (30 mL), and the PB (200 mg) at room temperature.

<sup>b</sup> Recycled PB: after oxidation reaction, PB was separated from the reaction mixture by filtration, and the isolated PB was oxidized by APS.

of secondary alcohols, we examined the various primary/secondary alcohols such as 4-methyl cyclohexanol, 2-butanol, and isopropyl alcohols using a PB catalyst (Table 2). Interestingly, all of the primary/secondary alcohols oxidized to give the corresponding aldehyde/ketone compounds at a moderate yield. In the ES polymer, the corresponding product of the primary alcohol is poorly produced (entry 2) and no reaction is observed in the oxidation of secondary alcohols (entry 4).<sup>15</sup> However, when catalytic amount of the PB (50 mg) was used with oxygen bubbling at 80 °C for 6 h, the yield of the benzaldehyde was increased drastically (entry 1) and secondary alcohols were efficiently oxidized (entries 5 and 6). As in the oxidation of HQ, these results show that oxidized form of PANI, PB, is a more powerful oxidant for secondary alcohols than ES. As expected, the oxidation of alcohols did not occur with fully reduced LB form of PANI.

The PB can be recycled without loss of activity or selectivity. As shown in Table 3, the yield of Q is very low when PB used for oxidation is used again without further treatment compared with that by fresh one (Table 3). However, when the recovered PB was regenerated by oxidation with oxidant such as ammonium persulfate (APS), the yield was drastically increased.

In conclusion, we have found that fully oxidized form of PANI, PB, is an effective solid oxidant for the dehydrogenative oxidation

of HQ and primary/secondary alcohols to Q or aldehyde/ketone, and it can be easily recovered and regenerated. The advantages of this environmentally benign and safe protocol include a simple reaction setup and chemo-selectivity. We are currently working on the reaction mechanism and the extension of the biological oxidation reaction for various glucose and heterocyclic compounds.

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