# Quinone Amine Polymers. IX. Attempts to Synthesize Polyamine–Benzoquinone Polymers Using Air and Oxygen as Oxidizing Agents

V. S. NITHIANANDAM and S. ERHAN*

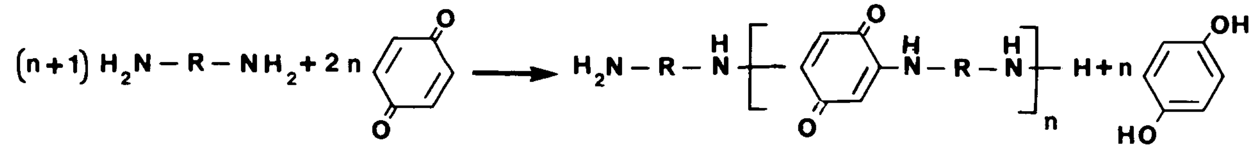
Center for Protein Research, Albert Einstein Medical Center, Philadelphia, Pennsylvania 19141

## SYNOPSIS

Attempts to synthesize Jeffamine D-400 : *p*-benzoquinone = 1 : 1 and later Jeffamine D-400 : hydroquinone = 1 : 1 oligomers, using air or oxygen as the oxidizing agent, have been only partially successful. Although oligomers that yield nontacky coatings are completely precipitable in water, only about 25% of these products are precipitable in water while 75% remains in suspension. These polymers yield tacky coatings, which suggests that neither air nor oxygen is capable of oxidizing hydroquinone to benzoquinone, which is necessary for the formation of the polymer. Hence, most of the oligomer chains are too short to precipitate in water.

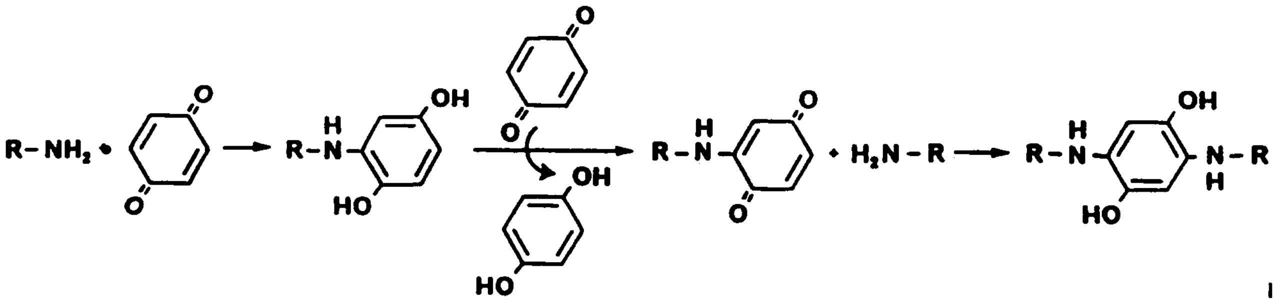
## INTRODUCTION

The reaction between diamines and benzoquinone produces linear polymers that bind to metals with sufficient affinity to displace water from wet, rusty steel surfaces[1]:



I

The reaction between amines and benzoquinone occurs in two steps: The first one yields a monosubstituted hydroquinone, through 1,4 addition. This has to be oxidized to monosubstituted benzoquinone before it can react with a second amine, again through 1,4 addition[1-3]:



II

The oxidation is normally effected by benzoquinone, which is already in the reaction mixture, because electron-donating substituents decrease the

---

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 42, 2385–2389 (1991)

CCC 0021-8995/91/092385-05$04.00

oxidation potential of benzoquinone.[4] For each benzoquinone molecule used in oxidation, a free hydroquinone is produced. Even though the stoichiometry of reaction (**I**) appears to show equimolar use of the amine and benzoquinone, the oxidation step needed for chain growth increases considerably the amount of quinone required. Indeed, just to obtain a tetramer, 16 benzoquinone molecules are needed! Not only does this represent a waste of a precursor, but also the creation of a potential problem, i.e., the ability of these polymers to bind to metals is due to chemisorption of quinone[5] and amine moieties, which occur in each repeat unit. The presence of free hydroquinones in the product could result in their competing with the quinones and amines found in the oligomers for the binding sites on the metals exposed to them. Consequently, it is quite natural to look for other oxidizing agents that will spare quinones and eliminate potential problems. Air and then oxygen are the first such agents that come to mind, and their effects on the synthesis of these oligomers were studied in some detail. The results of these studies are presented here.

## EXPERIMENTAL

Jeffamine D-400, a poly(oxpropylene) diamine, was obtained from Texaco Chemical Co. Benzoquinone, hydroquinone, and solvents used were purchased from Aldrich Chemical Co. and were used without further purification, except benzoquinone, which was recrystallized from ethanol. The reaction was followed with a Shimadzu UV 160U spectrophotometer. In this communication, different oligomers are identified by the input ratio of amine and the quinone.

### Preparation of Jeffamine D-400 : *p*-Benzoquinone = 1 : 1 Oligomer

*p*-Benzoquinone, 3.24 g (0.03 mol), was dissolved in 30 mL of ethanol, in a three-necked, round-bottom flask equipped with a reflux condenser, a gas introduction tube, a dropping funnel, and a stirrer. Twelve grams of Jeffamine D-400 (0.03 mol) was dissolved in 30 mL of ethanol and was added to quinone solution, kept at 55–60°C, all at once. Air was bubbled through the reaction mixture at a slow, steady rate for 8 h. Ethanol was removed by vacuum distillation, and the polymer was poured into water to precipitate it according to our established procedure. The product could not be precipitated completely, as is the case with the polymer used as a standard, which is made by reacting Jeffamine D-400 with benzoquinone with a ratio of 2 : 3. Hence, the reaction mixture was poured into petroleum ether and the precipitate washed thoroughly with hot petroleum ether and dried in a vacuum oven overnight.

### Preparation of Jeffamine D-400 : Hydroquinone = 1 : 1 Oligomer

Twelve grams (0.03 mol) Jeffamine D-400 was dissolved in 120 mL of ethanol in a round-bottom flask, and 3.3 g (0.03 mol) hydroquinone was dissolved in 33 mL ethanol and was added to the amine solution, at once. The temperature was raised to 60°C, air was passed through the reaction mixture for 7 h, and ethanol was distilled under vacuum. The product could not be precipitated completely in water as above. Hence, it was precipitated and washed extensively with petroleum ether.

### Preparation of Jeffamine D-400 : Hydroquinone = 1 : 1 Oligomer Using Catechol as Catalyst

Hydroquinone, 1.98 (0.018 mol), 0.22 g (0.002 mol) of catechol, and 8 g (0.02 mol) of Jeffamine D-400 were dissolved in 40 mL ethanol, in a round-bottom flask equipped with the usual reflux condenser, gas introduction tube, and stirrer. The reaction mixture was stirred at 60°C while bubbling oxygen through the reaction mixture for 2 h. Ethanol was distilled under vacuum, and the remaining syrup was poured into water. Only a small proportion, ca. 25%, was precipitated; the rest remained suspended in water.

## RESULTS

During our earliest studies performed on the reaction between diamines and benzoquinone, the product of Jeffamine D : 400-*p*-benzoquinone = 2 : 3 reaction, which has been shortened to PAQ (polyamine–quinone) = 2 : 3 in most of these communications, was found to have optimal coating characteristics for metals and alloys. The polymers produced nontacky, smooth, water-nonwettable coatings and were completely precipitable in water. Consequently, all other products obtained have been compared with PAQ = 2 : 3, and if the polymer was not precipitable in water, it was considered a failure because coatings made with these products have remained tacky after prolonged heat cure (6 h/150°C) even after addition of other diamines as hardeners, as has been done before.[6]

Even though PAQ = 1 : 1 was never satisfactory, we had expected that by using air oxidation, under similar conditions, we might be able to obtain products that were precipitable in water and also lacked the 290–295 nm absorption peak characteristic of hydroquinone.

Efforts to this end were unsuccessful. Increasing the reaction temperature to 85–95°C by using ethyl cellosolve as solvent, for 4 h, or adding the amine over a long period did not change the final result.

Shortly after air oxidation studies were started, the idea of attempting to obtain the same polymers starting from hydroquinone was conceived. The products obtained were similar to the ones obtained from benzoquinone and were unprecipitable in water. The coatings prepared, even though showing reasonable adhesion after addition of Ethacure 100 as hardener, were unsatisfactory.

Catechol, especially in the presence of amines, is autooxidized to *o*-benzoquinone by oxygen, with the production of hydrogen peroxide.[7] Since the oxidation potential of *o*-benzoquinone is higher than that of *p*-benzoquinone—0.792 *v* vs. 0.699 *v*—inclusion of a small amount of catechol in the reaction mixture was expected to improve the reaction. The results of actual experiments, however, did not support this anticipation. The products were not precipitable in water and yielded unsatisfactory coatings.

Before terminating these studies, the use of pure oxygen as the oxidizing agent was also tried. As soon as oxygen bubbling started, the reaction mixture appeared dark and the formation of the product was indicated by the appearance of 340 nm peak and practical disappearance of the hydroquinone peak that absorbs at 290–295 nm [Fig. 1(a, b)]. The product, however, was not precipitable in water. Precipitate was separated from the suspended material, washed, dried under vacuum, and weighed (2.6 g). The water was distilled from the suspended material, which was also weighed after drying (7.5 g). Thus, it is clear that nearly three-quarters of the product has too low a molecular weight to be precipitable in water. The UV spectra of both were

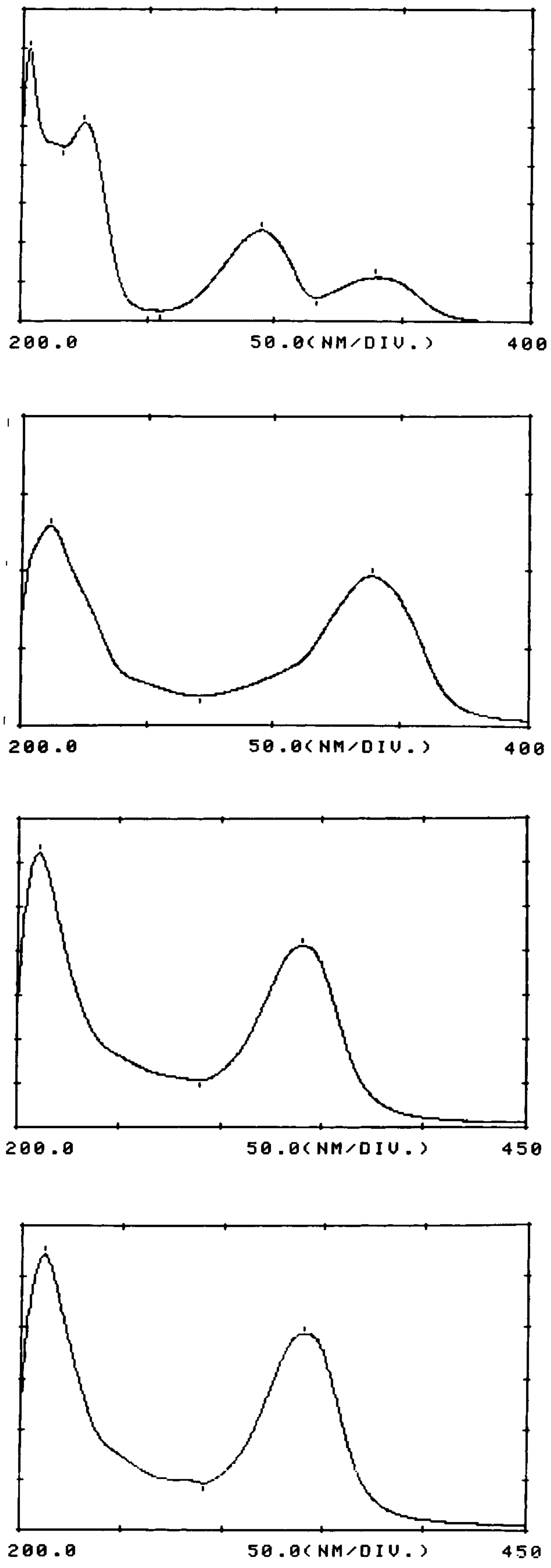


**Figure 1** (a) UV spectrum of reaction mixture containing a catalytic amount of catechol at 10 min. The 295 nm peak is characteristic of hydroquinone, and the 340 nm peak represents amine-substituted quinone. (b) UV spectrum of the same mixture after 90 min. The 295 nm peak is seen only as a shoulder. (c) UV spectrum of the product fraction that is water precipitable. (d) UV spectrum of the product fraction that is dispersed in water, after evaporation of water.

identical [Fig. 1(c, d)]. Extending the reaction period from 2 to 6 h did not have any effect.

The effect of catechol on hydroquinone oxidation was checked by bubbling oxygen through the reaction mixture that did not have any catechol for 3 h. The presence of hydroquinone in this product is seen in Figure 2(a). When catechol was added at this time, oxidation of hydroquinone was accelerated, and 90 min after addition of catechol, there was only a shoulder at 290 nm [Fig. 2(b)]. The product, nevertheless, was again only partially precipitable in water.

## DISCUSSION

These studies, which were started to reduce the amount of benzoquinone used in the preparation of polyamine–quinone oligomers to stoiochiometric ratio of 1 : 1, have produced some interesting results. It was known that a ratio of amine : quinone = 2 : 3 yielded the optimal products that were completely insoluble in water. Here, a large part of the quinone is used to oxidize the substituted hydroquinone and is itself reduced to free hydroquinone, which probably is held closely by the oligomer because the UV spectrum shows clearly the presence of hydroquinone, which absorbs at 290–295 nm.[1]

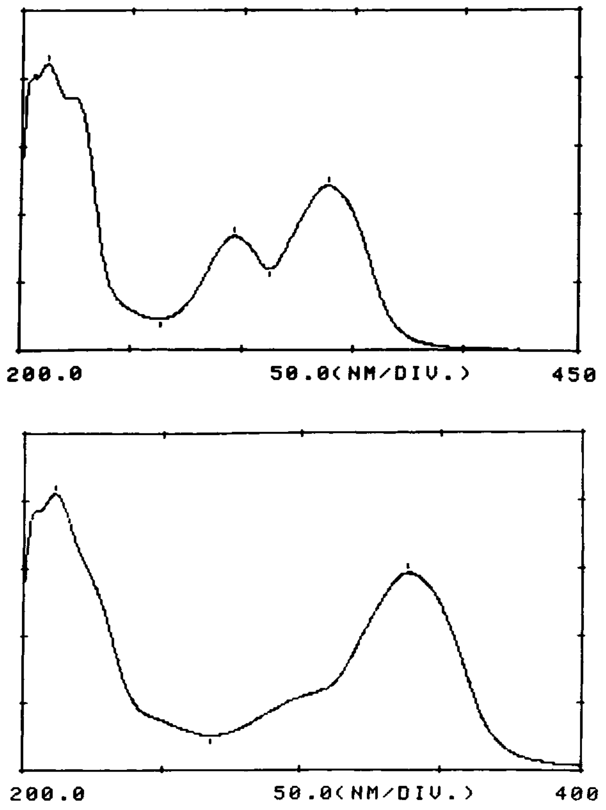


**Figure 2** (a) UV spectrum of the reaction mixture without catechol after 3 h of bubbling of oxygen, just before catechol was added. (b) UV spectrum of the reaction mixture 90 min after the addition of catechol.

But there is enough quinone excess that enables the chains to grow sufficiently to become insoluble in water. When, on the other hand, only a stoichiometric amount of benzoquinone or hydroquinone is used, mostly water dispersable and presumably lower molecular weight chains are produced. This suggests that neither air nor oxygen is capable of oxidizing hydroquinone to benzoquinone with sufficient rate, even in the presence of catechol, which had been demonstrated to autooxidize, when amines are present, to *o*-benzoquinone. Having a higher oxidation potential than that of *p*-benzoquinone, the *o*-benzoquinone should have been able to carry out this oxidation catalytically and efficiently. Unfortunately, this expectation could not be realized. On the other hand, an oxidizing agent like calcium hypochlorite produces perfectly satisfactory water-insoluble products starting either with benzoquinone or hydroquinone.[8] Switching from benzoquinone to hydroquinone provides two additional advantages: Benzoquinone is a more aggressive chemical, at least for some people, and hydroquinone is less expensive than is benzoquinone. Studies are being continued to find other conditions under which air or oxygen can be used to carry out this reaction.

The view that hydroquinone might be closely associated with the oligomer is supported by the results of thin-layer chromatography. Using a solvent consisting of 80% water-saturated ethyl acetate and 20% *n*-propanol, it was possible to separate a fraction that absorbs both at 295 and 245 nm, corresponding to hydroquinone and benzoquinone, respectively, from both water-precipitable and water-dispersed fractions (Nithianandam and Erhan, unpublished observation).

This observation explains why UV spectra of these products have a 295 nm absorbing peak. Our inability to remove these low molecular weight contaminants, despite extensive washing of the products, suggests that they might be held by the polymers through $\pi$–$\pi$ interactions.

Use of UV spectra exclusively in this study is based on our extensive experience with these polymers, which has proven this method to be the simplest and most telling procedure for these studies, even though it is not practiced by others. Alternative methods such as NMR spectroscopy, however, have also been used and have corroborated this conclusion.[2]

In conclusion, much to our dismay, it was not possible to use air or oxygen for the preparation of quinone–amine polymers, starting with stoichiometric amounts and saving quinone only for the synthesis of the polymers. This failure was due to the inability of air and oxygen to oxidize even the monosubstituted hydroquinone efficiently. This was an unexpected observation because amine substitution lowers oxidation potential of the quinone ring. Even the presence of *o*-quinone, which was expected to act as an oxidation catalyst, overcame the inability of these gases to oxidize hydroquinone.

## REFERENCES

1. K. Kaleem, F. Chertok, and S. Erhan, *Prog. Org. Coat.*, **15,** 63 (1987).
2. K. Kaleem, F. Chertok, and S. Erhan, *J. Polym. Sci. Chem.*, **27,** 865 (1989).
3. K. Kaleem, F. Chertok, and S. Erhan, *New Polym. Mater.*, to appear.
4. L. F. Fieser and M. Fieser, *Advanced Organic Chemistry,* Reinhold, New York, 1961, p. 845.
5. M. P. Soriaga and A. T. Hubbard, *J. Am. Chem. Soc.*, **104,** 2735, 2742 (1982).
6. V. S. Nithianandam, F. Chertok, and S. Erhan, to appear.
7. W. Brackman and E. Havinga, *Rec. Trav. Chim. Pays-Bas,* **74,** 1100 (1955).
8. V. S. Nithianandam and S. Erhan, *Polymer,* to appear.

*Received May 16, 1990*
*Accepted August 28, 1990*