Quinone–amine polymers: 10. Use of calcium hypochlorite in the syntheses of polyamine–quinone (PAQ) polymers

V. S. Nithianandam and S. Erhan*
Center for Protein Research, Albert Einstein Medical Center, Philadelphia, PA 19141, USA
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Calcium hypochlorite can be used successfully to prepare diamine–benzoquinone polymers starting with hydroquinone and the product precipitates in water completely, as the standard oligomer Jeffamine D-400: *p*-benzoquinone = 2:3. The product is completely free of hydroquinone which normally occurs in the standard oligomer.

(Keywords: diamine–benzoquinone polymers; calcium hypochlorite; hydroquinone)

INTRODUCTION

Polyamine–benzoquinone polymers (PAQ) have been shown to adhere to metals with sufficient affinity to displace water from a wet, rusty steel surface, to become non-wettable by water and resist most organic solvents after being cured chemically or thermally[1]. They are also resistant to salt spray, autoclaving and can be cleaned easily after biofouling. They adhere onto ordinary paints and all paints except water-based latexes can bind to these coatings, the failure of the latter being due to their inability to wet the polymer surface. Finally, they can be applied under water.

Aromatic polyetheramines yield polymers that are scarcely soluble in even the most powerful solvents except DMSO, DMF and sulphuric acid, but absorb only about 0.1% (w/w) moisture, after being immersed in water for 72 h, rivalling processable polyimides currently used in insulating electronic components[2].

The reaction between amines and benzoquinone occurs spontaneously, even below ambient temperature, and takes place, through 1,4 addition, as shown in *Scheme 1*.

The first step during the reaction is the formation of a mono substituted hydroquinone which has to be reoxidized to monosubstituted quinone before the second substitution, again through 1,4 addition, can occur.

Benzoquinone, which is present in the solution, can oxidize the monosubstituted hydroquinone because quinone oxidation potential is reduced by electron donating substituents[3]. With diamino compounds one obtains linear polymers; see *Scheme 2*.

Detailed characterization of the products, including n.m.r. studies, were made earlier to establish the correctness of the formulas given[1,2].

Formation of polyamine–benzoquinone polymers is also very easy. In many instances one does not even have to heat the reaction mixture. Depending on the properties of the amines and the quinones, one can produce a whole spectrum of polymers or oligomers from flexible to intractable. This does not mean, however, that this reaction cannot be improved. As seen in *Scheme 2* the polymers consist of repeating quinone–amine units: n moles of quinones for $(n+1)$ moles of amines, because these polymers always end with free amino groups, even when quinone is used in excess[1].

The simple stoichiometry indicated in *Scheme 2* however, fails to take into account the actual number of quinone molecules needed to oxidize the disubstituted hydroquinones that are formed as chain extension occurs. Thus, to obtain a tetramer one needs 16 *p*-benzoquinone molecules even though only four quinones are found in the oligomer, the rest being reduced to hydroquinones in the reaction mixture. As will be discussed later, the presence of free hydroquinone can be undesirable and in addition benzoquinone is wasted in the reaction. Consequently, use of other oxidizing agents to conserve benzoquinone is a reasonable approach. As oxidizing agents air, oxygen and various inorganic compounds such as chromates, permanganates, hypochlorites come to mind. One advantage of the use of a good oxidizing agent is the ability to use a less objectionable precursor, hydroquinone, in lieu of benzoquinone. Here we report the use of calcium hypochlorite in the preparation of polyamine–quinone (PAQ) oligomers, starting with hydroquinone. Its ability to oxidize hydroquinone and several of its derivatives has already been demonstrated[4].

MATERIALS AND METHOD

Jeffamine D-400 a poly(oxypropylene)diamine sample was obtained from Texaco. All other reagents were purchased from Aldrich Chemical Co. and used without further purification except benzoquinone which was recrystallized from ethanol. The progress of the reaction was monitored by a Shimadzu u.v. 160U spectrophotometer. Viscosity measurements were made with an Ubbelohde viscometer.

Preparation of polyetheramine–quinone oligomer (PAQ) from hydroquinone and Jeffamine D-400 = 1:1

Hydroquinone 8.8 g (0.08 mol) is suspended in 100 ml

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* To whom correspondence should be addressed

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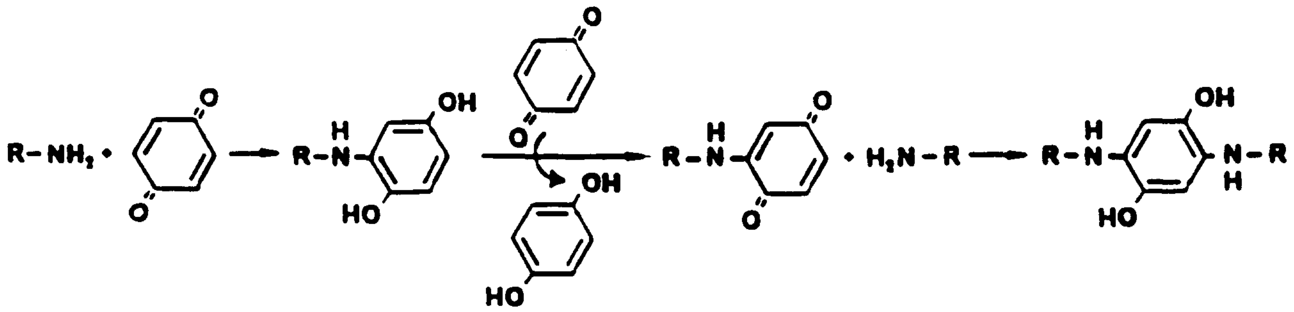
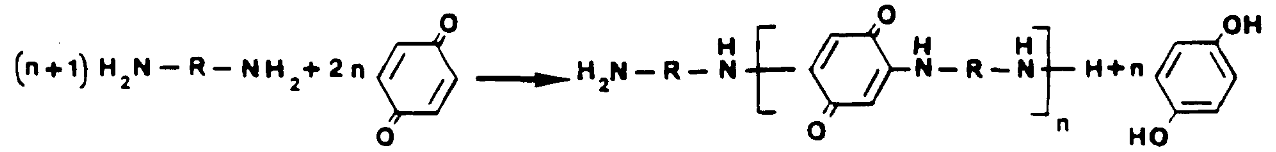


Scheme 1



Scheme 2

methylene chloride in a round bottom flask equipped with reflux condenser and a mechanical stirrer and 22.9 g (0.16 mol) calcium hypochlorite (65% available chlorine) is added to the suspension, with vigorous stirring, followed by 0.37 g (2.5 mol% of hydroquinone) phase transfer catalyst, benzyltrimethylammonium chloride and stirring continued under reflux. Samples are taken at intervals and the reaction is followed by u.v. spectroscopy. After about an hour all hydroquinone is oxidized to quinone. The reaction time is highly concentration dependent, with 200 ml of methylene chloride it takes two and a half hours to oxidize the same amount of hydroquinone.

When all hydroquinone is oxidized the reaction mixture is cooled to 20–30°C and 32 g (0.08 mol) Jeffamine D-400 in 100 ml of methylene chloride is added slowly to prevent an increase of the reaction temperature. The reaction mixture is stirred vigorously for 90 min at room temperature. Due to increase in viscosity it is necessary to have a mechanical stirrer. The reaction mixture is filtered and the precipitate is washed with 100 ml of methylene chloride.

The combined filtrate is evaporated under vacuum to remove methylene chloride. The remaining polymer is dissolved in ethanol or acetone and precipitated by pouring into water. This step is repeated several times and the polymer is dried in a vacuum oven at 50°C.

RESULTS

Preliminary studies using calcium hypochlorite as an oxidizing agent in the synthesis of Jeffamine D-400 based PAQs were encouraging. Consequently, attention was focused on the oxidation of hydroquinone and its derivatives to corresponding quinones using the same oxidizing agent[4]. The synthesis of the oligomer occurs with great ease whether one starts with benzoquinone or hydroquinone and can be followed by u.v. spectroscopy. Thus, in *Figure 1a* and *b* one sees the oxidation of hydroquinone to benzoquinone using calcium hypochlorite. *Figure 1c* and *d* show the spectrum 15 min and 2.5 h after the addition of the oxidizing agent. It is clear the reaction occurs very fast, 345 nm peak representing the product appears within 15 min and 295 nm peak characteristic of hydroquinone has been reduced to a shoulder by 15 min and keeps on decreasing with time. *Figure 1e* represents the spectrum of the standard oligomer with amine quinone = 2:3. Here no trace of hydroquinone is seen. 277 nm peak is due to amine substitution o- to oxygen. *Figure 1f* represents the reaction product precipitated, twice, with water.

From the start of these studies reaction product was obtained by pouring the reaction mixture into excess water both to precipitate the product and to remove water soluble reactants and reaction by-products. The precipitate was then washed thoroughly with water, sometimes after dissolving it in an appropriate solvent and reprecipitating with water. Also from the beginning the product of Jeffamine D-400:benzoquinone = 2:3 reaction was found to be the optimal product based on its characteristics after heat curing, i.e. a non-tacky, smooth and water non-wettable coating, hence all others have been compared with it.

After observing that air oxidation did not allow the synthesis of a product that lost its tackiness despite prolonged thermal curing, even after the addition of various diamines[5], several oxidizing agents were tried as alternatives. Calcium hypochlorite was found to be a satisfactory oxidizing agent that provided a product comparable to the standard starting with Jeffamine D-400 and *p*-benzoquinone = 2:3. There were, however, certain problems that had to be overcome. Because calcium hypochlorite is insoluble in organic solvents a phase transfer catalyst, benzyltrimethyl ammoniumchloride had to be used. If the catalyst is omitted a peak at 290 nm appears, suggesting that oxidation of the hydroquinone is not complete. *Figure 1g* represents the product obtained without the catalyst after 3 h at room temperature. The other problem encountered when hydroquinone is used was the inability to obtain a product that could be precipitated in water, if amine was added to the reaction mixture, from the beginning. This led to the addition of the amine after the oxidation of hydroquinone to quinone was completed, as assessed by u.v. spectroscopy. Inability of the product, formed when amine is added at the onset of reaction, to be precipitated

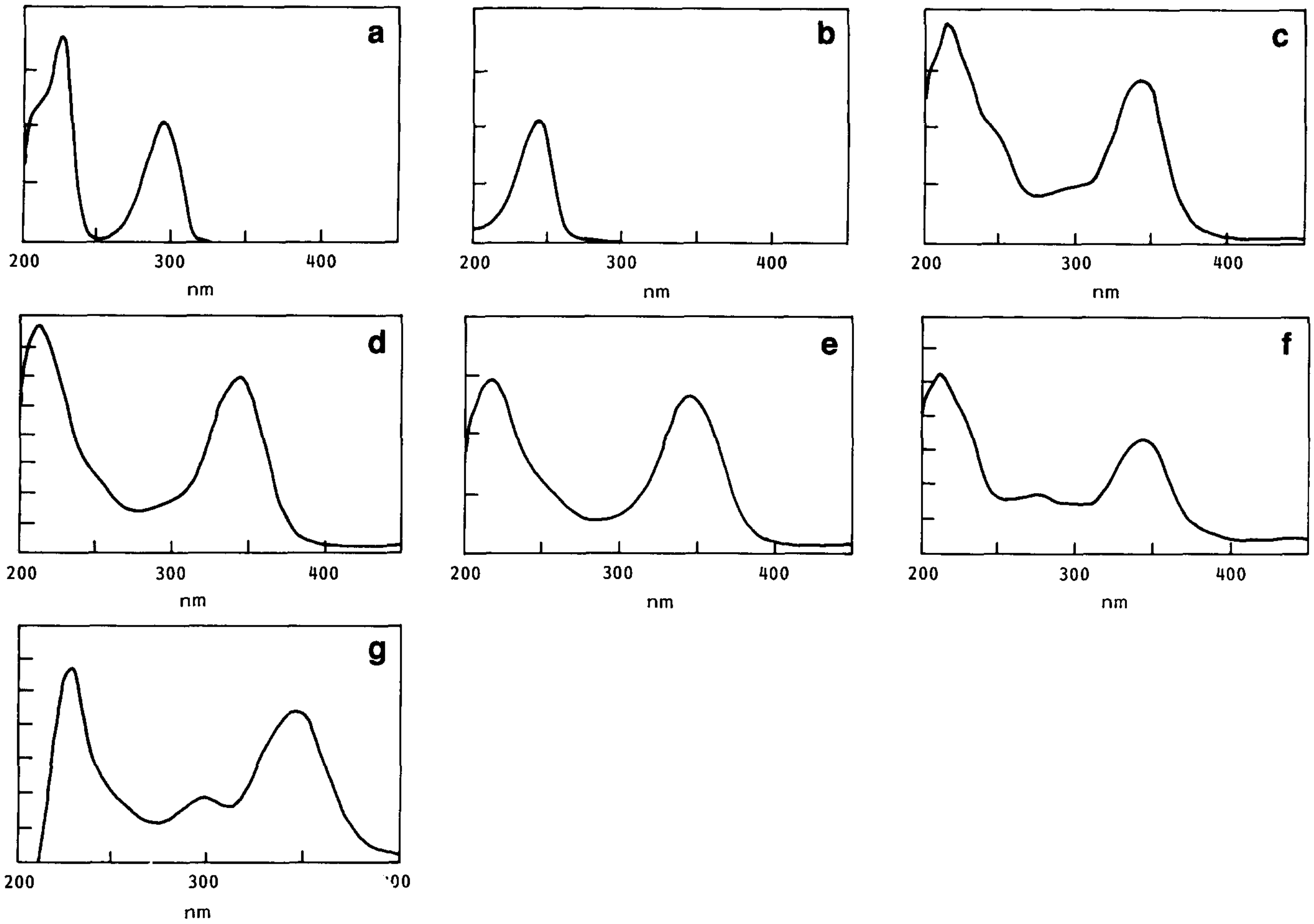


Figure 1 (a) U.v. spectrum of hydroquinone, before addition of calcium hypochlorite, showing 295 nm peak. (b) U.v. spectrum of the reaction mixture showing complete conversion of hydroquinone to benzoquinone which absorbs at 242–245 nm. (c) U.v. spectrum of the reaction mixture 15 min after the addition of Jeffamine D-400. Reaction product is already prominent at 345 nm and hydroquinone has been reduced to a shoulder. (d) Spectrum of the same mixture after 3.5 h. (e) U.v. spectrum of the standard oligomer prepared from Jeffamine D-400-benzoquinone = 2:3. (f) U.v. spectrum of the reaction product that was washed twice by precipitating in water. (g) U.v. spectrum of the product obtained from the reaction carried on for 3 h without the phase transfer catalyst, benzyltrimethylammonium chloride. Appearance of prominent 295 nm peak shows the presence of hydroquinone

quantitatively suggests the formation of lower molecular weight oligomers and is highly undesirable. Freshness of the oxidizing agent is critically important because it deteriorates rapidly after a container is opened and the reaction duration increases drastically and the oxidation of hydroquinone to benzoquinone will no longer be quantitative, even after 5 h.

The amount of oxidizing agent used is about 10% in excess of the stoichiometric requirement. If too large an excess is used the oligomer gels, probably through intermolecular crosslinking involving imino groups and quinone rings.

DISCUSSION

The great avidity of these polymers toward metals is due to chemisorption, whereby the free electrons of the amine nitrogens and quinone oxygens are donated to the electron-poor molecular orbitals of metals[6], because each repeat unit contains two imino nitrogens and two quinone oxygens. If there were free hydroquinone molecules left in the oligomer after polymerization, whether or not they were formed by the reduction of benzoquinone or remained unoxidized when hydroquinone is used as a precursor, it is quite likely that they would compete with the same species found in the product. Even though the product is extensively washed after its formation in the laboratory, it is highly unlikely that a similar purification will take place during large scale production, due to the expense involved. That hydroquinone is found in the product after extensive washing can be seen when spectra of benzoquinone and hydroquinone derived products are compared. The former usually has a 290–295 nm absorbing band characteristic of hydroquinone[1]. This can only happen either by hydroquinone being held by quinones found in the polymer or some of the substituted quinones found in the oligomer being reduced by the hydroquinone present in the reaction mixture. Thin layer chromatography performed on the final product using as solvent 80% water saturated ethyl acetate and 20% *n*-propanol mixture has succeeded to separate hydroquinone, which moves close to the solvent front (V. S. Nithianandam and S. Erhan, unpublished data). In contrast the latter does not have any 295 nm peak, clearly demonstrating that in the presence of a strong oxidizing agent all hydroquinones are oxidized to benzoquinone. Consequently, use of calcium hypochlorite or any other strong oxidizing agent is highly desirable because it enables one to use a less irritating precursor. This also happens to be more economical, as well as preventing potential competition which could reduce the adhesion of the product to metals.

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