

Quinone–amine polymers: 18

A novel method for the synthesis of poly(alkyl aminoquinone)s

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Sodium periodate can be used to prepare alkyl aminoquinones in good yield by oxidative amination reaction of hydroquinone. New studies have demonstrated for the first time that the same reagent can be used in the preparation of poly(alkyl aminoquinone)s from diamines and hydroquinone as demonstrated in the preparation of poly(ether quinoneamine). The polymer obtained is found to have similar spectroscopic (u.v. and i.r.) and analytical (TLC and viscosity) characteristics to the product prepared previously using excess quinone or calcium hypochlorite. © 1998 Published by Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

A new family of polymers, poly(aminoquinone) (PAQ), has been developed in recent years as effective anti-corrosive coatings^{1–9}. These polymers have extraordinary affinity towards metals, strong enough to displace water from wet rusted steel surfaces. Poly(aminoquinone) polymers perform even better when cured with other curing agents like diepoxides and isocyanates⁹. PAQ based coatings have many desirable characteristics like good flexibility, impact strength and corrosion resistance.

Poly(aminoquinones) and aminoquinones are conventionally prepared by the reaction of amines with excess of quinone according to *Schemes 1* and *2*.

This method has the disadvantage of not only poor utilization of starting materials, but also formation of large amounts of byproduct hydroquinone. It is possible to prepare PAQs without using excess benzoquinone by employing other oxidizing agents like calcium hypochlorite⁴. However, this reagent suffers from several disadvantages like inconsistent reaction time stemming from variation in reagent purity and in certain cases giving abnormal addition products⁶. Recently, we have discovered that sodium iodate can be used as the oxidizing agent for the synthesis of poly(aryl aminoquinone)¹⁰. Although sodium iodate could be used as the common oxidizing agent, it provides only moderate yield of 2,5 disubstituted quinone for alkyl amines. In the present work we describe the use of sodium periodate as the efficient alternative reagent for the synthesis of poly(alkyl aminoquinone)s.

EXPERIMENTAL METHODS

Jeffamine D-400, which is a poly(oxypropylene)diamine sample, was obtained from Texaco Chemical Co. *n*-Butylamine was a gift from BASF, USA; sodium periodate, hydroquinone, tetrahydrofuran (THF) and *N*-methyl pyrrolidinone (NMP) were of reagent grade purchased from either Aldrich or Fisher Scientific Co. and were used directly.

The progress of the reaction was monitored by a Shimadzu 160U u.v. spectrophotometer and thin layer chromatography. Thin layer chromatography was performed with Analtech silica gel plates (1000 μm) using the solvent mixture of chloroform and 96% ethanol (96:4). Inherent viscosity of dimethyl sulfoxide solution of polymers (3 g/dl) was measured with an Ubbelohde Viscometer at 30°C. I.r. spectra were taken with a Sargent Welch-Pye Unicomb model 3-200 spectrophotometer. Melting points were determined by Fisher-Jones apparatus.

Synthesis of 2,5-dibutylamino 1,4-benzoquinone

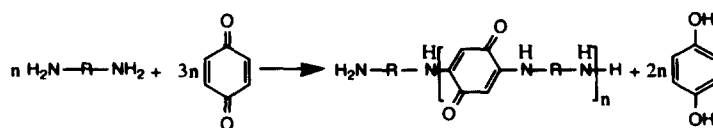
n-Butylamine (1.48 g, 0.020 mol) and hydroquinone (1.1 g, 0.01 mol) were dissolved in 20 ml solvent mixture of THF and NMP (80:20). Five drops of water were added to this solution. Sodium periodate (4.28 g, 0.02 mol) was added to the above solution gradually at room temperature (20–30°C) over 20 min with stirring. The reaction mixture was then heated to 55–60°C for 4 h. Then the reaction mixture was filtered and the filtrate was concentrated. The concentrated solution was diluted with 80 ml of cold water, when an orange coloured solid precipitated. The solid was filtered, washed with water and dried. Yield 72%. Crude product can be recrystallized from methanol to give crimson red crystals of 2,5-dibutylamino 1,4-quinone. Melting point (uncorr.) 160°C. Reported melting point 164°C¹¹. Repeated crystallizations did not improve the melting point.

Elemental analysis:	C	H	N
Calculated (%):	67.2	8.8	11.2
Found (%):	66.71	8.98	10.97

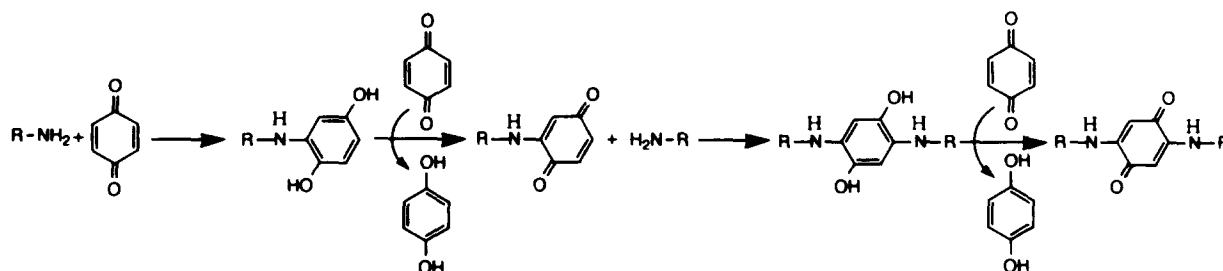
Synthesis of poly(ether quinoneamine) (PEQ)

The experiment described above was repeated with Jeffamine D-400 (8 g, 0.02 mol), hydroquinone (2.2 g, 0.02 mol) and sodium periodate (8.56 g, 0.04 mol). The filtrate obtained was poured into 500 ml of cold water. Semi-solid polymer was then washed extensively with water. Polymer was further purified by dissolving in methanol and reprecipitating in water. The final product was then dried under vacuum at 50°C.

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Scheme 1



Scheme 2

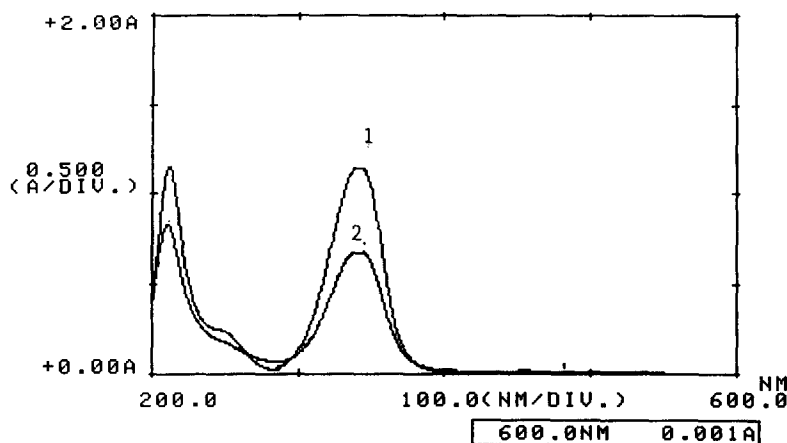


Figure 1 U.v. spectra of (1) 2,5-dibutylamino 1,4-benzoquinone and (2) poly(ether quinoneamine)

RESULTS AND DISCUSSION

2,5-Disubstituted benzoquinones can be prepared by two methods.

- (1) By substitution of reactive leaving groups like chloro, methoxy or hydroxy of quinone ring by amines.
- (2) More frequently used stepwise alternate 1,4 addition of amines to benzoquinone under oxidizing conditions.

PAQs are prepared by treating 1 mol of diamines with 3 mol of quinones. Since electron donating amine substituent reduces the oxidation potential of quinone ring, free quinone present in the solution readily oxidizes the intermediate monosubstituted hydroquinone to monosubstituted benzoquinone¹². Another molecule of amine is added to this monosubstituted benzoquinone leading to the formation of polymers. Each of these steps gives 1 mol of hydroquinone as the byproduct which has to be removed from the final product. It is known that use of other oxidizing agents, like calcium hypochlorite, will eliminate the need for excess quinone. This method, however, suffers from two major disadvantages. Rate of oxidation of hydroquinone to benzoquinone depends on the purity and

freshness of calcium hypochlorite. Absorption of moisture by this reagent over a period of time reduces the 'available chlorine' and hence the efficiency of the reaction. Secondly, calcium hypochlorite cannot be used for the synthesis of poly(aryl aminoquinone)s, probably due to the oxidation of arylamines by the reagent. Subsequently, sodium iodate has been shown as the preferred oxidizing agent for the preparation of poly(aryl aminoquinone)s¹⁰. This reagent could be used for the synthesis of both alkyl and aryl aminoquinones. However, only moderate yield of alkyl aminoquinones could be obtained by sodium iodate. For example, sodium iodate gave a 94% yield of 2,5-*o*-toluidino-*p*-benzoquinone upon refluxing a methanolic solution of 2 mol of *o*-toluidine and 1 mol of hydroquinone for 18 h. However, under identical reaction conditions, with *n*-butylamine only about 50% of 2,5-*n*-butylaminoquinone is formed. Thin layer chromatography showed the presence of unreacted *n*-butylamine and hydroquinone. In the present work, sodium periodate, a stronger oxidizing agent, was used for the synthesis of alkyl aminoquinone in good yield.

Formation of aminoquinones is monitored by the disappearance of the 295 nm peak due to the hydroquinone and the appearance of the 340 nm peak due to 2,5 diamino

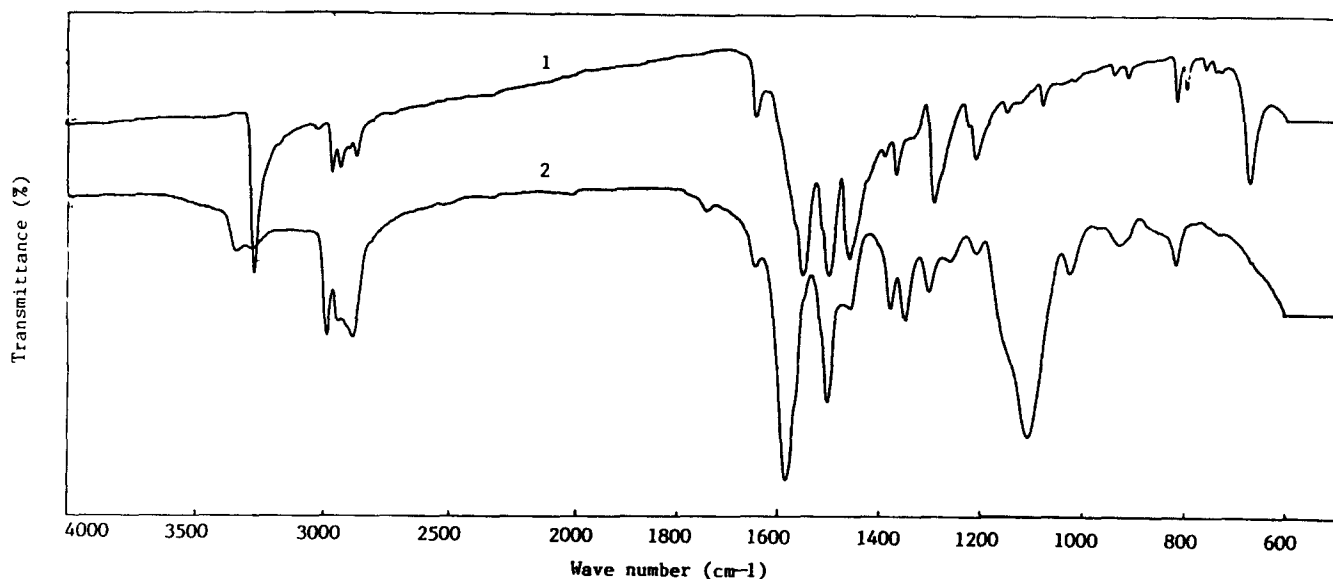


Figure 2 I.r. spectra of (1) 2,5-dibutylamino 1,4-benzoquinone and (2) poly(ether quinoneamine)

Table 1 Synthesis of 2,5-dibutylamino-*p*-benzoquinone and poly(ether quinoneamine)

No.	Reactants (mol) amine:HQ:oxidant ^a	Solvent (20 ml)	Reaction conditions	Result
2,5-Dibutylamino- <i>p</i> -benzoquinone				
1	0.02:0.01:0.02	THF	6 h at r.t.	Light orange coloured solid Yield 44% ^b
2	0.02:0.01:0.03	THF	6 h at r.t.	Dark orange coloured solid Yield 64%
3	0.02:0.01:0.02	NMP:THF 4:1	4 h at 60°C	Light orange coloured solid Yield 72%
4	0.02:0.01:0.03	NMP:THF 4:1	4 h at 60°C	Dark orange coloured solid Yield 86% ^b
PEQ				
5	0.02:0.02:0.04	NMP:THF 4:1	4 h at 60°C	Polymer with normal viscosity and solubility ^c
6	0.02:0.02:0.06	NMP:THF 4:1	4 h at 60°C	Polymer with lower solubility ^c
7	0.02:0.02:0.04	NMP:THF 4:1	12 h at 60°C	Slow reaction as judged by u.v. polymer with lower viscosity ^c

^a Five drops of water added to all the experiments except experiment no. 7

^b Isolated yields

^c Polymers obtained in the present method are compared with polymers from previous methods^{3,4}

substituted quinone moiety. Initial studies using sodium periodate as oxidizing agent in the synthesis of alkyl aminoquinone were encouraging. Model studies conducted using *n*-butylamine showed near total conversion of hydroquinone and formation of amine substituted benzoquinone by u.v. spectroscopy. Poly(ether quinoneamine) is prepared by the reaction of Jeffamine D-400 and hydroquinone under identical conditions. Aminoquinone products obtained are characterized by spectroscopy, thin layer chromatography and elemental analysis. Both 2,5-dibutyl aminoquinone and PEQ show a distinct u.v. peak at 340 nm characteristic of 2,5 diamino substituted quinone (Figure 1). Infra-red spectra have strong absorptions at 1640 cm⁻¹ for quinone carbonyl and at 3250–3350 cm⁻¹ for NH groups (Figure 2). The inherent viscosity of PEQ in dimethyl

sulfoxide at 30°C is 0.1056. This value is slightly higher than those obtained for PEQ prepared by other published methods^{3,4}.

Polymerization is conducted by reacting diamine and hydroquinone in a suitable solvent with oxidizing agent directly. After the filtration and solvent removal the polymer is neatly precipitated in water. This is in contrast to the earlier calcium hypochlorite method in which the reaction is conducted in two steps, first hydroquinone to benzoquinone and then addition of diamine to benzoquinone leading to polymerization⁴. Initial addition of amine in calcium hypochlorite reaction leads to very low molecular weight product. Sodium periodate is a strong oxidizing agent and hence it is sufficient to use 2 mol of periodate for 1 mol of hydroquinone. Increasing either the amount of sodium

periodate, or prolonging the reaction time only reduces the product quality in terms of solubility, viscosity and colour as shown in *Table 1*. The rate of oxidative amination is highly dependent on the solvents used in the reaction. The reaction can be conducted in a variety of solvents like alcohols, NMP, etc. Aminoquinone synthesis is extremely slow in THF, which is one of the best solvents for aminoquinone polymers. However, this obstacle can easily be overcome by using a mixture of THF and other solvents with trace amounts of water. Water itself can be used for the preparation of simple aminoquinones.

Our original aim of using a single oxidizing agent for the synthesis of both alkyl and aryl aminoquinone polymers is only partly realized. Sodium iodate which gives the best result for the synthesis of aromatic aminoquinones gives only a modest yield of alkyl aminoquinones. Sodium periodate, on the other hand, did not yield any poly(aryl aminoquinone) under the above mentioned conditions.

The great affinity of aminoquinone polymers towards 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 metals¹³. Conventional preparation of these polymers seems to contain some amount of simple hydroquinone molecules being held by quinone molecules found in the polymer⁴. These hydroquinone molecules are quite likely to compete with the polymer for metallic surface. Use of strong oxidizing agents to prepare these polymers enables one to conduct the reaction in equimolar quantities of diamine and hydroquinone. Hydroquinone is fully utilized for polymerization as shown in our previous studies⁴. Adsorption sites on metallic surfaces are occupied only by the polymer resulting in better adhesion. Our earlier studies have

demonstrated that PEQ coatings have excellent adhesion to metals⁹.

In conclusion, use of oxidizing agents like sodium iodate and periodate is very desirable for the synthesis of poly(aminoquinone)s since it enables us to use the less hazardous precursor hydroquinone instead of benzoquinone. Moreover, quite unlike the calcium hypochlorite method, the present method can tolerate the presence of moisture or even water in the solvents. These methods offer a more economical way of preparing these polymers since they avoid the use of excessive starting material, benzoquinone and recycling the generated hydroquinone.

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