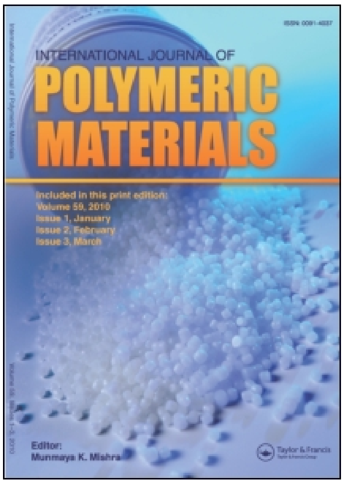

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Reddy, T. A. and Erhan, S.(1993) 'Preparation and Characterization of Reaction Products Between 2-Phenylquinone and Several Aliphatic Amines', International Journal of Polymeric Materials, 19: 1, 109 — 116

To link to this Article: DOI: 10.1080/00914039308012022

URL: http://dx.doi.org/10.1080/00914039308012022

Intern. J. Polymeric Mater., 1993, Vol. 19, pp. 109–116
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Printed in Malaysia

Preparation and Characterization of Reaction Products between 2-Phenylquinone and Several Aliphatic Amines†

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(Received July 1, 1992)

Polymers prepared by reacting diamines with quinones are known for their extraordinary affinity towards metals. This affinity is so strong that they can displace water from wet, rusty steel surfaces. Previously, methods were developed to use less expensive and less aggressive hydroquinone in lieu of benzoquinone. In this article we describe a series of compounds prepared by using 2-phenylquinone and various amines.

KEY WORDS Polymeric products, aliphatic amines, 2-phenylquinone

INTRODUCTION

During the past several years a family of polymers with extraordinary affinity towards metals strong enough to displace water from wet, rusty steel surfaces, were developed.[1–10] They were prepared by reacting diamines with quinones and depending upon the chemical nature of the precursors one obtains products with a wide range or properties, i.e., soluble to insoluble, flexible, tough to intractable, etc. The progress of the reaction, the purity of the products, i.e. whether any reaction precursors or reaction products are present in the product, can be followed by UV spectroscopy. Interestingly, although the UV spectrum of a compound is effected by many factors, such as substituents carried, solvents used pH, etc., major characteristics of the spectrum is preserved between the spectra of a compound taken by itself and when it is part of a polymer. Thus UV spectra provides a significant insight into the structure of a polymer.

Consequently when starting studies on a new series of diamino-quinone polymers, using 2-phenylquinone, several model compounds were prepared.

This communication describes, for the first time, reaction between 2-phenylqui-

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†This is Communication XI of the series "Quinone-amine Polymers."

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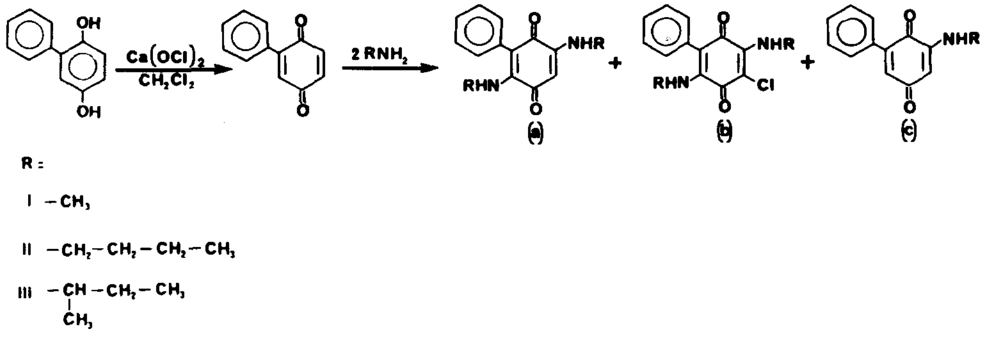

Proposed reaction scheme.

none and methylamine (I), *n*-butylamine (II) and sec-butylamine (III) and the characteristics of the reaction products.

RESULTS

Several years ago reaction conditions used to prepare the polymers were modified to be able to use hydroquinone, in the presence of an oxidizing agent, in lieu of benzoquinone because the former is a less aggressive and cheaper chemical and this modification allows one to use stoichiometric ratio between reactants rather than an excess of quinone, part of which is used as the oxidizing agent.[9,10]

Calcium hypochlorite was chosen as the oxidizing agent due to the ease of removal of the resulting salts.

The modified reaction conditions resulted in a two step reaction:

1. Oxidation of hydroquinone to benzoquinone,
2. Reaction of benzoquinone with diamine.

Oxidation of hydroquinone is accomplished in 2½ hours, at a temperature of 40–60°C, and can be monitored by UV spectroscopy. At the end of oxidation reaction mixture is allowed to cool to room temperatures, the diamine, dissolved in dichloromethane, is added and the reaction mixture is stirred at room temperature for several hours.

For this study the oxidation of 2-phenylhydroquinone was carried out as described above.

Since model compounds were being prepared with monoamines, for each mole of 2-phenylbenzoquinone 2 moles of amine was used except for methylamine, where due to its volatile nature three moles were needed to complete the reaction. The reaction of 2-phenylbenzoquinone followed the general reaction pattern producing diamino substituted phenylquinone, however, there were several unexpected byproducts. The crude product, after removal of the solvent, under vacuum, was dissolved in hot ethanol, and allowed to cool. The precipitate that formed was filtered, dissolved in chloroform and spotted on HP-TLC plates, and developed with chloroform, whereby two zones corresponding to two products were obtained. They were designated Ia and Ib; IIa and IIb and IIIa and IIIb for methylamine, *n*-butylamine and sec-butylamine derived products, respectively, and a is the band closest to the origin.

Ethanol soluble fraction contained one major and several minor, uncharacterized compounds again using HP-TLC.

The major product of the ethanol soluble fraction were designated Ic, IIc, and IIIc for methylamine, *n*-butylamine and sec-butylamine derived products, respectively.

All products were characterized using UV, IR, proton NMR and elemental analysis, the details of which are given under Experimental section.

The only difference between the **a** and **b** compounds in all three cases was the presence of a chlorine atom in compound **b** at 5 position of the quinone ring. This unexpected reaction was established by elemental analysis and ^{1}H-NMR. UV spectrum, too, showed a bathochromic shift of 5–8 nm, consistently in all three cases, as expected, although the magnitude of the shift was less than observed with simple quinone derivatives.[11]

H-NMR spectra of Ib, IIb and IIIb showed the absence of proton at 5 position while it was present in Ia, IIa, and IIIa. The presence of chlorine at 5 position also causes a considerable downfield shift in the positions of protons next to the amino group at 6 position, due to its electronegative nature. This effect is more evident in methylamine reaction products. In Ia chemical shift of *N*-methylprotons at 6 position appear as a doublet at δ 2.9 while in Ib they appear at 3.45. Phenyl group at 2 position, on the other hand, causes an upfield shift of *N*-alkyl protons, at 3 position, in comparison with *N*-alkyl protons at 6 position.

It is quite likely that chlorination takes place, through 1, 4 addition, after the formation of the model compounds because if the chlorination had taken place before, that chlorine would have been displaced by the amine.

Monosubstituted products Ic and IIIc were obtained in smaller quantities. Proton NMR spectra of each show two 1-proton singlets in the region of 5.7–6.7 assigned to quinoid ring protons. Their sharp singlet nature suggests that they are not occurring together which can be interpreted as the *N*-alkyl group occupying 6 position of the quinone ring in monosubstituted compounds. The chemical shift-values of *N*-alkyl protons of these compounds are identical with the *N*-alkyl proton values at 6 position in Ia and IIIa.

DISCUSSION

During the last 100 years, studies on quinone-amine reaction have established that the first step in the reaction is the formation of a mono-substituted hydroquinone. This has to be oxidized to monosubstituted benzoquinone before it can react with another amine, again through 1, 4 addition. Since amine substitution reduces the redox potential, some of the available quinone does act as the oxidizing agent, producing simultaneously an equivalent amount of hydroquinone. For this reason it is very difficult to obtain monoamine substituted benzoquinone under normal circumstances.

Compounds that carry free electrons, like quinones and amines, bonds to metals, including noble metals, through "chemisorption" with sufficient affinity to displace water.[12] Thus, the production of hydroquinone that also bonds to metals very strongly, during a reaction between a diamine and a quinone which leads to the formation of polymeric materials,[9] is undesirable, because it competes with the polymeric material for the available sites on the metal surface.

Consequently several years ago the procedure to prepare these polymeric materials was modified to utilize hydroquinone, instead of benzoquinone, in the presence of an oxidizing agent.[9,10] The choice for the oxidizing agent was calcium hypochlorite. One additional advantage of this modification was that it enabled us to use a stoichiometric ratio between the reactants, rather than an excess of quinone, a part of which was wasted as the oxidant.

The presence of calcium hypochlorite, then explains the occurrence of chlorinated by-products.

That the chlorine atom is not being involved in a reaction with an amine molecule, as would be expected, suggests that its introduction occurs after the amine addition has taken place.

It is quite unexpected to find, among the large number of products of the model reactions, monosubstituted quinones, albeit in smaller quantities, because in certain cases, a twofold excess of amine was used, in the presence of a strong oxidizing agent.

Before a systematic study is undertaken to explore the number and chemical nature of the by-products of this reaction one can only speculate that perhaps some quinones may have been substituted with three or four amines. The presence of a product with three amine substitutions, one through quinone carbonyl, during a reaction between 2-phenylquinone and 4-aminotoluene, appears to lend support to this speculation. (Reddy, T. A. & Erhan, S. unpublished observation). Since such an unusual structure was not encountered before, an extensive study is needed to confirm this conclusion.

Horspool *et al.*[13] and Davies and Frahn[14] have found about 50 products, many in trace quantities during the reaction between orthobenzoquinone and aliphatic as well as aromatic amines. Some of the products had quite unexpected structures, that could act as chain terminating molecules, in a polymerization reaction. One observation that suggests such "end-capping" by-products might also be formed during the reaction between *p*-benzoquinone and diamines is that the products formed have very low intrinsic viscosity of 0.05 or less. When a substitution polymerization is performed, however, between the same diamine and either 2.5-dichloro- or 2.5-dihydroxybenzoquinones one obtains products with inherent viscosities of 0.2–0.3. (Reddy, T. A., Nithianandam, V. S. and Erhan, S. unpublished observations).

EXPERIMENTAL

2-phenylhydroquinone, 2-phenylbenzoquinone, calcium hypochlorite (chlorine content 65%), and all solvents were purchased from Aldrich Chemical Co. *n*-Butylamine and sec. butylamine were obtained from BASF. Calciumhypochlorite was always kept in a vacuum dessicator.

The progress of reaction was followed with a Shimadzu UV-160 spectrophotometer after diluting reaction mixture with ethanol.

IR spectra were taken with a Pye-Unicam Model 3-200 spectrophotometer. Samples were dried and dissolved in chloroform and a thin film of the compound was prepared over the NaCl window.

HP-TLC Silica gel G1(1000 micron) plates were supplied by Analtech Inc. Melting points were determined with a Fisher-Johns instrument.

Elemental analyses were performed by the Galbraith Laboratories, Knoxville, TN.

NMR spectra were obtained using a 300 MH$_z$ Bruker Instrument at Temple University.

Oxidation of 2-phenylhydroquinone. 30 m mole 2-phenylhydroquinone, dissolved in 75 ml dichloromethane, was placed in a 3-necked round bottomed flask, fitted with a condenser, a dropping funnel and a mechanical stirrer. To this 60 mole solid calciumhypochlorite was added and the solution was heated to reflux under vigorous stirring. Oxidation was completed within 2–3 hours as judged by the disappearance of 2-phenylhydroquinone peaks and appearance of 2-phenyl benzoquinone peaks.

Reaction of 2-phenylbenzoquinone with aliphatic amines. The above reaction mixture was allowed to cool to room temperature and the amine (I, II, or III) (60 m mole) dissolved in 25 ml dichloromethane was added dropwise and the mixture was stirred for five hours at room temperature. The reaction mixture was allowed to settle overnight and the calcium salts were removed by filtration. The crude product was obtained, after removal of the solvent under vacuum, in 65–85% yield.

Methylamine reaction products. Due to volatility of the amine this reaction was run with a 90 m mole of amine.

Most of the crude product was insoluble, even in boiling ethanol. Insoluble product was dissolved in chloroform, spotted on preparative, HP-TLC plates and developed with chloroform. Two bands were obtained Ia and Ib which were extracted with chloroform:ethanol (1:1) solvent mixture, after the bands were scraped from the plates.

Ethanol soluble fraction yields a major and several minor products on HP-TLC, after removal of ethanol, dissolution in chloroform.

3,6 Dimethylamino-2-phenylbenzoquinone (Ia). Dark orange compound crystallized from chloroform after addition of ethanol until turbidity appears. m.p. 304–306°C (uncor.).

UV maxima, in ethanol 208 and 344 nm.

^{1}H-NMR ($CDCl_3$):2.4 (*d*, 3H at 3 pos), 2.9 (*d*, 3H at 6 pos), 5.35 (*S*, 1H at 5), 6.65 (*b*, 1H at 3 pos), 6.85 (*b*, 1H at 6 pos), 7.2–7.4 (*m*, 5H aromatic).

Elemental Analysis	C	H	N
Calculated for $C_{14}H_{14}N_2O_2$	69.42	5.79	11.57
Found	68.64	5.69	10.96

5-Chloro-3.6-dimethylamino-2-phenylbenzoquinone (Ib). Brown colored compound, m.p. 315°C (uncor.).

UV maxima in ethanol 209 and 349 nm.

^{1}H-NMR ($CDCl_3$): 2.4 (*d*, 3H at 3), 3.45 (*d*, 3H at 6), 6.88 (*b*, 1H at 3), 7.0 (*b*, 1H at 6), 7.15–7.32 (*m*, 5H aromatic).

Elemental Analysis	C	H	N	Cl
Calculated for $C_{14}H_{13}N_2O_2Cl$	60.65	4.69	10.11	12.63
Found	60.39	4.71	9.75	14.32

6-Methylamino-2-phenylbenzoquinone (Ic). Dark, brown crystals from chloroform: hexane = 1:1, m.p. 216–218°C (uncor.).

UV maxima, in ethanol, 205, 236 and 339 nm.

^{1}H-NMR ($CDCl_3$): 2.9 (*d*, 3H at 3), 5.6 (*S*, 1H at 5), 5.7 (*b.s* 1H at 6), 6.7 (*S*. 1H at 3), 7.4–7.55 (*m*, 5H aromatic).

Elemental Analysis	C	H	N
Calculated for $C_{13}H_{11}NO_2$	73.24	5.16	6.57
Found	73.10	5.41	6.57

n-Butylamine reaction products. The crude product was dissolved in boiling ethanol and allowed to cool. 50 mg of the precipitate was dissolved in chloroform, applied to preparative HP-TLC plates and developed with chloroform. Two products IIa and IIb were isolated from the plates, using chloroform-ethanol solvent mixture. 15.3 mg IIa and 33.7 mg IIb were obtained.

3,6 Di-butylamino-2-phenylbenzoquinone (IIa). Violet crystals from chloroform-ethanol. m.p. 142–144°C (uncor.).

UV maxima, in ethanol: 207.5 and 347 nm.

IR (smear): 3300 (—NH—), 1645 (C═O) and 1620 cm^{-1} (—C═C—)

^{1}H-NMR ($CDCl_3$): (Refer to Figure 1a). 0.95 (*t*, 3H at *a*), 1.45 (*m*, 2H at *b*), 1.65 (*m*, 2H at *c*), 3.2 (*d.t*, 2H at *d*), 6.85 (*b.s*, 1H at *e*), 5.4 (*s*, at *f*), 7.15–7.45 (*m*, at *g*); 0.75 (*t*, 3H at *a'*), 1.10 (*m*, 2H at *b'*), 1.45 (*m*, 2H at *c'*), 2.6 (*d.t*, 2H at *d'*), 6.7 (*b.s*, 1H at *e'*).

Elemental Analysis	C	H	N
Calculated for $C_{20}H_{26}N_2O_2$	73.62	7.98	8.59
Found	72.63	8.05	8.34

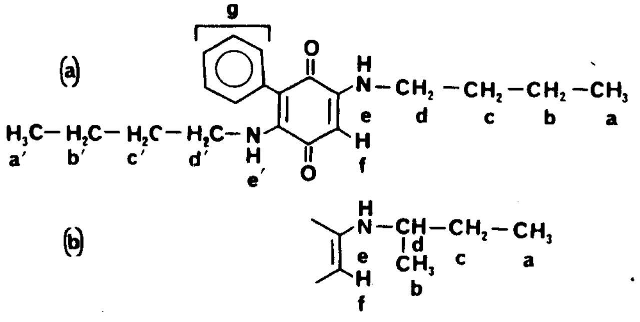

FIGURE 1 The assignment of NMR shifts to structure.

5-Chloro-3,6 di-n-butylamino-2-phenylbenzoquinone (IIb). Pink crystals from chloroform-ethanol. m.p. 148°C (uncor.).

UV maxima, in ethanol: 208 and 356 nm.

IR (smear): 3270 (—NH—), 1635-1 (C═O) and 1610 cm^{-1} (—C═C—) small shoulder.

^{1}H-NMR ($CDCl_3$): 0.98 (*t*, 3H at *a*), 1.45 (*m*, 2H at *b*), 1.68 (*m*, 2H at *c*), 3.87 (*q*, 2H at *d*), 7.15 (*b*, 1H at *e*), 7.18–7.43 (*m*, 5H aromatic); 0.78 (*t*, 3H at *a'*), 1.1 (*m*, 2H at *b'*), 1.35 (*m*, 2H at *c'*), 2.6 (*q*, 2H at *d'*), 6.9 (*b*, 1H at *e'*).

Elemental Analysis	C	H	N	Cl
Calculated for $C_{20}H_{25}N_2O_2Cl$	66.66	6.94	7.77	9.86
Found	66.10	7.05	7.66	not determined

Ethanol soluble fraction contains several products on TLC, the major fraction is likely to be the monobutylamino-2-phenylbenzoquinone, as has been established in methylamine reaction, although it has not been characterized.

Sec-Butylamine reaction products. The crude product was dissolved in boiling ethanol and allowed to cool. The precipitate was dissolved in chloroform and as done with *n*-butylamine product, two compounds were separated on TLC, IIIa and IIIb.

3,6 Di-sec-butylamino-2-phenylbenzoquinone (IIIa). Orange colored crystals from chloroform-ethanol. m.p. 154°C (uncor.).

UV maxima, in ethanol: 209 and 347 nm.

^{1}H-NMR: (refer to Figure 1b) 1.0 (*t*, 3H at *a*), 1.25 (*d*, 3H at *b*), 1.6 (*m*, 2H at *c*), 3.42 (*m*, 1H at *d*), 5.42 (*s*, 1H at 5 pos), 6.75 (*s*, 1H at *e*), 7.2–7.5 (*m*, 5H at *g*); 0.62 (*t*, 3H at *a'*), 0.9 (*d*, 3H at *b'*), 1.22 (*m*, 2H at *c'*), 2.9 (*m*, 1H at *d'*), 6.6 (*b.d*, 1H at *e'*).

Elemental Analysis	C	H	N
Calculated for $C_{20}H_{25}N_2O_2$	73.62	7.98	8.59
Found	73.89	8.15	8.72

5-Chloro-3,6-di-sec-butylamino-2-phenylbenzoquinone (IIIb). Light orange colored compound, from chloroform-ethanol. m.p. 168–170°C.

UV maxima, in ethanol: 210 and 355 nm.

^{1}H-NMR ($CDCl_3$): 0.95 (*t*, 3H at *a*), 1.25 (*d*, 3H at *b*), 1.6 (*m*, 2H at *c*), 4.65 (*m*, 1H at *d*), 7.05 (*b.d*, 1H at *e*), 7.15–7.42 (*m*, 5H at *g*); 0.62 (*t*, 3H at *a'*) 0.9 (*d*, 3H at *b'*), 1.25 (*m*, 2H at *c'*), 2.9 (*m*, 1H at *d'*), 6.85 (*b.d*, 1H at *e'*).

Elemental Analysis	C	H	N	Cl
Calculated for $C_{20}H_{25}N_2OCl$	66.67	6.94	8.59	10.74
Found	66.53	6.99	7.59	10.27

6-Sec-Butylamino-2-phenylbenzoquinone (IIIc). Gummy dark brown compound.

UV maxima, ethanol: 236.5 and 344.5 nm.

H-NMR ($CDCl_3$): 0.95 (*t*, 3H at *a*), 1.25 (*d*, 3H at *b*), 1.62 (*m*, 2H at *c*), 3.35

(*m*, 1H at *d*), 5.5 (*b.d*, 1H at *e*), 5.6 (*s*, 1H at 5 pos), 6.68 (*s*, 1H at 3), 7.15–7.55 (*m*, 5H at *g*).

Elemental Analysis	C	H	N
Calculated for $C_{16}H_{17}NO_2$	75.30	6.67	5.49
Found	74.74	6.99	6.35

CONCLUSION

It is quite reasonable to expect the characteristics of a compound, such as solubility, to depend on the chemical properties of the precursors. This had already been demonstrated for the diamines used in their syntheses.[5,6] In order to study the effect of quinone structure on the properties of the polymers it was decided to prepare and characterize appropriate model compounds, using monoamines. The rationale for this was based upon earlier observations which demonstrated that major UV absorption bands were identical for the model compounds as well as the polymers. Studies have already been initiated to prepare polymers with 2-phenyl- and 2-methylbenzoquinone and preliminary results indicate that binding affinity of the polymers towards metals have not been effected adversely.

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