

A Study of Coating Properties of Novel Poly(Amino-Quinone)s Prepared From 2-Methylbenzoquinone and 2-Phenylbenzoquinone*

T. ASHOK REDDY and S. ERHAN†

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

SYNOPSIS

Novel poly(amino-quinone)s were quantitatively prepared from *in situ* produced 2-methylbenzoquinone and 2-phenylbenzoquinone with Jeffamine D-400® in the presence of calcium hypochlorite as the oxidizing agent. These polymers were readily soluble in most of the organic solvents such as ethanol, acetone, tetrahydrofuran, chloroform, *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), and *N,N*-dimethylacetamide (DMAc). The coatings prepared from these polymers showed very good adhesion to metals, hardness, and flexibility even after curing at 110°C for 5 h. Particularly, coatings formulated with epoxy-novalac resin D.E.N-438 showed excellent corrosion resistance in artificial sea water and did not form any blisters. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

For the past several years, we have been studying poly(amino-quinone) (PAQ) polymers as coating materials because of their excellent corrosion resistance.¹⁻⁶ These polymers have demonstrated unusually strong affinity toward metal surfaces so that they can even be applied as coatings on wet, rusty, and unprepared metal surfaces. Most of these PAQ polymer coatings, when formulated with curing agents such as epoxy resins and alkyl titanates, can resist autoclaving with live steam and withstand 500 h of salt spray test without any blister formation or adhesion failure. In view of these interesting properties, further attempts have been made to prepare a new class of PAQ polymers using substituted benzoquinones as starting monomers.

In this article we report the synthesis, characterization, and coating properties of two new polymers, poly(amino-2-methylbenzoquinone) (MePAQ) and poly(amino-2-phenylbenzoquinone) (PhPAQ)

(Scheme 1). Both these polymers were prepared with *in situ* generated 2-methylbenzoquinone or 2-phenylbenzoquinone from their respective hydroquinones using calcium hypochlorite as the oxidizing agent and Jeffamine D-400® (polyoxypropylene diamine). Polymer coatings were chemically heat cured with ethylenediamine (EDA) and epoxy-novalac resin D.E.N-438 (Epoxy-438).

EXPERIMENTAL

Materials

2-Methylhydroquinone, 2-phenylhydroquinone, and 1,2-ethylenediamine were obtained from Aldrich Chemical Company. Jeffamine D-400® with nominal molecular weight of 400 was a gift from Texaco Chemical Company. Calcium hypochlorite was received from Fisher Scientific Company. Epoxy-novalac Resin D.E.N 438 was obtained from Dow Chemical Company and BYK-306 from Byk Chemie. UV spectra were recorded using a Shimadzu UV-160 U spectrophotometer and IR spectra were obtained on Pye-Unicam Model 3-200 spectrophotometer. Polymer viscosities were measured using an Ubbelohde viscometer and DMSO as solvent at a concentration of 0.5 g/dL at 30°C.

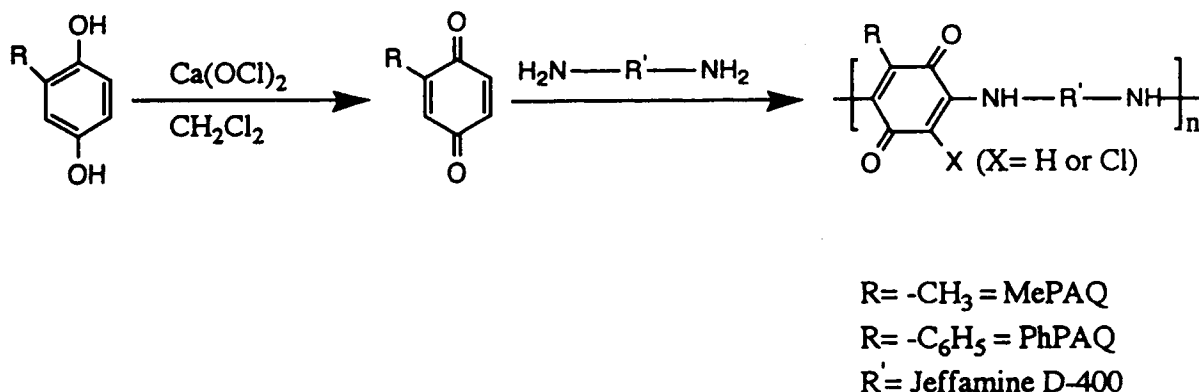
* This is communication XIV of the series "Quinone-amine polymers."

† To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 51, 1591-1595 (1994)

© 1994 John Wiley & Sons, Inc.

CCC 0021-8995/94/091591-05



Scheme 1

Methods

Synthesis of 2-Methylbenzoquinone-Jeffamine D-400® Polymer

To the solution containing 2-methylhydroquinone (6.2 g, 0.05 mol) dichloromethane (75 mL), calcium hypochlorite (14.3 g, 0.1 mol) was gradually added and the mixture was stirred for 2 h at room temperature. At this point UV showed characteristic absorptions for 2-methylbenzoquinone at 313 and 246 nm. Jeffamine D-400® (20.0 g, 0.05 mol) dissolved in 50 mL of dichloromethane was slowly added to the reaction mixture while reaction temperature was maintained constantly at room temperature and stirring was continued overnight. Reaction contents were allowed to settle and residual calcium salts were filtered. The filtrate was concentrated under vacuum and a dark gummy polymer obtained was reprecipitated by dissolving in dichloromethane and by adding an excess of hexane to it. Polymer yield 24.5 g (93.7%). UV (ethanol): 462, 345.5, and 214 nm. Viscosity (η_{inh}): 0.077 dL/g in DMSO at 30°C (concentration 0.5 g/dL).

Synthesis of 2-Phenylbenzoquinone-Jeffamine D-400® Polymer

To a 3-necked round bottom flask containing 2-phenylhydroquinone (9.3 g, 0.05 mol) in 75 mL of dichloromethane, calcium hypochlorite (14.3 g, 0.1 mol) was gradually added and stirring was continued for 2 h. At this stage the reaction mixture turns yellow which indicates the formation of 2-phenylbenzoquinone. To this reaction mixture Jeffamine D-400® (20 g, 0.05 mol) dissolved in 50 mL of dichloromethane was slowly added and stirring was continued for an additional 6 h at room temperature. The reaction was allowed to stand overnight and

calcium salts were removed by filtration. Most of the solvent was distilled out from filtrate and polymer was precipitated by pouring into an excess of hexane. The dark colored semisolid polymer obtained after reprecipitation was dried under vacuum. Yield: 27 g (92.2%). UV (ethanol) 345.5 and 207 nm. Viscosity (η_{inh}): 0.062 dL/g in DMSO at 30°C ($C = 0.5$ g/dL).

Coating Formulations and Curing

PhPAQ and MePAQ polymers were dissolved in a xylene/*n*-butanol (4 : 1) solvent mixture containing 2% of flow reagent BYK-306 and 1% of super-airout. For chemical curing either EDA or epoxy-novalac resin 438 was used in equal molar ratio, that is, per mole repeat unit either 1 mole of amine or epoxy resin was added. Overall solid contents for MePAQ was 60% and for PhPAQ was 70%. All Q-panels were degreased with trichloroethylene and dried. All the coating formulations were applied with wire wound applicators and were thermally cured at 110°C for 5 h.

Coatings Characterization

Film thickness was measured with a Model FN 252 Minitest Coating thickness gauge obtained from Gardco Company. The paint adhesion test (PAT) was performed according to ASTM-3359-85 method-D, by using a very coarse blade (3.0-mm spacing) six teeth cutter. A test for flexibility was carried out according to ASTM-D 1737-85 with a Pentagon Mandrel Bend Test Apparatus. Finally, the pencil hardness test was performed according to ASTM-D 3363 using pencil hardness gage H-501, supplied by Paul N. Gardner Co. Accelerated aging was performed according to ASTM-D-1183-70, procedure-D using substitute sea water. The test was carried

out for 1000 h, during which time coated panels were periodically checked for blister formation and adhesion failure.

RESULTS AND DISCUSSION

Polymer Synthesis

Polymerization was carried out using either one equivalent of 2-methyl or 2-phenylhydroquinone with one equivalent of Jeffamine D-400® and two equivalents of calcium hypochlorite as oxidizing agent in dichloromethane solvent at room temperature. This polymerization was conducted in two steps under heterogeneous conditions. In the first step, 2-methyl or 2-phenylhydroquinone was oxidized to its corresponding benzoquinone derivative and the reaction was monitored by UV spectrophotometry. At the end of oxidation, UV spectrum showed characteristic absorptions for 2-methylbenzoquinone at 313 and 246 nm and for 2-phenylbenzoquinone at 368, 231, and 202.5 nm.

In the next step, Jeffamine D-400® dissolved in dichloromethane was gradually added to the *in situ* formed benzoquinone derivative at room temperature. During the addition of amine the reaction color changes from yellow to dark brown indicating the formation of the amino-quinone derivatives. Because the 2-methylbenzoquinone reaction with amine was very slow the polymerization was carried out overnight to completion. In the case of 2-phenylbenzoquinone reaction with amine, UV spectrum of the reaction mixture instantaneously shows the characteristic absorptions due to the formation of the diamino-quinone derivative at 345 nm. The reactivity difference between the two monomers was probably due to the different electronic effect caused

by the presence of the methyl and phenyl groups on the quinone ring. The electron donating methyl group slows down the nucleophilic attack by amine at the C-3 position of the quinone ring. On the other hand the electron withdrawing phenyl group facilitates the amine addition at the same position. The purified MePAQ and PhPAQ polymers were characterized by UV and IR spectra and were comparable with the model compounds reported elsewhere.⁷ The UV spectra (Figs. 1, 2) of MePAQ and PhPAQ polymers showed characteristic absorptions due to the diamino-quinone derivative at 462, 345.5, and 214 nm and 345.5 and 207 nm, respectively. The IR spectra (Fig. 3) of these polymers showed a characteristic band at 3300 cm^{-1} for the —NH— stretching frequency and a shoulder at 1630 cm^{-1} for quinone carbonyl.

The formation of the polymer takes place in several stages. In the first instant the *in situ* formed 2-methyl or 2-phenylbenzoquinone undergoes an amine addition at the C-6 position to form a monoamino substituted hydroquinone. To enable the addition of second amino group at the C-3 position, the monosubstituted hydroquinone has to be oxidized to monosubstituted benzoquinone derivative in the presence of excess oxidizing agent. The addition of the second amino group and further oxidation of resulting poly(amino-hydroquinone) leads to the formation of poly(amino-quinone). During the polymerization about 65% of the quinone rings were chlorinated at the C-5 position demonstrated with model compounds.⁷

Inherent viscosities of MePAQ and PhPAQ polymers was measured in DMSO at 30°C and were in the range of 0.077 and 0.062 dL/g, respectively. Even though viscosities were low, these polymers could form free-standing thin films. Both the polymers

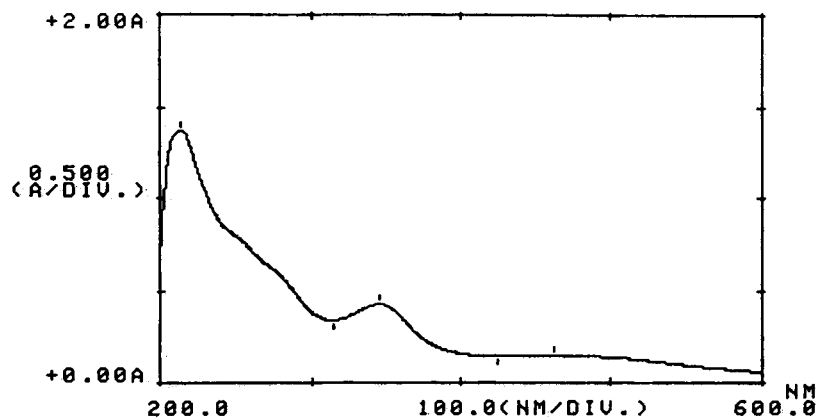


Figure 1 UV spectrum of MePAQ polymer in ethanol.

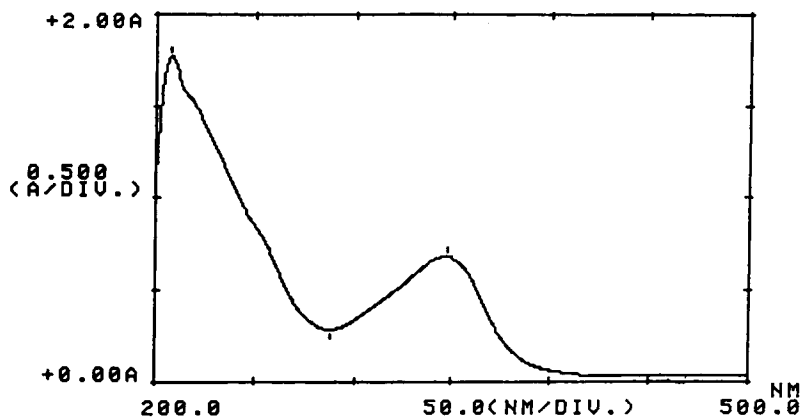


Figure 2 UV spectrum of PhPAQ polymer in ethanol.

were highly soluble in most of the organic solvents such as acetone, ethanol, tetrahydrofuran, chloroform, DMF, NMP, and DMAc.

Coating Formulations and Properties

MePAQ and PhPAQ polymers were dissolved in xylene/*n*-butanol (4 : 1) solvent mixture and applied to steel Q-panels using wire-wound applicators. For each polymer three different coating formulations were prepared. They were: (1) polymer without any added curing agent, (2) polymer with EDA, and (3) polymer with epoxy-novolac resin D.E.N 438. All coatings were allowed to dry overnight at room temperature and cured at 110°C for 5 h.

The test results of adhesion, hardness, flexibility, and accelerated aging are summarized in Table I. The film thickness of the coatings, measured with

a model FN252 Minitest coating thickness gage, varied from 0.66 to 1.3 mils. The PAT was done according to the ASTM-3359-83 method-B, except for MePAQ polymer coating; all other coatings had shown excellent adhesion to the metals and the edges of the coats were completely smooth and none of the squares of the lattice was detached. The PAT test results indicates that the addition of EDA or epoxy resin to MePAQ formulation increases its adhesion capability. Similarly, the pencil hardness test was performed according to the ASTM-D 3363 method, and it showed that the hardness of the coatings increases with the addition of curing agents. Finally the bend test results indicate that all the coatings had enough flexibility to be bent on a $\frac{1}{8}$ " pentagon mandrel.

For corrosion resistance studies, the scored coatings were immersed in artificial sea water prepared

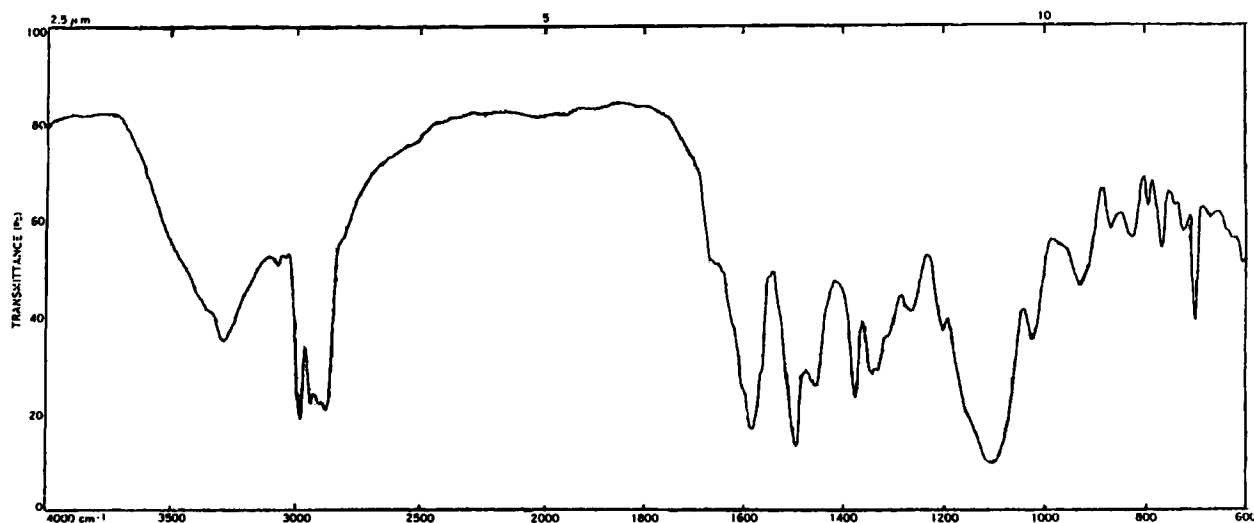


Figure 3 IR spectrum of PhPAQ polymer.

Table I Adhesion, Hardness, and Flexibility Properties of Cured Polymer Coatings

S.No.	Formulation	Film Thickness (mils)	PAT ^a	Pencil Hardness Test		Bend Test 1/8" Mandrel	Artificial Sea Water Immersion ^d
				Position ^b	Grade ^c		
1	MePAQ	0.98	4B, 4B, 5B	4	4H	Pass	40% blisters all over panel and no peeling
2	PhPAQ	1.03	5B, 5B, 5B	5	2H	Pass	Few blisters on the edges and no peeling
3	MePAQ-EDA (1 : 1)	0.66	4B, 5B, 5B	6	4H	Pass	50% blisters and no peeling
4	PhPAQ-EDA (1 : 1)	0.83	5B, 5B, 4B	6	4H	Pass	50% blisters and no peeling
5	MePAQ-Epoxy-438 (1 : 1)	1.15	5B, 5B, 5B	6	4H	Pass	No blisters and no peeling, best result
6	PhPAQ-Epoxy-438 (1 : 1)	1.3	5B, 5B, 5B	6	4H	Pass	No blisters and no peeling, best result

EDA, ethylenediamine. Epoxy-438, epoxy-novalac resin D.E.N-438.

^a Paint adhesion test.

^b Gardco pencil position.

^c Lead grade.

^d Immersed for 1000 h.

according to the ASTM-1183-70 procedure-D for 1000 h. Results of this test were varied for different formulations. MePAQ, MePAQ-EDA, and PhPAQ-EDA coatings showed about 40–50% blister formation all over the area but there was no peeling of the coatings. The failure of the EDA formulated coatings, attributed to the presence of the methyl or phenyl groups at the C-2 position of the quinone ring, may prevent reaction with the amino groups of the EDA. On the other hand very few blisters on the edges and no peeling of the coatings was observed for the PhPAQ formulation. In contrast to the above results, coatings formulated with epoxy-novalac resin D.E.N. 438, MePAQ-Epoxy, and PhPAQ-Epoxy, exhibited excellent resistance to the sea water. These coatings did not show any blister formation or extended corrosion underneath the coatings through the scored areas. The excellent performance of these coatings can be due to the high cross-linking density achieved through the epoxy-secondary amine reactions.

The strong adhesion of PAQ polymers to the metal surface can be explained based on the studies carried out by Soriaga and Hubbard,⁸ on the affinity of quinones and their derivatives toward the metals. The affinity of these compounds was attributed to

the contribution of the quinone molecule free electrons to the outer orbitals of the metal surface through the phenomenon called "chemisorption."

REFERENCES

1. K. Kaleem, F. Chertok, and S. Erhan, *Prog. Org. Coatings*, **15**, 63 (1987).
2. K. Kaleem, F. Chertok, and S. Erhan, *J. Polym. Sci. Polym. Chem. Ed.*, **27**, 865 (1989).
3. V. S. Nithianandam, F. Chertok, and S. Erhan, *J. Coatings Technol.*, **63**, 51 (1991).
4. V. S. Nithianandam, and S. Erhan, *Polymer*, **32**, 1146 (1991).
5. T. A. Reddy, V. S. Nithianandam, and S. Erhan, *Metallized Plastics 3: Fundamental and Applied Aspects*, K. L. Mittal, Ed., Plenum Press, New York, 1992, pp. 43–45.
6. T. A. Reddy and S. Erhan, *J. Polym. Sci. A, Polym. Chem.*, to appear.
7. T. A. Reddy and S. Erhan, *Intl. J. Polym. Mater.*, **19**, 109 (1993).
8. M. P. Soriaga and A. T. Hubbard, *J. Am. Chem. Soc.*, **104**, 2735 (1982).

Received July 22, 1993

Accepted August 24, 1993