

# Quinone–Amine Polymers. V. Syntheses and Solubilities of Several Diamine–*p*-Benzoquinone Oligomers (PAQ)

V. S. NITHIANANDAM, K. KALEEM, F. CHERTOK, and S. ERHAN\*

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

## SYNOPSIS

Several diamine–*p*-benzoquinone polymer/oligomers were synthesized to find those that exhibited superior properties, in addition to being able to displace water from wet, rusty steel surfaces. Unfortunately, many of these were found to be insoluble in most commonly used solvents and a few to be insoluble in all 34 solvents used in polymer solubility studies. The reason for this low solubility is believed to be the extremely regular structure of the polymers.

## INTRODUCTION

Polyamine–benzoquinone polymer/oligomers were shown to be able to adhere to metals and alloys with sufficient affinity to displace water from wet, rusty steel surfaces.<sup>1–3</sup> Some were also capable of resisting salt spray, autoclaving, being applicable under water,<sup>1</sup> and some absorbed only 0.1% (w/w) moisture when immersed in water for 96 h.<sup>2</sup>

The reaction occurs spontaneously through 1.4 addition leading first to a monosubstituted hydroquinone. This is oxidized to a monosubstituted benzoquinone, oxidation being affected by an available free benzoquinone, which then reacts with a second amine. A free hydroquinone is produced from the benzoquinone used in the oxidation. When di- or triamines are utilized a linear or 3-dimensional polymer results.<sup>1,2</sup> To take advantage of these unique capabilities, one has to be able to dissolve them in solvents that are acceptable environmentally and economically together with additives that allow optimal characteristics. During early studies, however, it became clear that solubility of these products was very low with many of the diamines, probably due to their very regular structures that allowed inter- as well as intramolecular hydrogen bond formation,

hydrophobic interactions as well as pi–pi interactions among the aromatic moieties. Consequently, it was decided to prepare polymers with different amines that looked promising, i.e., those amines that have a kink or branching in their molecules and study their solubilities. Polymers were also prepared with two different amines. Here the results obtained with single diamines are being reported while the next paper will detail studies with copolymers involving two amines.

## MATERIALS AND METHODS

The amines used and their sources are: ethylene diamine, 1,12-diaminododecane, *m*-phenylene diamine, 1,4-diaminocyclohexane 2,3-diaminopropionic acid, purchased from Aldrich Chemical Co. 1,3-Bis(3-aminophenoxy) benzene (APB) was bought from National Starch. The Ethacure 100 sample was received from Ethyl Corp. Jeffamine<sup>†</sup> D-400 and D-2000 samples were obtained from Texaco. The 2,4-Diamino-5-*tert*-butyltoluene sample came from Air Products and the trimethylhexamethylene diamine sample was received from Huels America. *p*-Benzoquinone and all solvents were

\* To whom correspondence should be addressed.

<sup>†</sup> Jeffamines are di- and trifunctional polyoxypropylene di- or triamines, represented by D- and T-, respectively. Their nominal molecular weights are designated by the numbers following the letters.

purchased from the Aldrich Chemical Co. All compounds were used as received except *p*-benzoquinone, which was recrystallized from ethanol.

UV spectra were obtained with a Hitachi-Perkin Elmer Model 200 UV spectrophotometer; viscosity

measurements were made with a Ubbelohde viscometer. Solubilities were determined as usual by suspending a weighed sample in different solvents, allowing them to stand with stirring, removing the insoluble and weighing.

**Table I Diamine-*p*-Benzoquinone Reaction Conditions and Yields**

Amine	Amine : pBQ	Solvent	Concn (% w/v)		Reaction Time		Drying		Yield
			pBQ	Amine	(°C)	(h)	(°C)	(h)	
1. Ethylenediamine	1 : 3 <sup>a</sup>	THF	10	10	30	1 $\frac{3}{4}$	60	24	97
2. Ethylenediamine	1 : 2 <sup>b</sup>	THF	18	16	66	4	60	24	63
3. Ethylenediamine	1 : 2 <sup>c</sup>	THF	18	16	66	20	70	24	52
4. Ethylenediamine	2 : 3	THF	18	16	66	4	70	24	53
5. Ethylenediamine	1 : 1 <sup>d</sup>	EtOH	14	12	66	4 $\frac{1}{4}$	70	24	32
6. 1,12-Diaminododecane	1 : 3 <sup>e,f</sup>	THF	10	10	30	1 $\frac{3}{4}$	30	24	71
7. <i>m</i> -Phenylenediamine	1 : 3 <sup>g,h</sup>	THF	10	10	30	1 $\frac{3}{4}$	60	24	100
8. <i>m</i> -Phenylenediamine	1 : 3 <sup>h,i</sup>	THF	10	10	66	4 $\frac{1}{2}$	60	24	100
9. 2,4-Diamino-5- <i>tert</i> - butyltoluene	1 : 3 <sup>h,j</sup>	THF	10	10	30	3 $\frac{3}{4}$	60	24	100
10. 1,4-Diaminocyclohexane	2 : 3 <sup>h,k</sup>	THF	10	10	66	4 $\frac{1}{2}$	60	24	89
11. Trimethyl- hexamethylene- diamine <sup>l</sup>	2 : 3 <sup>h,m</sup>	THF	10	10	66	4 $\frac{1}{4}$	60	3	100
12. Ethacure-100 <sup>n</sup>	2 : 3 <sup>h</sup>	THF	10	10	66	4 $\frac{1}{4}$	40	24	58
13. Jeffamine D-2000 <sup>o</sup>	2 : 3 <sup>h</sup>	THF	10	10	66	4 $\frac{1}{4}$	55	24	—
14. Jeffamine D-400 <sup>o,p</sup>	2 : 3	EtOH	7	16	78	3	50	5	—
15. 1,3-Bis(3-aminophenoxy) benzene	1 : 3 <sup>q</sup>	EtOH	6	6.5	78	3	50	3	80
16. 4,4'-diaminophenyl ether	1 : 3 <sup>r,s</sup>	EtOH	1		78	3	50	5	82
17. Lysine	1 : 3 <sup>a</sup>	EtOH : H2O = 10 : 7	5	3	78	3	60	24	—
18. 2,3-Diaminopropionic acid	1 : 3	EtOH : H2O = 7 : 3	5	3	78	4	60	24	—

<sup>a</sup> A precipitate formed during reaction.

<sup>b</sup> Amine was added to quinone solution at 0–5°C during 50 min and then refluxed for 4 h.

<sup>c</sup> Precipitate was digested with boiling water for 12 h.

<sup>d</sup> Air was bubbled through the mixture during refluxing. Due to the sensitivity of THF towards oxidation ethanol was used as the solvent.

<sup>e</sup> The amine was added directly because of its very sparse solubility in THF, in small portions, but more THF was added to flask to make the final amine concentration 10%.

<sup>f</sup> Product precipitates out; recovered by centrifugation and washed extensively with THF.

<sup>g</sup> After water, cold acetone and petroleum ether were also used to wash the precipitate.

<sup>h</sup> During the addition of amine the temperature was kept below 30°C.

<sup>i</sup> Wash water contained hydroquinone (UV) after usual washing. The precipitate was extracted with ether in a Soxhlet apparatus, for 12 h. Weight loss 5%.

<sup>j</sup> A waxy solid was precipitated in water. Since wash water had benzo- and hydroquinone (UV), the precipitate was dissolved in THF and reprecipitated with water several times.

<sup>k</sup> Product precipitated during reaction and was washed extensively with THF.

<sup>l</sup> A mixture of 2,2,4-trimethyl- and 2,4,4-trimethylhexamethylenediamine.

<sup>m</sup> Product still contains ca. 5% hydroquinone despite extensive washing.

<sup>n</sup> A mixture of 2,4- and 2,4-diamino-3,5-diethyltoluene.

<sup>o</sup> A mixture of polyoxypropylene diamines; hence yield was not calculated.

<sup>p</sup> *Prog. Org. Coatings*, **15**, 63 (1987).

<sup>q</sup> *J. Polym. Sci. Chem.*, **27**, 865 (1989).

<sup>r</sup> Product precipitates during reaction.

<sup>s</sup> Product contains a considerable amount of unreacted amine; the yield was not calculated.

### General Procedure for the Preparation of Quinone-Amine Polymers

The required amount of *p*-benzoquinone was dissolved in THF, in a three-necked round-bottom flask equipped with a reflux condenser, dropping funnels, a gas introduction tube, and a mechanical stirrer. Unless indicated otherwise, the final concentration of the quinone and the amine was 10% (w/v). The corresponding amount of amine, too, was dissolved in THF, unless stated otherwise, and was added into the benzoquinone solution over 15 min, keeping the temperature of the mixture below 30–35°C. The mixture was either stirred for a specific period, as given in Table I, at 30°C or was refluxed, with constant stirring. In rare cases the product precipitated out during stirring, even during the addition of the amine.

Normally, at the end of reaction period, most of the THF was removed under vacuum and the product was precipitated by pouring the mixture into excess water. The precipitate was isolated generally by filtering, except with 1,12-diaminododecane, where the product was isolated by centrifugation. The precipitate was extensively washed with water or other solvents, when indicated, to remove unreacted amine, benzoquinone, and the reaction by-product hydroquinone. The end point for washing usually is indicated by the wash water becoming colorless. In certain instances, the precipitate had to be redissolved in an appropriate solvent and reprecipitated several times to remove those compounds. UV analyses of the wash water is a convenient way to check the presence of benzoquinone 245 nm and hydroquinone 290 nm. The presence of amine can be tested with ninhydrin reaction.

The cleaned precipitate was then dried in an oven for a certain period, always under vacuum.

### RESULTS

These studies were performed to find conditions under which soluble products could be obtained with the highest yields. Consequently, many parameters were varied, but certain steps remained the same such as the use of the most adequate solvent, THF, removal of this under vacuum, precipitation of the product by pouring into water, with very few exceptions, and drying the product. Some amines, such as 1,12-diaminododecane, are sparsely soluble in THF as well as other solvents; hence it had to be added directly into benzoquinone solution. Generally raising the reaction temperature did not contribute to higher yields.

Table II Solubility Profiles of Diamine-Benzoquinone Reaction Products, in % (w/w)

Solvents	Polymers																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Acetone	0.04	0.03	0	0.06	0.04	0.28	1.80	1.23	Sol	Swell	1.11	n.d. <sup>d</sup>	Sol	Sol	0	0	0	0
<i>n</i> -Butanol	0.05	0.05	0.17	0.22	0.01	n.d.	n.d.	0.09	0	0	1.09	n.d.	Sol	Sol	0	0	0	0
Chloroform	0	0	0	0	0	0.12	n.d.	n.d.	Sol	Swell	5.83 <sup>a</sup>	n.d.	0	0	0	0	0	0
DMA	0.67	1.08	1.00	0.91	1.40	0.11	6.56	6.99	Sol	Sol	9.34 <sup>b</sup>	n.d.	Sol	Sol	Sol	0	0	0
DMF	0.51	1.27	1.10	0.99	1.15	0.21	4.32	7.06	Sol	Sol	4.56	n.d.	Sol	Sol	Sol	0	15.0	0
Dioxane	0.30	0.08	0.05	0.05	0.02	0.11	2.96	1.29	Sol	Sol	2.85	n.d.	Sol	Sol	Sol	0	0	0
DMSO	1.80	3.02	2.28	3.05	3.15	0.30	7.25	14.0	Sol	Swell	16.26	n.d.	Sol	Sol	Sol	Sol	0	0
Ethanol	0.04	0	0.12	0	0.05	0.1	0.56	0.32	Sol	Sol	n.d.	n.d.	Sol	Sol	Sol	0	0	0
MEK	0.11	1.03	0.11	0.09	0.09	0.32	2.48	0.91	Sol	Sol	3.74 <sup>c</sup>	n.d.	Sol	Sol	Sol	0	0	0
NMP	4.86	1.41	0.87	0.78	1.13	0.38	8.36	7.99	Sol	Swell	8.9	n.d.	Sol	Sol	Sol	0	0	0
THF	0.10	0.06	0.14	0.09	0.09	0.29	3.29	3.09	Sol	Sol	3.11	n.d.	Sol	Sol	Sol	0	0	0
Xylene	0	0	0.02	0	0.04	n.d.	n.d.	n.d.	Sol	Sol	n.d.	n.d.	0	0	0	0	0	0
Concd sulfuric acid	4.1	n.d.	n.d.	n.d.	n.d.	Swell	0.65	n.d.	n.d.	5.85	6.91	n.d.	n.d.	n.d.	n.d.	Sol	0	0

<sup>a</sup> Coats glass.

<sup>b</sup> Film formation.

<sup>c</sup> Coats glass.

<sup>d</sup> Due to very low solubility in preliminary experiments individual determinations were not made.

**Table III Solubility of Some Diamine-*p*-Benzoquinone Oligomers in Solvent Mixtures % (w/w)**

	Oligomers					
	1	6	8	9	10	11
Solvents (v/v)	—	—	—	—	—	—
Chloroform : toluene = 1 : 1	—	0.24	—	—	—	—
Nitrobenzene : THF = 1 : 1	—	0.04	—	—	—	—
Methanol : nitrobenzene = 1 : 1	1.09	—	—	—	—	—
DMSO : nitrobenzene = 1 : 1	1.34	—	—	—	—	—
MEK : SHFN <sup>a</sup> = 1 : 1	—	—	0.01	Sol	0.06	2.32 <sup>b</sup>
<i>n</i> -Butanol : xylene = 1 : 4	—	—	0.10	Sol	0.29	—

<sup>a</sup> Superhigh flash naphta.

<sup>b</sup> Coats glass.

Products of lysine, 2,3-diaminopropionic acid, and APB were obtained during earlier studies and have been included here to provide additional information.

In an effort to find solvent combinations that might solubilize these compounds, solubility parameters of the two least soluble polymers—ethylene diamine and 1,12-diaminododecane—were calculated using Small's method<sup>4</sup> and Hoy's most recent tables.<sup>5</sup> Table II shows the solubility of these polymers in several solvents. A 2-dimensional solubility map was then constructed for each of the polymers.<sup>6</sup> The most likely solvent combinations were used with these products, and the results are given in Table III. Unfortunately, due to very high value of their solubility parameters, it is impossible to find solvents that can solubilize them.

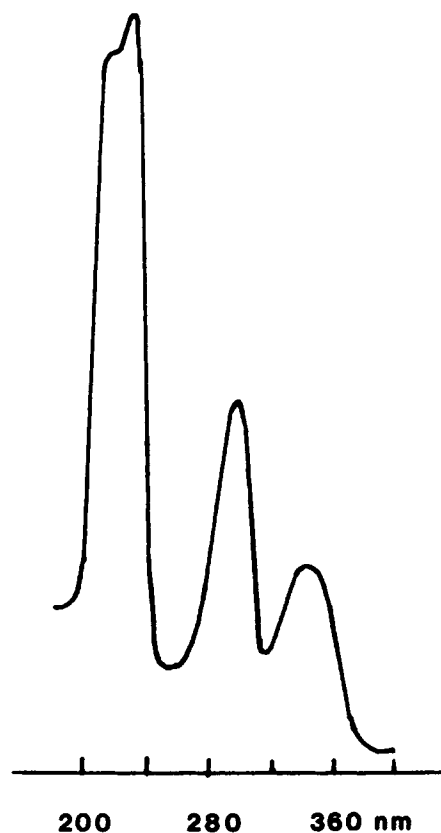
All of the polymers obtained share the absorption maxima seen in Figure 1 with the exception of *m*-phenylenediamine and Jeffamine D-2000 products (Table IV). Inherent viscosities of these compounds show that they are oligomeric in nature (Table V).

## DISCUSSION

It has already been established that when quinone reacts with polyamines linear chains are formed through two successive 1,4 additions.<sup>1,2</sup> The reaction proceeds with the intermediate formation of a monosubstituted hydroquinone which is oxidized by a quinone molecule to a monosubstituted benzoquinone because electron donating substituents lower the oxidation potential of substituted hydroquinone.<sup>7</sup>

These polymers owe their great affinity towards metals, to chemisorption,<sup>8</sup> and represent a class of compounds that hold great promise for many in-

dustrial applications. These include, but are not limited to, their being used as primers for metals exposed to elements, as their resistance to salt spray for long periods—ca. 2000 h (unpublished observation)—and their autoclavability, clearly demonstrate. Since they can displace water, they probably represent the only truly moisture resistant coatings.



**Figure 1** The UV spectrum, of 1,4-diaminocyclohexane-*p*-benzoquinone reaction product. The 340–350 nm band represents disubstituted benzoquinone.

**Table IV Absorption Maxima of Diamine-Benzoquinone Oligomers**

Oligomers	Maxima (nm)						
1-5	—	226	240	—	—	—	339
6	—	226	—	295	—	—	339
7, 8	—	226	240	268 <sup>a</sup>	—	308	—
9	—	227	—	—	296	—	350
10	—	224	—	—	294	—	343
11	—	224	—	—	293	—	343
12	215	—	—	—	295	—	340
13	211	—	—	—	—	—	343

<sup>a</sup> Appears as shoulder.

**Table V Inherent Viscosities of Some Diamine-Benzoquinone Reaction Products**

Amine	
Jeffamine D-400	0.0714
2,4-Diamino-5- <i>tert</i> -butyl toluene	0.0349
<i>m</i> -Phenylenediamine	0.0530
1,3-Bis(3-aminophenoxy)benzene	0.0704

Since even when they are cured they have reactive  $\begin{matrix} \text{H} \\ | \\ \text{—N—} \end{matrix}$  and  $\text{—OH}$  or  $\text{=O}$  groups, they can function as moisture-resistant adhesion promoters. They can be developed into adhesives that are capable of adhering to unprepared surfaces, etc. Our preliminary studies show that lap shear joints, prepared with these compounds, utilizing Epon 828 show no decrease in tensile strength after being immersed into water for 90 h. Hence it is quite natural to explore the possibilities that exist in different compositions and characterize them. Foremost among these characteristics is their solubility because it is much easier to work with a soluble product than with an insoluble one which requires special techniques to be utilized.

It is clear from the data presented that only a few amine-quinone combinations have adequate solubility; the structural requirements for solubility are hard to pinpoint.

It appears that if the amine functions are separated by flexible, long chains, one obtains good solubility—Jeffamine D-400 and Jeffamine (R) D-2000. However, 1,12-diaminododecane is practically insoluble whereas *tert*-butyltoluenediamine has excellent solubility. Although aliphatic ether amines provide good solubility, one aromatic ether amine is again practically insoluble. Ethylenediamine product was insoluble in any of the standard 34 solvents used in the coating industry. This study was performed

by the DuPont Co. Branched chains were expected to interfere with molecular order and yield soluble products, but trimethylhexamethylene diamine was not as soluble as expected.

Furthermore, some of the products are also infusible, such as lysine and diaminopropionic-acid-based compounds; however, TGA shows that both begin to lose weight around 200°C (Erhan, unpublished observations).

The low solubility of the aliphatic diamine series, from ethylene diamine to 1,12-diaminododecane, has been observed before, in a study of the heat-conducting capacity of these compounds.<sup>9</sup>

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