

Poly(amino-quinone)s: A new class of polymers for anticorrosive applications

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Metals or steel reinforced concrete structures, that are not by themselves inert to chemical attack (corrosion) from the environment in which they are designed to serve, can very rarely be protected by metallic coatings [1]. The normal protection under such conditions will be provided by a non metal, often by a polymer coating. Each polymer so used has its own limitations—chemical or thermal, which must be considered. Therefore, in any case, a combination of two or more properties in a given polymer is required to provide necessary ultimate protection to the metal or steel present in the concrete.

An ideal corrosion-resistant coating would be the one that can adhere to a wet surface, resist moisture and temperature changes, is capable of binding to metals as well as siliceous materials under wet conditions, and resists autoclaving [2]. The polymers for this application should also be chemically compatible with other known engineering plastics for flexible use.

Our own work in this area is concerned with the identification and the development of hydrophobic polymers for corrosion resistance applications. Hitherto, most of the polymers used for this application are directly or indirectly based on acrylic, vinyl, epoxy, polyurethane, etc. We have focussed our attention on two aspects, viz., (i) to explore the use of hydrophobic polymers as precursors to corrosion resistance coatings and (ii) to evaluate them in inhibitor formulations.

Among the many polymers presently used in corrosion resistance application, poly(amino-quinone)s (PAQ) is a unique class in the context of protecting metallic surfaces as they readily bind to the metal with sufficient affinity to displace water. This feature of PAQ opens up new vistas in protecting metal surfaces that form the part of ship hulls and steel reinforcement bars from sea water corrosion and fouling.

One of the major attractive features of this class of polymers is its preparation from a host of amines and quinones available in plentitude. Hitherto known methods of synthesizing [3–5] this class of polymers by condensation polymerization involve several approaches and usually takes two or three steps [Scheme 1].

However, the above synthesis is not free from problems such as:

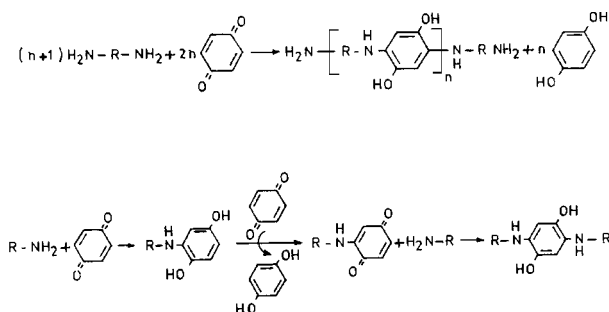
1. the polymer formation occurs spontaneously between amine/diamines and benzoquinone (BQ); firstly, it yields a monosubstituted hydroquinone (H₂Q) through 1,4-addition. This needs to be reoxidized to monosubstituted benzoquinone before it can react with

the second amine, again through 1,4-addition. Excess BQ is needed to oxidize the disubstituted hydroquinones that are formed as the chain propagation occurs, the rest being converted to H₂Q as waste. Further, the H₂Q competes with PAQ in binding to the metal and hence needs to be eliminated.

2. the strategy for enhancing the utilization of BQ molecules warrants the use of strong oxidizing agents such as calcium hypochlorite which in turn needs a phase transfer catalyst, since PAQ formation is usually carried out in non-aqueous media.

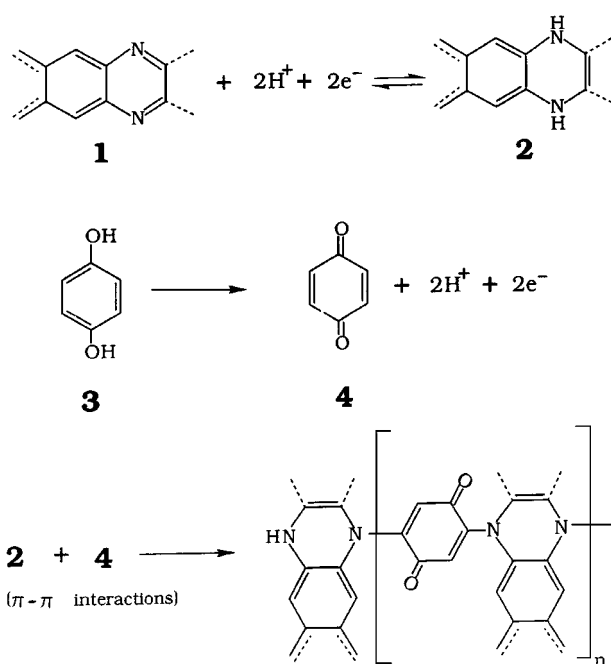
We have overcome the above problems by resorting to an electrochemical approach wherein the complete utilization of BQ from the precursor H₂Q is ensured in the aqueous medium itself [6] without employing an oxidizing agent, assisted by phase transfer. It also affords adherent films of ladder-type PAQ polymers of varying thickness, as explained in the Scheme 2. In this paper, we report the characteristics of the PAQ synthesized from o-phenylenediamine and hydroquinone and its polyblends and some interesting aspects of the PAQ properties relevant to anti-corrosive formulations.

Table I shows the salient features of PAQ electro-synthesized using the above approach. Importantly, the key IR characteristic band at 1650 cm⁻¹ due to the quinoneimine interaction in the PAQ is observed in our studies (which is otherwise not discernible if the amine precursor is a polyetherimine [2]) on the electrochemically synthesized polymer samples. Its adsorption on mild steel surface is also revealed by Fourier Transform IR spectroscopy [7]. To render them suitable in coating formulations with sufficient mechanical strength and flexibility, the compatibility of PAQ with known commercial polymers is evaluated through DSC analysis and the data are given in Table I. The observation



Scheme 1 Condensation of mono- and di- amines with benzoquinone.

ELECTROSYNTHESIS OF PAQs :



Scheme 2 Electrochemical synthesis of poly(amino-quinone) using o-phenylenediamine and hydroquinone.

that a single T_g for the polyblend formed confirms their compatibility. This facilitates formulation of suitable surface coatings for mild steel. Incidentally, the electrochemical method enables (a) continuous coating of wires; and (b) coating the rods by dipping in solutions of polyblends of electrochemically synthesized PAQs.

The use of PAQs as corrosion inhibitors, as examined by us, is also an exciting application. PAQs meet the specific requirements such as the ability to form defect free and compact-barrier type film through chemisorptive interactions with the metal surface, thus promoting monolayer/multilayer formation. This has been successfully tested [7, 8] in acids like H_2SO_4 and HCl

TABLE I Characteristics of PAQ and its blends

1. Solubility	Acetone, ether, tetrahydrofuran
2. UV-Vis spectrum	$\lambda_{max} = 340$ nm (characteristic of PAQ)
3. Infrared	1650 cm^{-1}
4. Gel permeation chromatography	$M_n = 1150$
5. Compatibility with other commercial polymers (glass transition temperature ($T_g \pm 0.2^\circ\text{C}$) values are given in parentheses)	PAQ alone (343.0°C) PAQ + POLYOL ^a (1 : 1) (454.3°C) PAQ + PE (1 : 1) (391.2°C) PAQ + ER-6097 (1 : 3) (453.4°C) PAQ + ER-6097 (1 : 1) (443.4°C) PAQ + ER-6084 (1 : 3) (426.3°C) PAQ + ER-6084 (1 : 1) (413.4°C)

PE: Polyethylene (Spectroscopy grade, Merck); ER: Epoxy resin.

ER-6084: ~Epoxy equivalent: 900; Mix ratio with polyamide: 80 : 20; Amine value of polyamide: 280–320 mg KOH/g.

ER-6097: ~Epoxy equivalent: 2000; Mix ratio with polyamide: 90 : 10; Amine value of polyamide: 280–320 mg KOH/g.

^aAcrylic-type.

through studies of self-corrosion, dynamic polarization, electrochemical impedance spectroscopy, hydrogen permeation measurements and supported further by spectroscopic and surface examination. Thus, we find that PAQ serves as an excellent corrosion resistant material to formulate anticorrosive products meeting the following criteria, as observed in our extensive studies:

- hydrophobicity
- high efficiency at lower concentration
- lower hydrogen permeation current values [7]
- good solubility
- effective use at different pH levels
- compatibility with known commercially available polymers and
- easy incorporation as liquids or dispersible solid into desired polymer system.

Vaccaro and Scola [9, 10] have evaluated fluorinated amino-quinone polymers as coupling agents and adhesion promoters for stainless steel/epoxy. They were also found to improve durability of metal/epoxy/metal joints. The improvement is thought to be caused by the formation of a strong bond between the amino-quinone compounds and the metal surface (through adsorption or chelation of the amino-quinones by the metals). The secondary amines present in these compounds react with the epoxy resin, rendering the bond even more stable. More recently, by the use of electrochemical impedance spectroscopy it was demonstrated that a hydroxyethyl amine-quinone containing polyurethane absorbed considerably less moisture than poly(ethyleneterephthalate), poly(ethylene naphthate) or an aromatic polyamine (Aramid) [11]. Modification of the amine or diamine for improved solubility for applications as adhesion promoters or corrosion inhibitors would be a natural extension of the present technology. Modification of the amino-benzoquinone system to amino-hydroquinone system would provide corrosion inhibitors and adhesion promoters with significantly better electron-donor properties for interaction with metal surfaces. The electron donor properties of amino-quinones are due to the presence of π electrons associated with the quinone rings and the unshared electron pairs on the adjacent oxygen and nitrogen atoms. These available electrons are believed to have a strong interaction with metal surfaces [12], such as steel, thereby protecting the metal surface from corrosion, or improving the adhesion between the metal surface and the polymeric adhesives.

Several adducts and polymers have been synthesized using amino-quinones: (a) naturally occurring catecholic protein polymers [13, 14], synthetic aliphatic amino-p-benzoquinone polymers [2, 15, 16], benzoquinone-amine modified polyurethanes [17–19] and heterocyclic benzoquinone polymers [7] form corrosion resistant coatings on steel and iron surfaces. It is likely that in the future, the versatile chemistry of amino-quinones will make it possible to evolve synthetic schemes to form adhesive films of different functions (e.g. conducting, semi-conducting or insulating barriers) by combining the self-assembly approach of Katz [20], Lukkari [21] and the chemistry of

organosilanes, employed by Ooij [22]. In fact, our as-yet unpublished results of the *in-situ* conductivity measurements have shown that the PAQ polymers retain sufficient conductivity ($\sim 10^{-6} \text{ S m}^{-1}$) even on electrochemical reduction in a pH range of 1 to 5.

Our current efforts directed to (i) the implementation of the above schemes; and (ii) the protection of other metal surfaces such as aluminum and zinc are underway. It is imperative that the chemistry of this class of polymers can be tailored to suit different corroding substrates. In our opinion, the PAQ-based blends hold great promise for advanced corrosion protection coating technologies.

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