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Electrochemically Synthesized Polymer of the Plant Substance Embelin (2,5-Dihydroxy-3-Undecyl-1,4-Benzoquinone)

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Abstract

Among the possible new materials for microelectronics, quinones have a number of significant advantages. Similarly, polymers with quinone functionality possess biodegradability. Because natural polymers are promising candidates for functional materials for the future, we have initiated studies on the polymers of natural products. In the present study, a natural quinone (a plant substance) extracted from *Embelier libes* distributed in the Kerala state of India was electrochemically polymerized and its properties were investigated. The redox activity, electrical conductivity, and biodegradability are discussed.

Index Entries: Embelin; polymerization of embelin; biodegradable polymers; quinone polymer; conducting polymer.

Introduction

Biodegradable polymers have received enthusiastic attention in the recent past in view of waste management. The general acceptance for biodegradable polymers will depend not only on the products meeting the specifications but also on acceptance by a widely diverse group of people including environmentalists, legislators, and consumers. In this context, natural polymers are likely to play the major role in the development of biodegradable polymers since they are not perceived to leave toxic or harmful residues in the environment *(1)*. The natural polysaccharides chitin and chitosan have been the subject of extensive research for a number of years *(2)*. Other natural polysaccharides that are of commercial interest are curdlan, dextran, hyaluronic acid, and xanthan gum. Biodegradable thermoplastic materials have been produced by chemically grafting olefinic

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monomers to natural polymers such as starches, proteins, lignin, and cellulose *(3–6)*. In the present study, we report the features of an electrochemically synthesized polymer of a plant substance—embelin. Embelin is 2,5-dihydroxy-3-undecyl-1,4-benzoquinone, a plant substance extracted from *Embelier libes* distributed in the Kerala state of India.

Materials and Methods

Unless otherwise specified, all chemicals used were E Merck guaranteed reagent grade products. Electropolymerization was carried out in a cylindrical undivided cell using stainless steel electrodes and under argon atmosphere. The cell was filled with a suitable electrolyte, and electrolysis was carried out at a constant current density that was increased over a period of 2 to 3 h to a maximum of 3.5 mA/cm^2. After approx 5 h, the polymer formed on the cathode *(7)*. The polymer removed from the electrode was washed with acetonitrile and dried. The yield was 85–90%. This material was insoluble in all common solvents, and although initially black it became light brown on exposure to the atmosphere; no melting point was observed up to 673 K. Doping was effected during the electropolymerization itself by incorporating appropriate metallic cations into the electrolyte. Infrared (IR) spectra were recorded on a Shimadzu IR 408 spectrophotometer using KBr pellets. Diffuse reflectance ultraviolet spectra were recorded on a Varian Cary 13 spectrophotometer using MgO as the standard.

For conductivity measurements, the polymer was compacted into 0.008-m-diameter, 0.001-m-thick pellets in a hydraulic press at a compaction pressure of 250 kg/m^2 using a Carver hydraulic press. Electrical contact was provided to the pellet by means of silver paint/gold deposit, and the conductivity was measured using an assembled Hall Van der Pauw system. Biodegradability tests on the synthesized polymer were carried out at 303 K in a 500-ppm activated sludge *(3)*. The crude activated sludge was obtained from the sewage treatment plant at Chennai Metrowater Supplies and Sewerage Board. Polymer films (initial weight about 2×10^{-5} kg) (1×2) 10^{-2} m^2 wide and 0.006–0.010 m thick were placed in 0.1 L of an aqueous solution of the activated sludge and then incubated at 303 ± 2 K with shaking for several weeks. Samples were removed once a week, washed with water, and dried in vacuum and the weight was measured.

Results and Discussion

Figure 1 shows the IR spectrum of embelin and that of the polymeric embelin. They are distinct from each other, indicating structural variation in the polymer as compared with that of the monomer (i.e., embelin). The IR spectrum of the polymer shows a strong absorption at 1650 cm^{-1} associated with the quinone carbonyl group. Other absorptions include (cm^{-1}) 2926(s), 1749(s), and 1465(s). The absorptions at 2926(s) and 1465 could be attributed to the CH_2 groups, while that at 1749 cm^{-1} is attributable to the carboxyl group, probably of an esoteric functionality. Residual absorptions

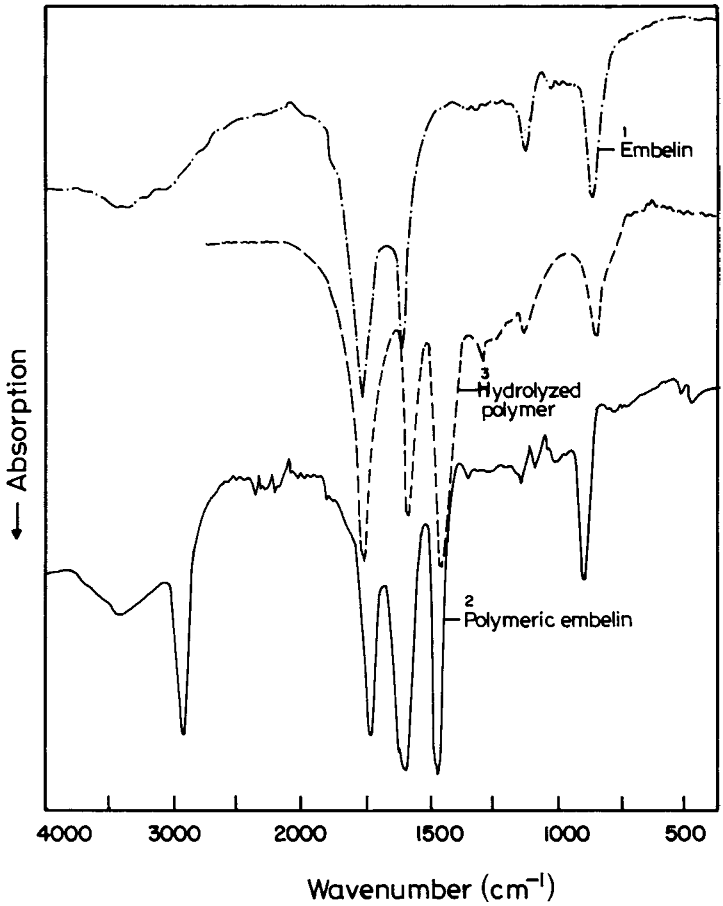


Fig. 1. IR spectrum of (1) embelin (2) polymeric embelin, and (3) hydrolyzed polymeric embelin.

remaining above 2950 cm^{-1} are presumably owing to hydration water left after drying at 373 K. The presence of esoteric linkage was confirmed by the IR spectrum of the polymer after equilibrating it in 50% H_2SO_4 for 4 h; the absorption from the free carboxylic acid group was exhibited (Fig. 1, curve 3) at 1760 and 1440 cm^{-1} *(8)*.

Biodegradability

From the IR spectra it is evident that the synthesized polymeric embelin has two types of components: a quinone component and an alkyl ester component, both of which are essential for biodegradability. The role of quinone functionality as a photosensitizer for biodegradability has been well established *(9–13)*. The hydrolytic enzymatic degradation of esters is also well known *(14–16)*.

We therefore tested the biodegradability of the polymeric embelin in terms of weight loss over a period of weeks. An average weight loss of 60%

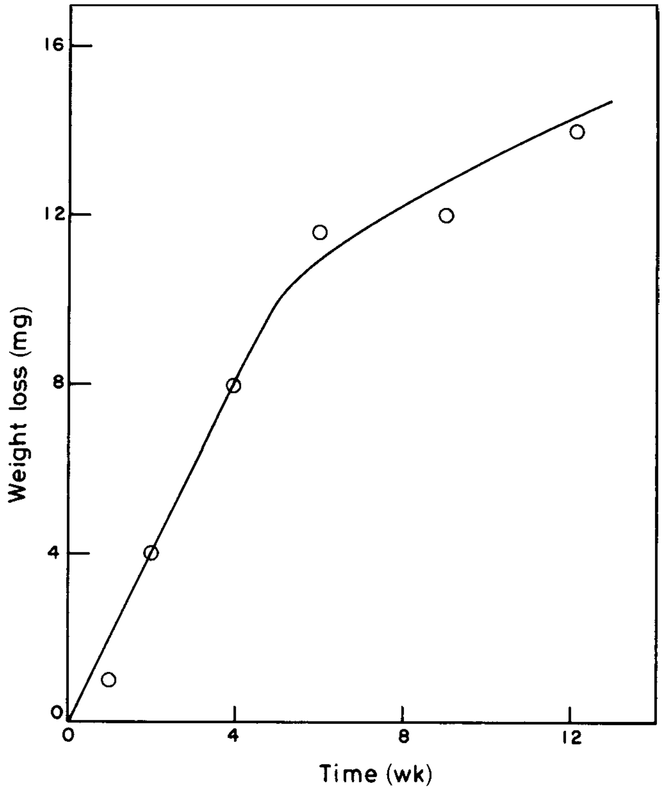


Fig. 2. Weight loss of polymeric embelin in the biodegradability tests over a period of weeks.

was achieved within 8 wk, indicating good biodegradability (Fig. 2). In the absence of activated sludge, degradation of the material was absent.

Redox Activity

The cyclic voltammogram of the polymeric embelin exhibits a reversible couple in the vicinity of 0 V vs saturated calomel electrode (SCE) (Fig. 3). The potential of this redox couple falls within the range of reduction of quinone *(17)*. The cyclic voltammogram in Fig. 3 is in fact a multiple cyclic voltammogram. There is a considerable change in the area covered under the cyclic voltammogram over repeated cycling. This observation indicates that the electrochemical reaction does not occur steadily in the system. Furthermore, there is a drastic difference in the extent of area reduction between the cathodic and anodic segments. Such a difference is of direct relevance to the choice of materials for rechargeable batteries *(18)*.

At more negative potentials, another couple is also observed (Fig. 4); the peaks of this cyclic voltammogram are unequal and also accompanied by a shoulder, revealing that the process is not a simple reversible redox process. Probably the peak could be associated with the reduction in the carboxyl functionality (as revealed by the IR spectrum) in the polymeric

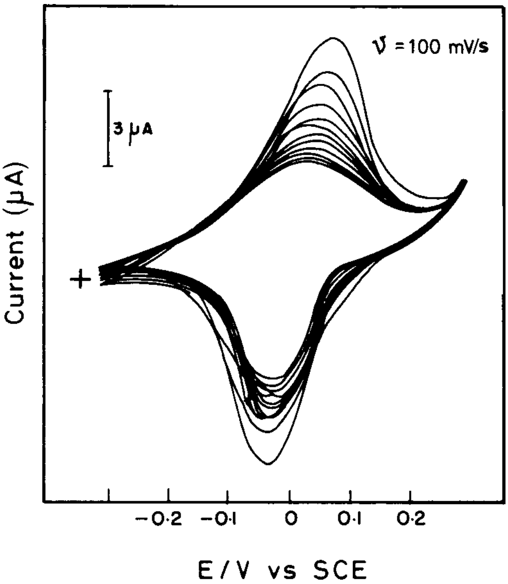


Fig. 3. Multiple cyclic voltammogram of polymeric embelin.

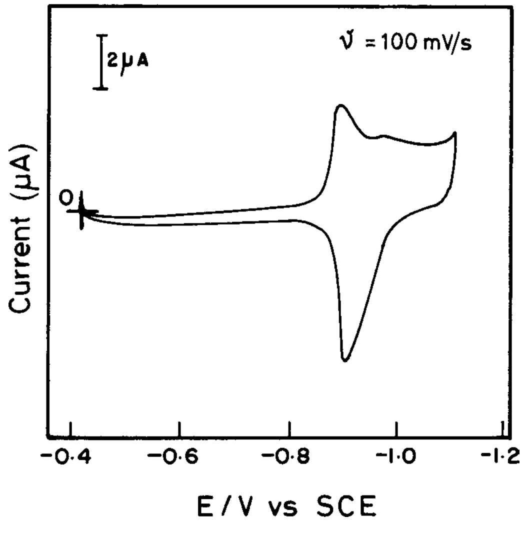


Fig. 4. Cyclic voltammogram of polymeric embelin at more negative potentials.

embelin. The redox activity is generally coupled to proton activity near the electrode surface. Such a proton coupling is well known to occur in $2H^+$/2e redox couples *(19,20)* of hydroquinones *(21,22)*, polyanilines *(23–25)*, and mercaptan systems *(26,27)*. Polymerization as well as depolymerization are determined by the proton coupling *(28)*. Therefore, the cyclic voltammogram in Fig. 4 at more negative potentials could be reminiscent of a reductive depolymerization mode of the polymeric embelin. However,

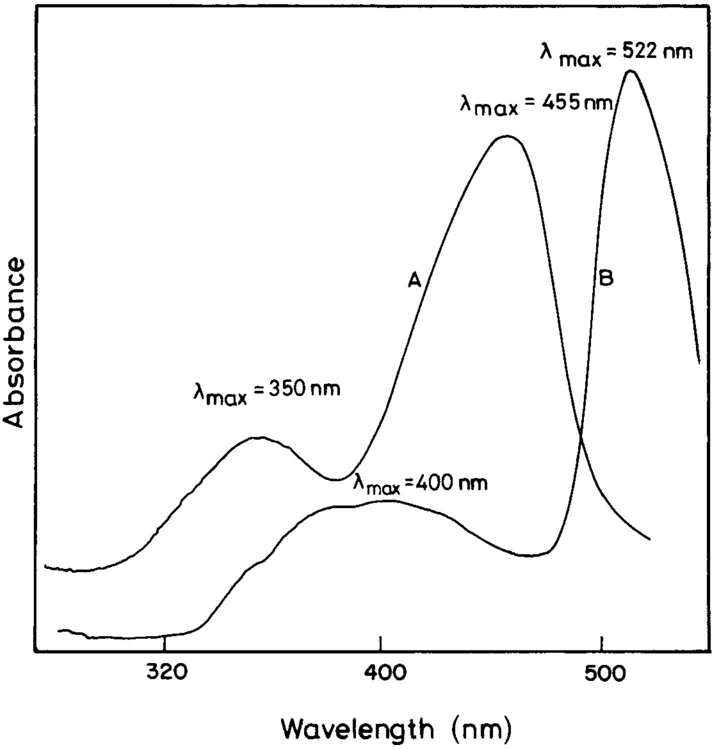
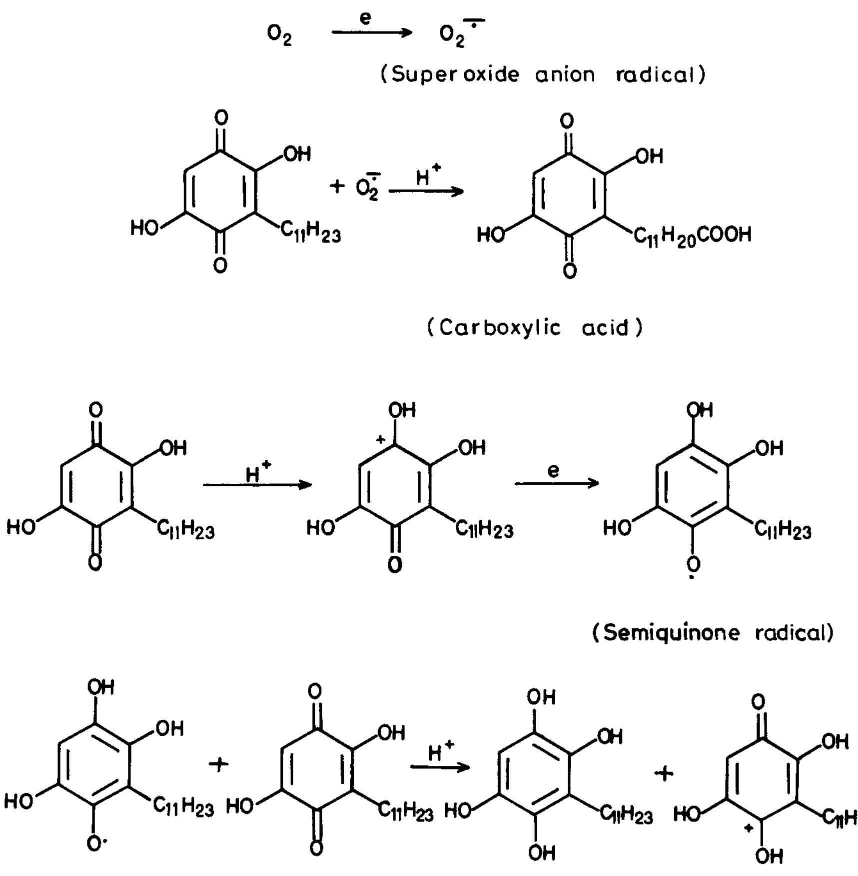


Fig. 5. Diffuse reflectance spectrum of (A) undoped polymer and (B) tin-doped polymer.

a complete interpretation of the cyclic voltammogram deserves detailed investigation.

Electrical Conductivity

The electrical conductivity of the polymeric embelin was found to be $4.3 \times 10^{-6}\ \Omega^{-1}/\mathrm{cm}$, a value indicative of good electrical conductivity. Doping of the polymer with Li^+ by established procedures *(28)* enhanced the conductivity to $3.7 \times 10^{-4}\ \Omega^{-1}/\mathrm{cm}$. Electrical conductivity is a measure of the ease of flow of electricity through the polymer. Although the scheme proposed for the formation of polymer indicates a nonconjugated extensivity in the polymer structure, the magnitude of the electrical conductivity ($4.3 \times 10^{-6}\ \Omega^{-1}/\mathrm{cm}$) indicates the possibility of a different polymerization mode. A further possibility of enhanced electrical conductivity could emanate from structural factors in the same nonconjugated mode. The number of monomer units in a given polymer, the nature and strength of crosslinkages, spatial distribution including intralamellar distance, aggregation number, and activation barrier are some of the parameters that determine the electrical conductivity of a polymer. That the electrical conductivity of polymeric embelin is of high order stresses the need for a detailed study on its electrical conductivity.

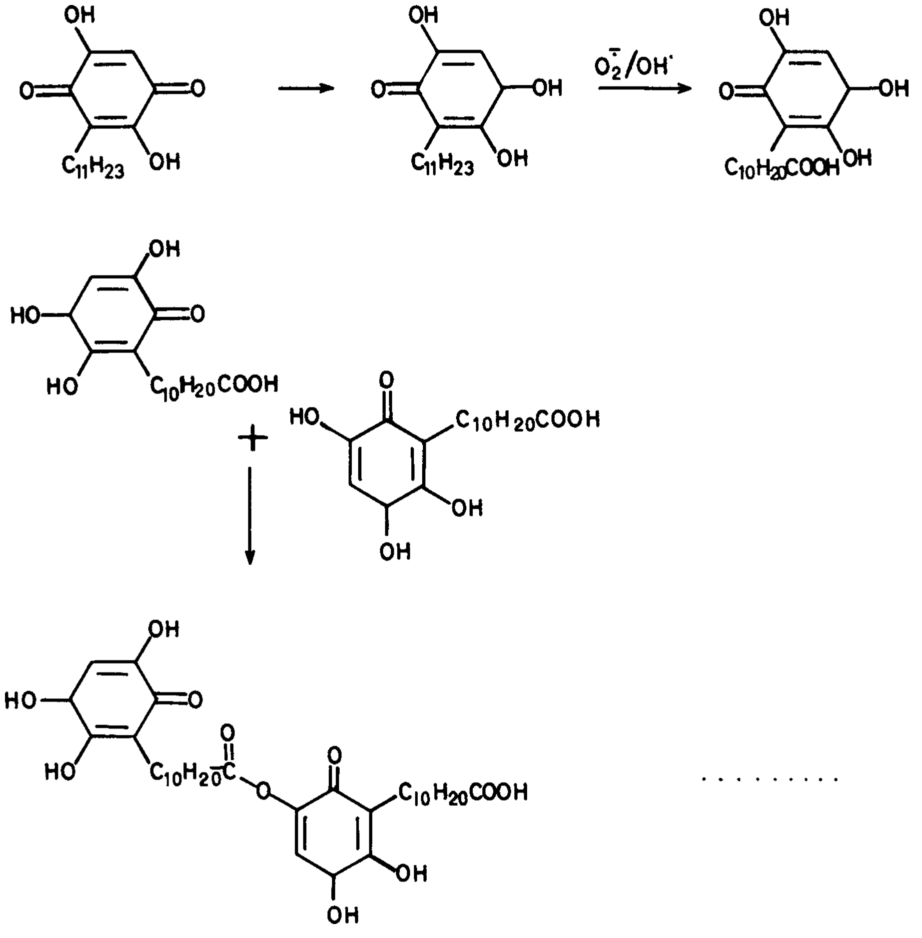


Scheme I. Electroreduction of oxygen to superoxide anion radical and reduction of embelin to the semiquinone and oxidation of the alkyl side chain to the terminal carboxylic acid.

The diffuse reflection spectra of the undoped polymer (Fig. 5, curve A) shows intense absorption supporting extended electron clouds (i.e., delocalization in the molecule of polymeric embelin). Intense absorption as exhibited by the polymer is presented in Fig. 5. Whereas it does not exclusively represent electron delocalization along the polymer chain, it does indicate extensive distribution of electron density. Doping studies have been conducted, and we have found significant shifting to shorter frequencies depending on the kind and extent of doping. The results are being published elsewhere. A representative spectrum of a tin-doped polymer is presented in Fig. 5, curve B.

Mechanism of Electropolymerization

On the basis of the aforesaid features, the following mechanism could be proposed tentatively for the electropolymerization process (Schemes I–III). The reduction in oxygen at the cathode *(29)* generates the superoxide

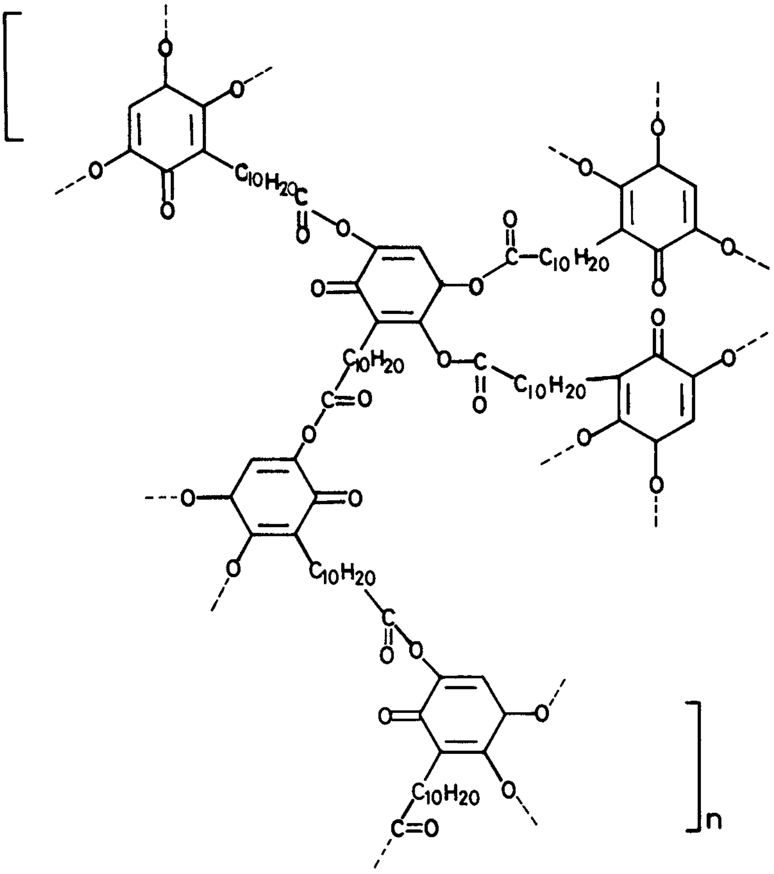


Scheme II. Linear polymerization mode of embelin.

anion radical $O_2^{\cdot -}$, which is the oxidant effecting carboxylation at the alkyl side chain of embelin. Semiquinone formed by electroreduction of embelin (Scheme I) can undergo condensation with the carboxylic acid derivative to form the polymer as in Schemes II and III.

Conclusion

A plant substance, embelin, was electrochemically polymerized and some of its basic properties were studied. The results obtained in this preliminary investigation indicate that the material would be found extremely useful in the development of functional polymers for electronics, batteries, as well as packaging. We are continuing further studies on the polymeric embelin.



Scheme III. Cross-linking polymerization mode of embelin.

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