

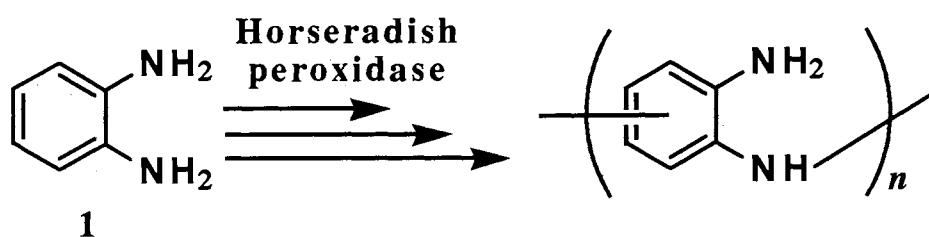
Enzymatic Oxidation Polymerization of *o*-Phenylenediamine

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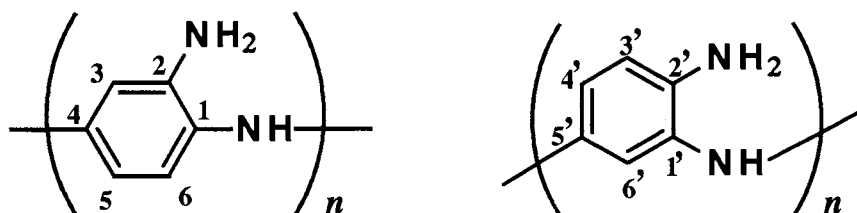
Enzymatic oxidation polymerization of *o*-phenylenediamine using horseradish peroxidase as a catalyst was carried out in an aqueous organic solvent. Polymeric materials with average molecular weight of 20 000 were obtained. The structure of the polymer was found to be composed mainly from imino-2-aminophenylene unit from  $^{13}\text{C}$  NMR analysis.

Polymerization normally requires a catalyst, an initiator, or irradiation to induce the reaction. In most cases, are used radical initiators, UV irradiation, cationic or anionic initiators, and various transition metal catalysts such as Ziegler-Natta catalysts or olefin metathesis catalysts. Until recently, however, polymerization from the standpoint of enzymatic catalysis had not been achieved. Very recently, we have succeeded in the first synthesis of cellulose by *enzymatic polymerization* of  $\beta$ -D-cellobiosyl fluoride utilizing cellulase as catalyst via a non-biosynthetic path.<sup>1)</sup> In this study, we extended the scope of the *enzymatic polymerization* to an oxidation polymerization of *o*-phenylenediamine (**1**) using a horseradish peroxidase catalyst. In relevant to the present study, polymerizations of aniline<sup>2)</sup> and 4-phenylphenol<sup>3,4)</sup> using an enzyme catalyst have been reported.



Oxidation polymerization of **1** was carried out in a mixture of 1,4-dioxane and phosphate buffer (pH 7.0) at room temperature.<sup>5)</sup> Horseradish peroxidase (Wako Pure Chemical Ind., LTD.) and hydrogen peroxide were used as catalyst and a source of an oxidizing agent, respectively. The polymerization of **1** in hydrogen peroxide without the enzyme gave oligomeric products (Yield = 67%, Mw = 800). In the GPC chart of the products obtained by the polymerization using the enzyme, on the other hand, a new another peak appeared at the lower elution time, indicating the formation of polymers with higher molecular weight (Mw = 20 000).

The polymeric portion was separated from the reaction mixture by using HPLC. From  $^{13}\text{C}$  NMR analysis of the polymer, the structure of the polymer was found to be constructed mainly from imino-2-aminophenylene unit:  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ )  $\delta$  102(C3 and C6'), 126-128(C5, C6, C3', and C4'), 143-145(C1, C2, C1', and C2'). In the polymerization of **1** by a Fe-chelate complex<sup>6)</sup> or by electrolysis,<sup>7)</sup> the resulting polymer showed mainly a ladder structure with phenazine rings and contained an insoluble portion. It is to be noted, however, that the present polymer is of a linear structure and soluble in a highly polar solvent such as DMF and DMSO. The product polymer is a poly(aniline) derivative, and hence, may find applications as electrically conductive polymers.



Further investigations on the mechanism of the present polymerization are now in progress.

#### References

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- 5) The polymerization was carried out as follows. Under air, 1.08 g (10 mmol) of **1** and 10 mg of horseradish peroxidase were dissolved into 80 mL of 1,4-dioxane and 20 mL of phosphate buffer (pH 7.0). The polymerization started by the addition of 230  $\mu\text{L}$  (2 mmol) of hydrogen peroxide (30%) at room temperature. The same amount of hydrogen peroxide as further added 4 times at one hour interval. After 24 h, the solvents were evaporated under reduced pressure. The remaining black powder was collected and washed with water. Polymeric materials were separated by using HPLC (eluent, acetone; flow rate, 6.0 mL/min; column, Inertsil PREP-ODS (GL-Science Inc.)) (Yield 33%).
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