



Co-polymerization of MTPC (methylene tri *p*-cresol) and *m*-cresol using CiP (*Coprinus cinereus* peroxidase) to improve the dissolution characteristics of the enzyme-catalyzed polymer

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ABSTRACT

MTPC (Methylene tri *p*-cresol) and *m*-cresol were copolymerized by *Coprinus cinereus* peroxidase in aqueous acetone. Although MTPC did not dissolve completely in the aqueous acetone, copolymerization was achieved owing to the radical transfer between solute and solid surface. Various polymerized products with different molecular weights and hydroxyl values were synthesized depending upon reaction compositions (ratio of MTPC to *m*-cresol and buffer to acetone). Poly(MTPC-*m*-cresol), a copolymer of MTPC and *m*-cresol, was mixed with a diazonaphthoquinone derivative to form a new type of photoresist, a thin film of which was formed on a silicon wafer and immersed in alkaline solution (tetramethylammonium hydroxide) to measure speed of dissolution. Poly(MTPC-*m*-cresol), with higher hydroxyl value (over 80%), showed remarkably improved dissolution characteristics (dark loss in alkaline solution decreased by almost half), which is prerequisite for sensitive photoresist polymer.

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1. Introduction

Photoresists are essential chemicals in semiconductor processing, LCD (liquid crystal display) processing, and many printing processes, with a rate of consumption that has steadily increased over the years [1]. Various polymers are currently being investigated as new photoresists because of the demand for high resolution and imagery, however, most conventional photoresists are still mainly composed of novolac resin and DNQ (diazonaphthoquinone) photoactive compounds. Most conventional novolac resins are synthesized by polymerizing various phenolics (*o*-cresols) with formaldehyde to produce resins with excellent film-forming properties, good adhesion, etch resistance, and high solubility in alkaline solution. However, the toxic properties of the formaldehyde used have led to considerable research efforts to find alternative routes to their synthesis.

Enzymatic polymerization of phenolics using peroxidase has been intensively studied [2,3,4] with several advantages over conventional polymerization having already been reported. Recently,

we reported a successful enzymatic polymerization using the fungal peroxidase, CiP (*Coprinus cinereus* peroxidase), for the synthesis of polycardanol and poly(bisphenol A) [5,6]. Although the poly(bisphenol A) showed good resolution as a photoresist, its dissolution characteristics were not satisfactory because the poly(bisphenol A) had a lower hydroxyl value compared with that of conventional novolac resins. The ratio of the phenylene bond, not the oxyphenylene bond, must be increased to elevate the hydroxyl value of resulting polymer. Template polymerization using PEG can yield a polymer with a much higher hydroxyl value [7,8], however, separation of the pure polymer from the template-polymer complex is extremely difficult, thus polyphenol was not feasible as a photoresist polymer. In this paper copolymerization between MTPC (methylene tri *p*-cresol) and *m*-cresol was tried to increase the number of hydroxyl group per chain. Significant increase of OH-number per chain was achieved although there was a limit to elevate the hydroxyl value. The resulting copolymer (MTPC/*m*-cresol) showed much improved dissolution characteristics.

2. Experimental

2.1. Production and purification of the fungal peroxidase

C. cinereus IFO 8371 was used as the peroxidase-producing strain. The medium for the production of the peroxidase contained

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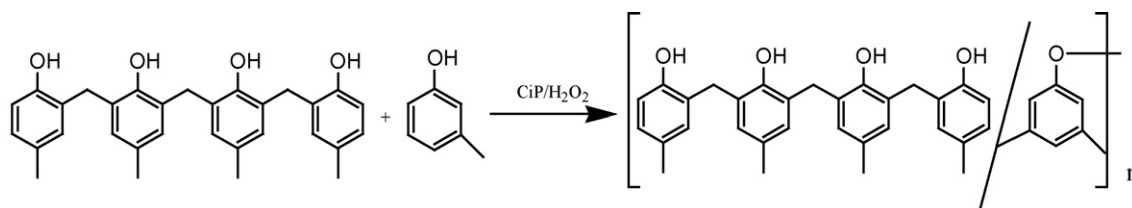


Fig. 1. Scheme of copolymerization of MTPC and *m*-cresol using CiP.

30 g/L glucose, 5 g/L peptone (Difco Lab., USA), and 3 g/L yeast extracts (Difco Lab., USA). The details of the production and purification of the fungal peroxidase have been previously reported [5]. Finally, the purified CiP was concentrated to a final concentration of 20,000 U/mL for the polymerization of bisphenol A.

2.2. Enzymatic copolymerization of MTPC and *m*-cresol

The reaction scheme for the copolymerization of MTPC (Waco Chemicals, Germany, CAS No 20837-68-7) and *m*-cresol (Aldrich, USA) is shown in Fig. 1. All the chemicals including MTPC and *m*-cresol were used as received without further purification. The typical enzymatic copolymerization of MTPC and *m*-cresol was carried out as follows: 3.24 g of MTPC and 2.16 g of *m*-cresol (20 mmol) were suspended in a mixture of 100 g acetone and 150 g phosphate buffer (100 mM, pH 7.0). 100,000 units of CiP were then added to the reaction mixture and stirred for 5 min. The reaction was initiated by adding 15% H₂O₂ solution (20 mmol) continuously at a rate of 4.0 mmol/h at 20 °C with gentle stirring for 5 h. After that, the reaction mixture was centrifuged at 5000 rpm and the supernatant decanted. The settled materials (white powdery) were washed three times with aqueous methanol (50:50, v/v) to remove any unreacted monomer and buffer. The washed material was dried *in vacuo* to give poly(MTPC–*m*-cresol).

2.3. Evaluation of peroxidase-catalyzed poly(MTPC–*m*-cresol) as a photoresist resin

The photoresist thin film was prepared on a silicon wafer by spin-coating from a 27 wt.% PGMEA (propylene glycol monomethyl ether) solution of the poly(MTPC–*m*-cresol) and a photosensitizer (PS-105, Koyo Chemicals, Japan) (80:20 wt.%). The resulting film was immersed in 2.38% TMAH (tetramethylammonium hydroxide) solution for 60 s. The differences in thickness before and after immersion were measured by employing Nanospec (NSR-19c MCS2, Nikon, Japan). The dissolution rate of the coating film (dark loss) was calculated from the differences in thickness.

2.4. Analytical methods

Peroxidase activity (U/mL) was measured as follows. Several microliters of the reaction solution were added to 2 mL of a 0.18 mM solution of ABTS (2,2'-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid)) in 50 mM phosphate-citrate buffer (pH 5.0). One microliter of a 15% H₂O₂ solution was added to initiate the color generation reaction. One unit of peroxidase was defined as the amount of enzyme required to catalyze the conversion of 1 μmol of ABTS ($\epsilon = 34,700 \text{ cm}^{-1} \text{ M}^{-1}$) per min at 25 °C. The molecular weights of the poly(MTPC–*m*-cresol) were determined by GPC (gel permeation chromatography). GPC analysis was carried out using a refractive index detector under the following conditions: PL4 mixed BB columns (TOSOH, Japan) and tetrahydrofuran as a solvent at 1.0 mL/min. The calibration curves for the GPC analysis were obtained using polystyrene standards. The hydroxyl

value was measured by titration methods using acetic anhydride [9].

3. Results and discussion

3.1. Peroxidase-catalyzed copolymerization of poly(MTPC–*m*-cresol)

In this study, peroxidase derived from *C. cinereus* and hydrogen peroxide were used as a catalyst and oxidizing agent, respectively. Polymerization of MTPC was not successful in any aqueous organic solvent mixture including methanol, ethanol, 2-propanol, acetone, and DMSO. Any significant increase of molecular weight in the MTPC reaction was not observed, implying that CiP was not able to generate a radical on the MTPC given its steric bulk interfering with its approach towards the reactive site of the peroxidase. Copolymerization of MTPC with *m*-cresol was attempted in an effort to obtain the polymeric product of MTPC since *m*-cresol is known to be polymerized easily through peroxidase-catalysis [10]. As shown in Table 1, the effects of the aqueous organic solvent mixture on the CiP-catalyzed copolymerization of MTPC–*m*-cresol were studied. In the hydrophilic aqueous solvent mixture (low log *P*, DMSO), the copolymerization did not take place at all. On the other hand, CiP yielded the polymerized product having a higher molecular weight in the relatively hydrophobic aqueous solvent mixture (high log *P*), as compared to that produced in the other solvents. Surprisingly, while MTPC was only suspended in aqueous acetone or aqueous 2-propanol, copolymerization of MTPC–*m*-cresol was accomplished successfully to yield polymeric product. This implies that the radical transfer between *m*-cresol radical and suspended but still particulate MTPC still takes place rapidly. Considering *m*-cresol was polymerized in aqueous DMSO mixture, radical transfer between MTPC and *m*-cresol was not thought sufficiently performed in aqueous DMSO mixture. Since radical transfer is known to depend on the radical lifetime, radical lifetime may be shorter in aqueous DMSO mixture rather than aqueous acetone or aqueous 2-propanol [11]. Fig. 2 shows the relationship between the log *P* of the organic solvent and the molecular weight of the poly(MTPC–*m*-cresol) whose polymerization was catalyzed by CiP in a mixture of organic solvent and phosphate buffer. An organic solvent that is too hydrophilic can penetrate and replace the water bound on the protein, possibly disturbing the authentic three dimensional protein structure [12]. A

Table 1

Effects of solvent on the peroxidase-catalyzed copolymerization of MTPC and *m*-cresol

Solvent	Yield (%)	Mn	Mw	Log <i>P</i>
DMSO	0	–	–	–0.69
Methanol	92.9	1536	2,633	–0.32
Ethanol	95.0	1902	3,794	0.056
Acetone	92.8	1866	7,530	0.23
2-Propanol	98.2	2446	10,293	0.42

MTPC (2.16 g) and *m*-cresol (3.24 g) were copolymerized by CiP in various aqueous organic solvents (buffer:solvent = 60:40, w/w).

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