Selective photooxidation of chlorophenols with molecularly imprinted polymers containing a photosensitizer

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Molecularly imprinted polymers containing a photosensitizer, rose bengal (RB), were synthesized *via* a polymerization of methacrylic acid (MAA) as a functional monomer and chlorophenols as template molecules. The polymeric sensitizers promote selective oxidation of target chlorophenol in water with molecular oxygen under visible light irradiation ($\lambda > 530$ nm). This is due to the selective attraction of the target substrate onto the molecular recognition site on the polymer followed by efficient oxidation of the substrate by a singlet oxygen produced by the photoexcited RB units located in the vicinity of the recognition site.

1. Introduction

The design and development of polymers and polymeric materials containing a photosensitizing unit have attracted much attention in photochemical organic transformation,[1] because the polymer microenvironment provides various functions,[2] such as accumulation of substrates,[3] stabilization of photoexcited sensitizers and activated molecular oxygen (O_2),[4] and efficient energy transfer to substrates.[5]

Molecularly imprinted polymers (MIP) that exhibit high selectivity and affinity to the predetermined substrate are a rapidly growing research focus.[6] The special binding sites are produced by the self-assembly of a template molecule and monomers with specific functional groups, followed by cross-linking copolymerization. After polymerization, the template molecule is removed from the polymer, leaving the microcavities and recognition sites that, in terms of size and shape functionality, are complementary to that of the templates. The MIP methods possess several advantages including low-cost, simple and convenient preparation, storage stability, and durability to heat and pressure.[7] MIP materials have therefore been applied in various areas, such as separations,[8] catalysis,[9] sensors,[10] drug delivery systems,[11] and artificial antibodies.[12] There are, however, only two reports of MIP applied in photoreactions;[13] semiconductor TiO_2 particles coated with MIP promoted selective photocatalytic decomposition of target substrates.

Herein, we report an another example of MIP applied in a photoreaction. We synthesized a MIP containing an organic photosensitizer and used it for selective photosensitized oxidation of chlorophenols in water with O_2. Rose bengal (RB) was employed as a sensitizer, which produces a singlet oxygen ($^1O_2$) by an energy transfer from the photoexcited RB to O_2.[14] The RB-containing MIP was synthesized with methacrylic acid (MAA) as a functional monomer, ethylene glycol dimethacrylate (EGDMA) as a crosslinker,[15] and chlorophenol (2-chlorophenol (2CP), 3-chlorophenol (3CP), or 4-chlorophenol (4CP)) as a template substrate. We found that the respective RB-containing MIP synthesized with each template substrate, IP-*x* (*x* = 2CP, 3CP, or 4CP), selectively oxidizes the target substrate, while the polymer prepared without a template (NIP) shows no selectivity. We describe that the substrate-selective oxidation by IP-*x* is due to the selective attraction of the target substrate onto the molecular recognition site located in the vicinity of the RB units.

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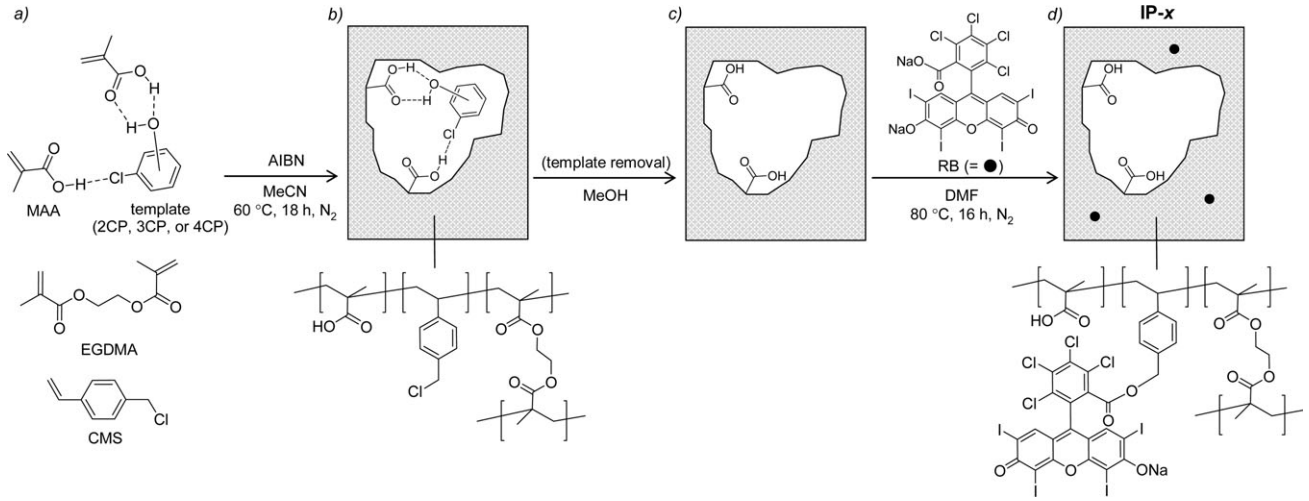
2. Experimental section

2.1 General

All of the reagents used were of the highest commercial quality, which were supplied from Wako, Aldrich, and Tokyo Kasei and used without further purification. Water was purified by the MilliQ system. IP-*x* and NIP were synthesized according to the procedure summarized in Scheme 1 and as follows.

2.2 Synthesis of polymers

IP-*x* were synthesized as follows: each template substrate (2CP, 3CP, or 4CP; 0.043 g, 0.33 mmol) and MAA (0.230 g, 2.70 mmol) were dissolved in MeCN (3 ml) and stirred at room temperature for 30 min. 4-Chloromethylstyrene (CMS; 0.025 g, 0.17 mmol), EGDMA (1.290 g, 6.5 mmol), and AIBN (0.033 g, 0.20 mmol) were added to the solution and degassed twice by freeze–pump–thaw cycles. The solution was kept at 60 °C for 18 h under dry nitrogen. The solid formed was recovered by filtration and washed thoroughly with MeOH to remove the template. The obtained solid (0.2 g) and RB (0.027 g, 0.027 mmol) were added to DMF (3 ml) and stirred at 80 °C for 16 h under dry nitrogen. The resulting solid was recovered by filtration and washed thoroughly with MeOH to remove free RB, affording IP-*x* as pink solids. NIP was synthesized in a similar manner to that of IP-*x* without the template substrate. The amount of RB units on the respective polymers were determined by absorption spectra of the unreacted RB during the synthesis; 1.8×10^{-5} mol g^{-1} (IP-2CP),



Scheme 1 Synthesis of RB-containing molecularly imprinted polymer, IP-*x* (*x* = 2CP, 3CP, or 4CP).

1.0×10^{-5} mol g^{-1} (IP-3CP), 1.45×10^{-5} mol g^{-1} (IP-4CP), and 1.19×10^{-5} mol g^{-1} (NIP), respectively.

2.3 Photoreaction

Each polymeric sensitizer was added to a buffered aqueous solution (5 ml; pH 10; consisting of 0.025 M $NaHCO_3$ and 0.011 M NaOH) containing substrates within a Pyrex glass tube (capacity: 20 ml). Each tube was sealed using a rubber septum cap, and O_2 was bubbled through the solution for 5 min. The tube was photoirradiated with magnetic stirring by a high-pressure Hg lamp (100 W; Eikohsha Co. Ltd., Osaka, Japan),[16] filtered through a Corning color filter (CS3-67) to give light wavelengths of $\lambda > 530$ nm. The light intensity at 530–630 nm (through the filter) is 317 mW m^{-2}, and the temperature of the solution during photoirradiation is 298 K. Substrate concentrations were determined by GC-FID (Shimadzu GC-14B).

2.4 Analysis

Diffuse reflectance UV-vis spectra were measured on a UV-vis spectrophotometer (Jasco Corp.; V-550 with Integrated Sphere Apparatus ISV-469) using $BaSO_4$ as reference. Absorption spectra were measured on a UV-visible photodiode-array spectrophotometer (Shimadzu; Multispec-1500) at 298 K. IR spectra were measured on an FT-IR-610 infrared spectrophotometer (Jasco Corp.) using a KBr disk.

3. Results and discussion

The RB-containing polymers, IP-*x*, were synthesized with target chlorophenols as the template substrates, according to the procedure summarized in Scheme 1. A functional monomer, MAA, was polymerized in the presence of template chlorophenol (2CP, 3CP, or 4CP), CMS, and a crosslinker, EGDMA. Removal of templates from the resulting polymer followed by an introduction of RB units to the polymer gives rise to IP-*x*, as pink solids. Fig. 1 shows diffuse reflectance UV-vis spectra of IP-*x*. All of these polymers demonstrate a distinctive absorption at 500–600 nm, assigned to the RB units.[17]

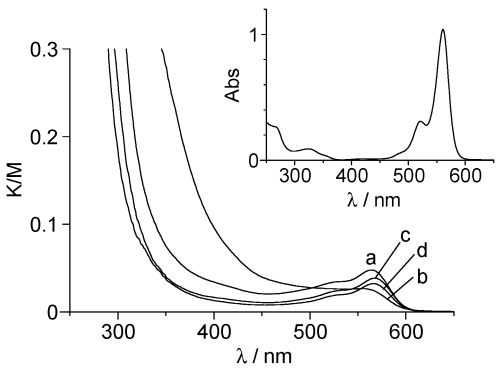


Fig. 1 Diffuse reflectance UV-vis spectra of (a) IP-2CP, (b) IP-3CP, (c) IP-4CP, and (d) NIP. (Inset) absorption spectrum of RB (9.4 μM) in MeOH at 298 K.

Fig. 2a and b show IR spectra of IP-2CP and NIP, respectively. Both spectra show three distinctive absorptions assigned to –COOH groups of the MAA units; C=O stretching vibration at *ca.* 1700 cm^{-1}, O–C–O absorption at *ca.* 1200 cm^{-1}, and –OH stretching vibration at *ca.* 2900 cm^{-1}.[18] As shown in Fig. 2b, NIP synthesized without a template molecule shows two additional absorptions at 3554 and 3289 cm^{-1}, which are assigned to the monomeric and dimeric –COOH groups of the MAA units, respectively.[18] In contrast, as shown in Fig. 2a, IP-2CP shows no dimeric –COOH absorption at 3100–3300 cm^{-1}. During the polymerization, the –COOH groups of MAA units associate with –Cl and –OH groups of the template chlorophenols *via* a hydrogen bonding interaction (Scheme 1a and b). This suppresses the dimerization of –COOH groups. The hydrogen bonding interaction between –COOH groups and template chlorophenols is confirmed by absorption spectra. As shown in Fig. 3c, MAA monomer measured with 2CP shows a red-shifted absorption at >230 nm as compared to the sum of the spectra for MAA and 2CP (d).[19] This clearly supports the hydrogen bonding interaction between MAA and template chlorophenols (Scheme 1a and b).

The photosensitization activity of IP-*x* was estimated with $^1O_2$ oxidation of phenol and chlorophenols (2CP, 3CP, and 4CP).

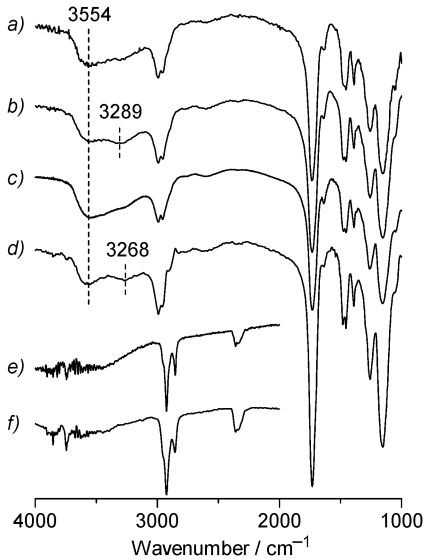


Fig. 2 IR spectra (KBr) of (a) IP-2CP, (b) NIP, (c) IP-2CP measured with phenol, (d) IP-2CP measured with 2CP, (e) phenol, and (f) 2CP. The spectra (c) and (d) were measured according to the following procedure: phenol or 2CP (2 mg) was added to MeCN (10 ml) containing IP-2CP (1 mg) and stirred at 298 K for 1 h. The solvent was removed by evaporation. The resultant and KBr (0.1 g) were ground and used for preparation of KBr films.

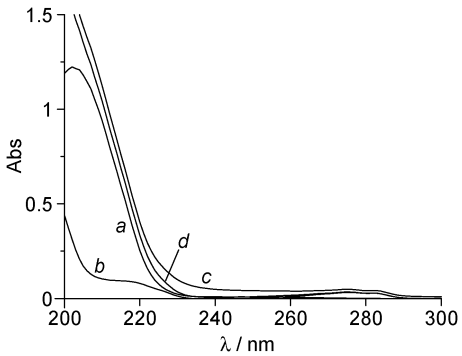


Fig. 3 Absorption spectra of (a) MAA (8.0×10^{-5} M), (b) 2CP (8.0×10^{-5} M), and (c) the mixture of MAA (8.0×10^{-5} M) and 2CP (8.0×10^{-5} M). (d) The sum of the spectra of (a) and (b).

The respective IP-*x* (1 mg; containing *ca.* 0.01 μmol RB units) was added to a buffered aqueous solution of pH 10 containing these substrates (each 10 μmol), and the solution was photoirradiated at $\lambda > 530$ nm in the presence of O_2. Fig. 4 (black bar) shows the conversions of substrates obtained with respective sensitizers. With unpolymerized RB as a sensitizer (a), conversions of phenol, 2CP, 3CP, and 4CP are similar (*ca.* 35%). With IP-*x* and NIP (Fig. 4b–e), conversions of all substrates are lower than that obtained with RB. This is because energy transfer from the excited state RB units to O_2 ($^1O_2$ formation) and oxidation of substrates by $^1O_2$ occur heterogeneously. However, IP-*x* shows specifically high conversion for the corresponding chlorophenols that were used as templates for polymer synthesis; for example, IP-2CP shows *ca.* 10% conversion of 2CP, while showing lower conversions of other substrates (<5%). The results clearly indicate that the respective IP-*x* promotes selective oxidation of target chlorophenol.

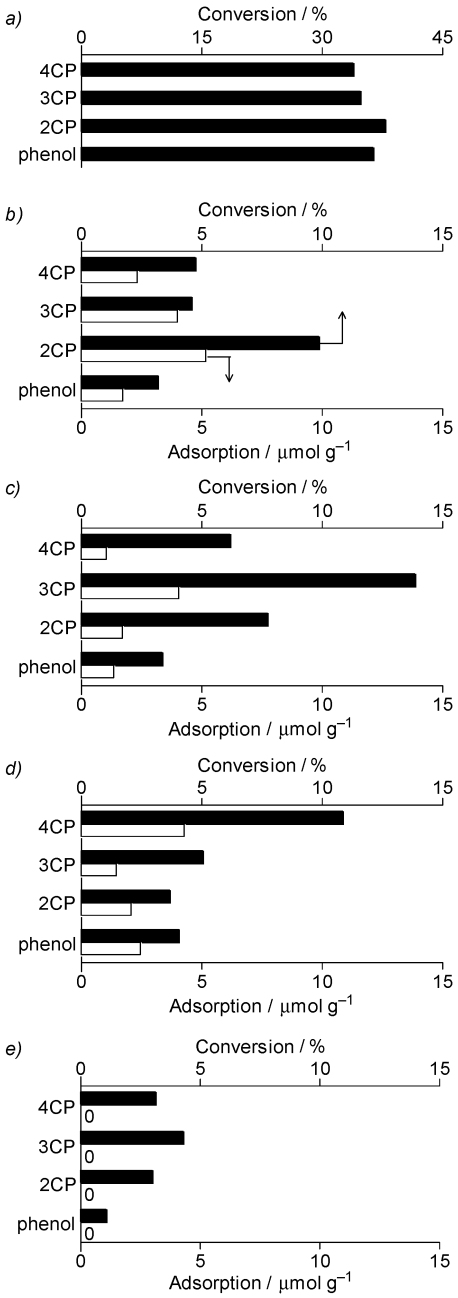
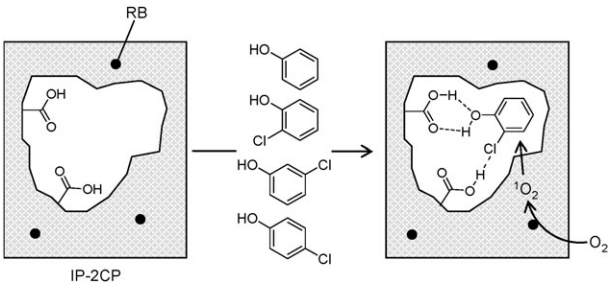


Fig. 4 (Black bar) Conversion of substrates during photoirradiation ($\lambda > 530$ nm) with respective sensitizers, (a) RB (0.01 μmol), (b) IP-2CP, (c) IP-3CP, (d) IP-4CP, and (e) NIP, where the photoirradiation time is 30 min for (a) and 3 h for (b)–(e). The reaction conditions: IP-*x* or NIP (1 mg containing 0.01 μmol RB units), substrates (each 10 μmol), buffered aqueous solution (pH 10, 5 ml), 298 K. (White bar) amount of substrates adsorbed onto the polymers during stirring the solution for 3 h at 298 K without photoirradiation.

The selective photooxidation of target chlorophenol by IP-*x* is due to the selective attraction of the substrate to the molecular recognition site on the polymer. This is confirmed by adsorption experiments. Fig. 4b–e (white bar) shows the amount of substrates adsorbed onto IP-*x* while stirring the solution at 298 K for 3 h without photoirradiation. The results reveal that the respective IP-*x* adsorbs the corresponding



Scheme 2 Schematic representation of the mechanism for selective $^1O_2$ oxidation of chlorophenols on IP-*x* (the above is the case for IP-2CP).

chlorophenol selectively. The selective interaction between the template chlorophenol and the recognition site on IP-*x* is confirmed by IR analysis. As shown in Fig. 2c, IP-2CP measured with phenol shows a spectrum similar to that of IP-2CP itself (Fig. 2a). However, as shown in Fig. 2d, IP-2CP measured with 2CP shows a new absorption at 3268 cm^{-1}, which is assigned to a hydrogen bonding between –COOH groups of the MAA units and –Cl and –OH groups of 2CP.[20] The results clearly indicate that the recognition sites on IP-*x* selectively attract the target substrate.

The mechanism for selective $^1O_2$ oxidation of target chlorophenol on IP-*x* can be explained as Scheme 2. The molecular recognition sites generated within IP-*x* attract the target chlorophenol selectively *via* a hydrogen bonding interaction. $^1O_2$ is produced by an energy transfer from the photoexcited RB units to O_2 and oxidizes the substrates during the diffusion within its lifetime. However, as reported,[21] the diffusion of $^1O_2$ is significantly suppressed within polymer matrices. The target substrate attracted to the recognition site on IP-*x* is therefore oxidized efficiently by $^1O_2$, which is produced by the RB units located in the vicinity of the recognition site. This results in selective $^1O_2$ oxidation of the target chlorophenol on IP-*x*.

4. Conclusions

Molecularly imprinted polymers containing rose bengal (IP-*x*) were synthesized and used as photosensitizers for $^1O_2$ oxidation of chlorophenols in water. These polymers promote selective oxidation of targeted chlorophenol that was used as a template for polymer synthesis. Adsorption experiments and IR analysis reveal that selective interaction between target substrate and the recognition site promotes selective $^1O_2$ oxidation.

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