Synthesis, characterization and application of a novel polymer solid photosensitizer

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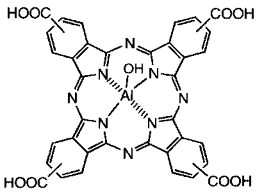
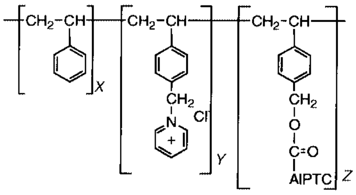
A new water-insoluble polymer solid photosensitizer, prepared from an aluminium(III) tetracaboxyphthalocyanine and poly(styrene-*co*-chloromethylstyrene), has a photosensitizing ability for the photo-oxidation of phenol with singlet oxygen.

The photo-oxidation reactions of sulfides,[1,2] thiols,[3,4] phenols[5–7] and other organic compounds[8–11] have been reported using various low molecular weight photosensitizers such as Rose Bengal, Methylene Blue, porphyrins and phthalocyanines. Although these photosensitizers show high reaction activity, they are difficult to remove from the reaction cell because they are homogeneous. The use of polymer solid photosensitizers is expected to overcome this problem. Compared with low molecular weight photosensitizers, however, there are few reports on the application of polymer solid photosensitizers to photo-oxidation reactions.[12–14] Here, we describe the synthesis and characterization of a new water-insoluble polymer solid photosensitizer prepared from an aluminium(III) tetracaboxyphthalocyanine and poly[(styrene)-*co*-(4-chloromethylstyrene)] (polymer-AlPTC). Furthermore, the photo-oxidation of phenol is investigated in aqueous solution.

The poly[(styrene)-*co*-(4-chloromethylstyrene)] (St-*co*-CMSt) was prepared by free-radical copolymerization of styrene and 4-chloromethylstyrene with benzoyl peroxide as initiator in bulk. The degree of copolymerization was styrene:chloromethylstyrene = 0.8:0.2 (molar percentage), determined by elemental analysis and ^{1}H NMR. Gel permeation chromatography (GPC) measurements using polystyrene standards showed an average molecular weight of 8.0×10^4. The preparation of polymer-AlPTC was carried out as follows. St-*co*-CMSt (2.0 g) and aluminium(III) tetracarboxyphthalocyanine[3] (0.05 g) were heated at 90 °C for 24 h under a nitrogen atmosphere in a mixture of freshly distilled DMSO (20 ml) and acetone (10 ml). An excess of pyridine (20 ml) was added, and the heating was continued for 24 h. After the unreacted pyridine and acetone were completely removed by evaporation, the solution was slowly poured onto vigorous stirring Et_2O. The light green precipitate was filtered, washed with Et_2O, and then dried *in vacuo* for 12 h. The pure polymer-AlTPC, which is identified by elemental analysis, FTIR, and absorption spectrum measurements,[15] is shown below.



AlPTC



$X : Y : Z = 0.800 : 0.198 : 0.002$

Polymer-AlPTC

The absorption spectrum of the polymer-AlPTC in DMF showed an absorption maximum at 688 nm with a molecular absorption coefficient of *ca.* 40 000 in the visible region, which almost corresponded with that of AlPTC.[3] Although the copolymer of styrene and pyridiniomethylstyrene, corresponding to the parent copolymer of the polymer-AlPTC, is water-soluble, the polymer-AlPTC is water-insoluble. This is because the polymer-AlPTC has a structure which is partially bridged by AlPTC.

The photo-oxidation experiments were performed at 25 °C in an oxygen-saturated aqueous solution of pH 7, adjusted using a KH_2PO_4/Na_2HPO_4 buffer. A sample tube containing 2.0×10^{-6} mol dm^{-3} AlPTC or 0.84 mg polymer-AlPTC film (the same molarity as AlPTC) and 2.0×10^{-4} mol dm^{-3} phenol in aqueous solution (3 ml) was bubbled with oxygen for 10 min, and the capped sample solution was irradiated with a 300 W slide projector equipped with a UV cut-off filter ($\lambda > 440$ nm). The reaction was monitored by UV–VIS absorption spectrum measurements and also followed by GC and FTIR analyses.

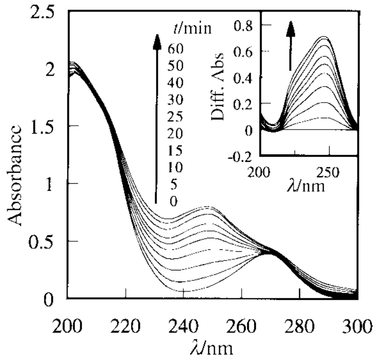


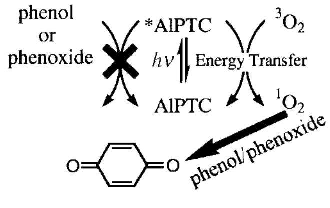
Fig. 1 Absorption spectral changes in an aqueous solution of polymer-AlPTC and phenol at pH 7 upon visible light irradiation. Inset: differential absorption spectral changes.

Table 1 Initial formation rates at pH 7 for polymer-AlPTC and AlPTC systems

	Initial rate[a]/mol dm^{-3} min^{-1}	[BQ][b]/mol dm^{-3}
Polymer-AlPTC[c]	1.05×10^{-6}	3.39×10^{-5}
NaN_3[cd]	1.71×10^{-9}	2.03×10^{-7}
Under Ar	—	—
AlPTC	—	—

[a] Experimental errors are within ±5%. [b] After irradiation for 120 min. [c] In oxygen-saturated aqueous solution. [d] $[NaN_3] = 2.0 \times 10^{-4}$ mol dm^{-3}.

Upon visible light irradiation of an oxygen-saturated aqueous solution of phenol and polymer photosensitizer, a new absorption band around 248 nm, characteristic for 1,4-benzoquinone (BQ),[14] increased. Fig. 1 shows the absorption spectral change in the heterogeneous reaction solution upon visible light irradiation at pH 7, and the initial formation rates of 1,4-benzoquinone are summarized in Table 1 In the presence of NaN_3 as



Scheme 1

a singlet oxygen quencher, the reaction rate and the amount of BQ formed are very small, and BQ does not form under Ar. Moreover, the absorption spectral change was not observed in the dark. These facts indicate that the present reaction is induced by excitation of the sensitizer itself and is the oxidation of phenol with singlet oxygen generated as shown in Scheme 1. Surprisingly, the photo-oxidation reaction using AlPTC photosensitizer, corresponding to the low molecular weight model complex, did not occur in a homogeneous aqueous solution at pH 7.[16] The polymer-AlPTC has hydrophobic segments (styrene residues) and positively charged segments (pyridinium residues) in the polymer backbone. These residues would concentrate phenol and/or phenoxide anion through hydrophobic and electrostatic attraction. Furthermore, the polymer-AlPTC can be readily separated by filtration from the reaction solution.

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Notes and references

1 W. Spiller, D. Wöhrle, G. Schulz-Ekloff and J. Stark, *J. Photochem. Photobiol.*, 1996, **95**, 161.

2 D. Wöhrle, W. Spiller, G. Schneider, G. Schulz-Ekloff and J. Stark, *J. Inf. Rec. Mater.*, 1994, **21**, 1.

3 G. Schneider, D. Wöhrle, W. Spiller, J. Stark and G. Schulz-Ekloff, *Photochem. Photobiol.*, 1994, **60**, 333.

4 D. Wöhrle, G. Schneider, J. Stark and G. Schulz-Ekloff, *J. Mol. Catal.*, 1992, **75**, L39.

5 H. E. Gsponer, C. M. Previtali and N. A. Garcia, *Toxicol. Environ. Chem.*, 1987, **16**, 23.

6 M. C. Palumbo and N. A. Garcia, *Toxicol. Environ. Chem.*, 1988, **17**, 103.

7 R. Gerdes, D. Wöhrle, W. Spiller, G. Schneider, G. Schnurpfeil and G. Schulz-Ekloff, *J. Photochem. Photobiol. A: Chem.*, 1997, **111**, 65.

8 R. C. Straight and J. D. Spikes, in *Singlet Oxygen, Vol. IV*, ed. A. A. Frimer, CRC Press, Boca Raton, 1985, p. 91.

9 J.-L. Ravanat, M. Berger, F. Benard, R. Langlois, R. Ouellet, J. E. van Lier and J. Cadet, *Photochem. Photobiol.*, 1992, **55**, 809.

10 X.-F. Zhang and H.-J. Xu, *J. Photochem. Photobiol. B: Biol.*, 1994, **24**, 109.

11 J. D. Spikes, J. E. van Lier and J. C. Bommer, *J. Photochem. Photobiol. A: Chem.*, 1995, **91**, 193.

12 V. Iliev, A. Ileva and L. Bilyaska, *J. Mol. Catal. A: Chem.*, 1997, **126**, 99.

13 F. Amat-Guerri, M. Carrascoso, M. Luiz, A. T. Soltermann, A. Biasutti and N. A. Garcia, *J. Photochem. Photobiol. A: Chem.*, 1998, **113**, 221.

14 M. Nowakowska and M. Kepczynski, *J. Photochem. Photobiol. A: Chem.*, 1998, **116**, 251.

15 For AlPTC-polymer, elemental analysis: C: 79.55; H: 7.29; N: 2.07%, FTIR of polymer film: 1687 (COOH) and 1711 cm^{-1} (COO–CH$_2$–), and UV–VIS spectrum in DMF: $\lambda_{\max}$ = 688 nm and $\varepsilon_{\max}$ = 40500 mol^{-1} dm^3 cm^{-1}. Even when the polymer-AlPTC was immersed into water for 1 month, the polymer and unreacted AlPTC were not observed in water. Therefore, the polymer-AlPTC is completely water-insoluble and does not contain the unreacted AlPTC.

16 For AlPTC system, the photo-oxidation reaction was carried out in a homogeneous aqueous solution because of its water-solubility.

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