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Development of an eco-friendly optical sensor element based on tetraphenylporphyrin derivatives dispersed in biodegradable polymer Effects of substituents of tetraphenylporphyrins on HCl detection and biodegradation

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Abstract

Composite films of 5,10,15,20-tetraphenylporphyrin ($TPPH_2$) derivatives containing electron-releasing groups such as alkyl and alkoxy group embedded in various biodegradable polyesters (BDPE) matrices were prepared and their optical response to hydrogen chloride (HCl) gas were examined in comparison with nonbiodegradable polymers (NBDP) matrices. Absorbance of the Soret- and Q-bands for $TPPH_2$ derivatives-BDPE composite films are reversibly, more sensitive to sub-ppm levels of HCl gas than those for those-NBDP composite films. A high sensitivity to sub-ppm levels of HCl gas was achieved by using a 5,10,15,20-tetra(4′-butoxyphenyl)-porphyrin ($TP(OC_4H_9)PH_2$)-poly(ε-caprolactone) (PCL) composite film.

Keywords: Optochemical gas sensor; Biodegradable polyesters; Porphyrin; Hydrogen chloride; Enzymatic degradation; Environmental monitoring

1. Introduction

In the last decade, the detection of sub-ppm levels of hydrogen chloride (HCl) in nitrogen, as might be leaked from the adsorbing towers at a semiconductor factory, has become desirable. HCl is generated from incineration plants and has been identified as hazardous for people in working places, with a short period exposure limit of 5 ppm.

We have recently reported that the sensitivity and response behaviors to low ppm levels of HCl gas were strongly influenced by substituents for 5,10,15,20-tetraphenylporphyrin ($TPPH_2$) derivatives, the used polymer matrix and an addition of a plasticizer to the sensor [1]. However, the addition of a plasticizer result some deterioration with time in sensitivity due to phase separation of plasticizer and polymer, i.e., the difference in solubility parameter polymer and plasticizer, as reported by Mills et al. [2]. In addition, plasticizer such as dioctyl phthalate (DOP) is endocrine-disrupting chemicals (EDC) and polymer matrices such as poly(alkyl acrylate) (PAA), poly(alkyl methacrylate) (PAMA) and polystyrene (PSt) are low biodegradable. To solve these problems, it is required to use eco-friendly polymers as a matrix without plasticizer for environmental safety. In our recent study, for use as eco-friendly polymer, i.e., biodegradable polyesters (BDPE), such as poly(ε-caprolactone) (PCL), poly(butylene succinate adipate) (PBSA) and poly(butylene adipate terephthalate) (PBAT), which are considered as the most promising materials, since these polyesters are commercially produced and degraded in soil, and compost after their sensing life has

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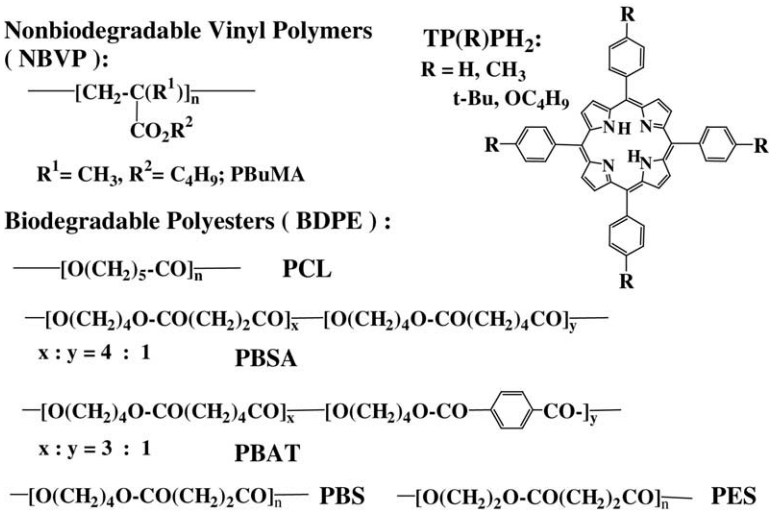

Fig. 1. Structure of polymer matrices and TP(R)PH_2.

been over [3]. In this study, the substituent effect for $TPPH_2$ derivatives (TP(R)PH_2), i.e., electron-releasing groups like alkyl and alkoxy group on optical HCl gas sensing characteristics (sensitivity, response and recovery behavior) by using TP(R)PH_2–BDPE composite films, in comparison with nonbiodegradable polymers (NBDP) matrices such as poly(alkyl methacrylate) were examined. In addition, we examined an enzymatic degradability of BDPE in order to study an influence of TP(R)PH_2-additive on the degradability of BDPE.

2. Experimental

2.1. Composition of the elements

Molecular structures of polymer matrices and electron-releasing groups substituted 5,10,15,20-tetraphenylporphyrins (TP(R)PH_2) (R = CH_3, *t*-Bu, OC_4H_9) are shown in Fig. 1. These polymers are characterized by using ^{1}H NMR (400MHz, JEOL ECP 400) and GPC (HITACHI, L-6200). And their glass transition temperatures (T_g) were measured by means of DSC (Rigaku, DSC-8230). Porphyrins (TP(R)PH_2) were synthesized by Adler's method [4] and assigned with NMR (JEOL, ECP-400), and other spectroscopic methods. The known concentration of porphyrin in chloroform or toluene and that of polymer matrix in chloroform were mixed and sensor-composite films were prepared by spin-coating these solutions on alumina substrates (1 cm × 1 cm) and then were dried at 70 °C in vacuo to remove the solvent. The composite film was ca. 1.5-μm thick by using a SEM (JEOL, JSM-5200). The crystalline structure of biodegradable polyesters films was analyzed by wide-angle X-ray diffraction (WAXD) (Rigaku, RINT 2200) and the degree of crystallinity was measured with the aid of the Ruland method [5].

2.2. The sensor structure and measurement

The apparatus for the HCl detection are described in our previous report [1]. The element was located directly in the gas stream. The chamber and gas-flow system were manufactured with polytetrafluoroethylene. Concentration of HCl gas was controlled by mixing of 11.0 ppm HCl standard gas (balanced by N_2), and N_2 gas and the total flow rate was controlled to 200 cm^{-3} ml^{-1} and stainless steel bodied needle valves had to be used to control the flow rate and mixing ratio. Filtered light from a D_2/I_2 lamp (350–800 nm, 15 w, MC-964, Otsuka electronics) was guided into a Y-type fiber and irradiated on a sensor element, and the reflected light was analyzed using a spectro multichannel photodetector (MCPD-1000 and 3000, Otsuka electronics). The spectrum (I_0) of the composite film in N_2 was first measured and used as the standard reference for measuring the spectrum ($I//I_0$) of the film. The reflectance (%) is defined as $100I/I_0$. All measurement was performed at 45 °C.

2.3. Enzymatic degradation of (TP(R)PH_2)–polymer composite films

Enzymatic degradation was carried out with or without 5 units/ml of a lipase PS from Amano Medicine manufacture at pH 7.0 and 37 °C for a fixed time. The degradability of TP(R)PH_2–polymer composite films was evaluated on the basis of the weight loss or the total organic carbon (TOC, HIRANUMA, TOC A-2000) measurement of them after filtration of hydrolyses solutions by a Millipore filter (0.2 μm). Before and after degradation test, topological changes of the surfaces of (TP(R)PH_2)–polymer composite films were observed using a SEM.