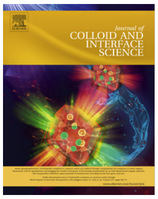
Journal of Colloid and Interface Science 532 (2018) 210–217

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis



Regular Article

Synthesis and activity characteristics of visible light responsive polymer photocatalyst system with a styrene block copolymer containing TiO_2 gel

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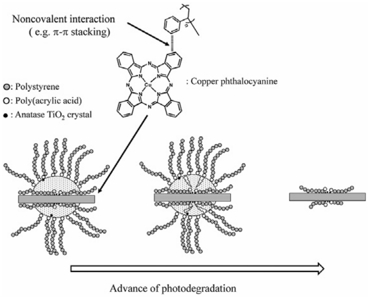
GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 June 2018
Revised 21 July 2018
Accepted 27 July 2018
Available online 31 July 2018

Keywords:
Polymer photocatalyst
Block copolymer
Titanium dioxide gel
Copper phthalocyanine

ABSTRACT

A polymer photocatalyst system was synthesized using a poly(styrene-*block*-acrylic acid) (PS-*b*-PAA) containing TiO_2 gel without calcination, and its activity characteristics were assessed with methylene blue (MB) photodegradation test in water under visible light irradiation. The initial photodegradation activity was controllable by the polymer chain length and PAA/PS molar ratio. The longer polymer chain length provoked the activity decrease by macromolecular crowding effect. The lower molar ratio did an increase in the photocatalytic surface area by generation of a large number of anatase TiO_2 crystal nuclei, leading to the activity increase. The copper phthalocyanine (CuPc) loading remarkably improved the activity. A higher active site was formed on the interface and showed good recycling performance.

1. Introduction

Organic pollutants discharged from industrial effluents have frequently created a serious problem for the global environment. Photocatalysis has been employed for the degradation [1–6]. Titanium dioxide (TiO_2) is well-known as photocatalyst and has been extensively studied about the photocatalytic activity [7,8]. The organic pollutants have been completely decomposed by TiO_2 under UV irradiation [9]. On the other hand, the photocatalytic activity has been inefficient in using a visible light source such as sunshine. TiO_2 does not absorb above 385 nm wavelength, the development of TiO_2 having absorption in the longer wavelength has been required to use visible light source [10]. Many researchers have been enthusiastically working on making TiO_2 responsive to visible light with dye sensitization [10–13], coupling with other semiconductor [14–16], doping atoms [17–19], etc. Among them, the dye sensitization with CuPc is an inexpensive and efficient one [10,13]. Phthalocyanine is adequate for the sensitizing dye because of low toxicity and high resistance to chemical attack such as radical reaction. In particular, the combination with a nanosized TiO_2 shows excellent photocatalytic activity under visible light irradiation [10,13,20–22]. On the other hand, some investigators have reported that a nanosized TiO_2 was harmful to lung and

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https://doi.org/10.1016/j.jcis.2018.07.119

DNA [23–25]. The exposed usage of nanosized TiO_2 may be a problem from the viewpoint of environmental compatibility. Development of non-toxic CuPc-sensitized and nanosized TiO_2 (CuPc-TiO_2) will be required in the future.

In our previous work, a novel encapsulated TiO_2 gel nanoparticle was prepared with a PS-*b*-PAA polymer micelle [26]. The TiO_2 gel contained anatase phase without calcination process and showed methylene blue photodegradation activity in water under visible light irradiation. It has an equilibrium between solid and ion states as follows [27,28]:

$$TiO^{2+} \rightleftharpoons TiO_2$$

The equilibrium tends to ion side with pH decreasing. Therefore, the encapsulated TiO_2 gel can be dissolved as ion with an acid water. The properties are available for the solution of the nanosized TiO_2 problem. The pH in the TiO_2 gel and micelle strength are adjustable by the PAA/PS molar ratio and/or polymer chain length, leading to controlling the photocatalyst activity. In addition, if CuPc is incorporated into the micelle, a large improvement of the photocatalyst activity in visible light irradiation is expected.

In this study, the polymer photocatalyst systems were synthesized using some kinds of PS-*b*-PAA containing TiO_2 gel, and their MB photodegradation tests were performed in water under visible light irradiation. Moreover, the CuPc loading effects were studied using them. The activity characteristics and recycling efficiency were assessed by MB photodegradation test using a UV–Vis spectrometer. The TiO_2 gel domain size, distribution and shape were observed by a Field-Emission type Transmission Electron Microscope (FE-TEM).

2. Experimental

2.1. Materials

Styrene (St), α-methylstyrene (α-MeSt), *tert*-butylacrylate (*t*BA), LiCl and tetrahydrofuran (THF: super dehydrated and stabilizer free), dichloromethane (CH_2Cl_2), trifluoroacetic acid (TFA), diethyl ether, hexane, titanium isoproxide (TTIP), 2-propanol, HCl and benzene were purchased from Wako Pure Chemical Industries, Ltd., respectively. *sec*-Buthyllithium (*sec*-BuLi) and CuPc were purchased from Sigma-Aldrich Co. LLC., respectively. The St, α-MeSt and *t*BA were dried over calcium hydride for 24 h and distilled under reduced pressure before use. The TTIP was distilled under 0.15 MPa at 115 °C and was used. Others were used without further purification.

2.2. Synthesis of poly(styrene-block-acrylic acid)

Poly(styrene-*block*-acrylic acid) (PS-*b*-PAA) was synthesized according to Yamada et al. report [28]. The synthesis procedure was shown in Fig. 1. Initially poly(styrene-*block*-*tert*-butylacrylate) (PS-*b*-*t*BA) was synthesized by living anion polymerization and then was hydrolyzed to obtain PS-*b*-PAA. The detailed procedure was shown as follows.

PS-*b*-*t*BA synthesis: An initiator of living anion polymerization was synthesized with α-MeSt and *sec*-BuLi in THF solvent. The first step polymerization was conducted at −78 °C for 30 min in a stirred 100 ml glass reactor under nitrogen by using THF, LiCl and St, and then second step polymerization was performed at −78 °C for 30 min by the addition of *t*BA. In order to change the molecular weight, the amounts of the initiator and LiCl were varied.

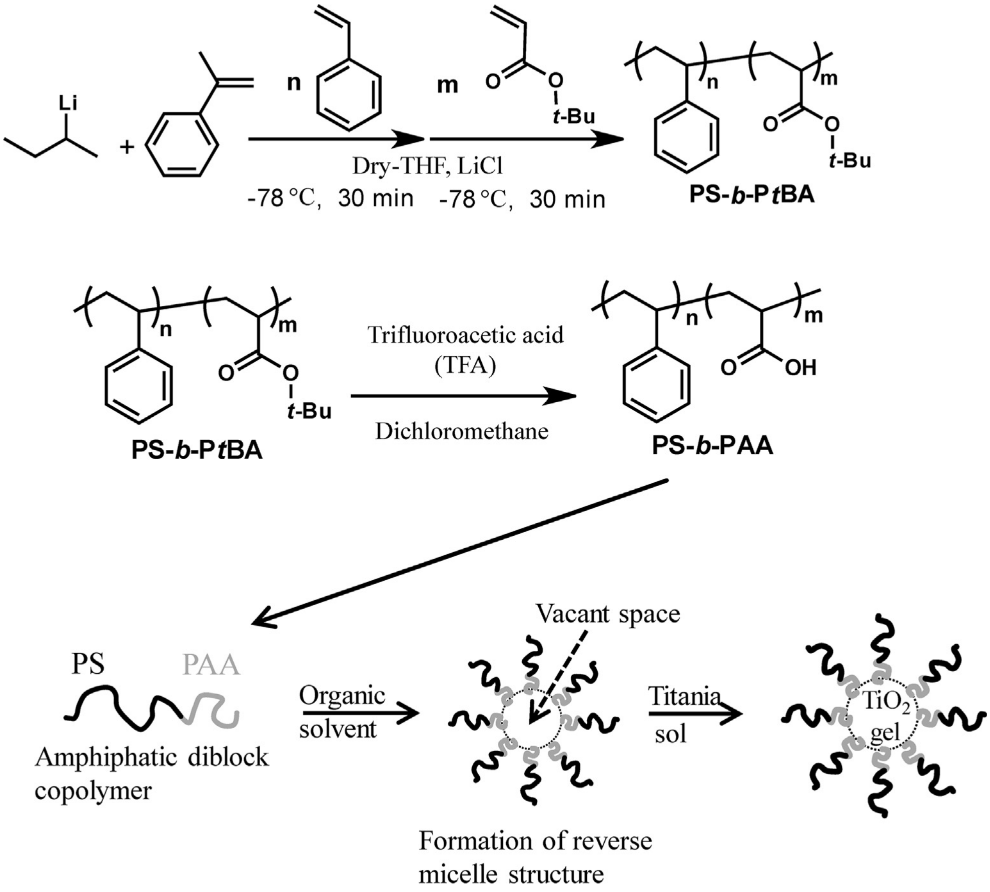

Fig. 1. Synthetic schemes of PS-*b*-PAA containing TiO_2 gel.