



Cationic and free radical polymerization initiated by a visible-light sensitive complex based on the photocatalytic decarboxylation of carboxylic acid

Wanfeng Liao, Xiuyuan Ni*, Yulan Zhou

State Key Laboratory of Molecular Engineering of Polymer, Department of Macromolecular Science, Fudan University, Shanghai 200433, China



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ABSTRACT

The photopolymerization with important application has usually used the organic initiators sensitive to ultraviolet light. In this work, we designed a new visible-light initiator complex composed of iron doped TiO₂ (TiO₂:Fe_{x%}, x = 1, 5, and 10), succinic acid and iodonium salt (Ph₂I⁺PF₆⁻). The ternary complex was proved to efficiently initiate both cationic ring-opening polymerization and free radical polymerization. The mechanism studies with solid-state ¹³C-nuclear magnetic resonance (¹³C NMR) and gas chromatography-mass spectrometer (GC-MS) clearly presented that the TiO₂:Fe_{x%} nanoparticles catalyzed the decarboxylation of succinic acid in the pathway of photo-Kolbe reaction. Meanwhile, Ph₂I⁺PF₆⁻ could serve as an electron acceptor. The reaction kinetics of epoxy resin and epoxy-acrylate hybrid resin were measured by the attenuated total reflection-Fourier transformation infrared (ATR-FTIR) spectroscopy.

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1. Introduction

Photopolymerization technology, which is chiefly based on the free radical and cationic polymerization, has been broadly used for manufacturing dental materials, ink, UV curable coating, electronic devices and varnishes [1–5]. The initiation mechanisms of both free radical and cationic polymerization have been studied in details [6,7]. With light irradiation, the photoinitiators are excited to give rise to free radical and protonic acid intermediates, which further initiate the polymerization of alkene monomers and epoxide, respectively. Recently, cationic-free radical hybrid polymerizations have received extensive interest for the application of fabricating composites with balanced properties [8,9]. However, those photoinitiators for both free radical and cationic polymerization are always confined to be UV sensitive. For instance, the typical initiators like 1-hydroxycyclohexyl phenyl ketone and the traditional cationic photoinitiators, such as diphenyliodonium hexafluorophosphate (Ph₂I⁺PF₆⁻), mainly absorb UV light at the wavelength lower than 400 nm [10,11]. Now, a visible-light induced polymerization has received great attention due to the low-cost utilization of sunlight [12–14]. Another advantage is that the monomers can be solidified conveniently at the natural condi-

tion to prepare materials, which makes it necessary to develop novel visible-light initiators.

Semiconductor materials have been used frequently in photocatalytic process [15–18]. Among these semiconductor materials, TiO₂ is a promising candidate due to its high chemical stability, good photocatalytic activity and low toxicity [19–23]. For instance, in response to the UV excitation, the electron-hole pairs as active charge carriers are produced at the surface of TiO₂ nanoparticle. These charge carriers can oxidize acetic acid, instantly converting it into CH₃ radical intermediate and CO₂. This reaction was named as photo-Kolbe, which was found by Bernhard Kraeutler and Allen J. Bard in 1978 [24]. The CH₃ radical intermediate is reactive enough to initiate free radical polymerization, as reported in our previous work [25,26]. Moreover, we have obtained that aliphatic carboxylic acid (such as acetic acid, propionic acid, and so on) and TiO₂ as a binary initiator complex can initiate free radical polymerization [26], which is comparable to the efficiency of traditional free radical initiators. The TiO₂-based polymerization has an advantage of using aqueous medium, avoiding the pollution caused by organic solvent. However, pure TiO₂ nanoparticles have a weak absorption in the visible light region. It is of great potential and academic significance to develop the new visible-light sensitized initiator complex by using modified TiO₂ [27,28].

In the decarboxylation of carboxylic acid at the surface of TiO₂, carboxylic acid is oxidized by the charge carrier at the surface of TiO₂ and the reaction gives rise to protons (H⁺) as part of the

* Corresponding author.

E-mail address: xyjni@fudan.edu.cn (X. Ni).

intermediates [25,26]. This H^+ intermediate will be reduced by the photo-generated electron through the proton-coupled electron transfer (PCET) reaction, which can avoid high energy intermediate [29]. As is well known, $Ph_2I^+PF_6^-$ is one of the traditional cationic photoinitiators for epoxy resin [30,31]. It also can be used as good acceptor for electron from photocatalytic reactions [32]. Using $Ph_2I^+PF_6^-$ as the electron acceptor probably increases the reaction efficiency of the photocatalytic decarboxylation due to the separation of the electron-hole pairs. The recombination of the electron-hole pairs should be suppressed due to the electron is accepted by $Ph_2I^+PF_6^-$. To the best of our knowledge, the decarboxylation of carboxylic acid is not actualized by using visible-light sensitive semiconductor. The photocatalytic decarboxylation accompanied by $Ph_2I^+PF_6^-$ also has not been attempted as yet.

In this study, we have developed the new visible-light initiator complex to initiate cationic and free radical polymerization. Iron doped TiO_2 ($TiO_2:Fe_{x\%}$), succinic acid and $Ph_2I^+PF_6^-$ ($TiO_2:Fe_{x\%}/succinic\ acid/Ph_2I^+PF_6^-$) was applied as the ternary visible-light initiator complex. Diglycidyl hydrogenated bisphenyl A (DGHBA) as a typical epoxy resin and trimethylolpropane triacrylate (TMPTA) as a typical acrylate resin were selected for the cationic and free radical polymerization, respectively. The ternary complex of $TiO_2:Fe_{x\%}/succinic\ acid/Ph_2I^+PF_6^-$ was analyzed about the photocatalytic reaction intermediates. The polymerization kinetics of DGHBA and the DGHBA-TMPTA mixture were studied by attenuated total reflection-fourier transformation infrared (ATR-FITR) spectroscopy, respectively. The results showed that the ternary complex of $TiO_2:Fe_{x\%}/succinic\ acid/Ph_2I^+PF_6^-$ is a promising visible-light sensitive initiator for cationic and free radical polymerization.

2. Experimental

2.1. Materials

The reagents used in this study, $FeCl_3 \cdot 6H_2O$, titanium isopropoxide, tert-Butyl benzene and acetone were purchased from Sinopharm chemical reagent Co, Ltd. Succinic acid, $Ph_2I^+PF_6^-$ and N-tert-Butyl-Alpha-phenylnitron (PBN) were acquired from Aladdin, Shanghai. 1, 4- ^{13}C succinic acid and 2, 3- ^{13}C succinic acid were supplied by Icon Isotopes. DGHBA (JE-8430) was purchased from Jiadida new material Co, Ltd, Shenzhen. TMPTA (Agisyn-2811) were purchased from Curease chemical Co., Ltd, Shanghai. All the reagents were used as received.

2.2. Synthesis of $TiO_2:Fe_{x\%}$ nanoparticles

$TiO_2:Fe_{x\%}$ was prepared by sol-gel method using titanium isopropoxide (TIPO) as titania precursor [33,34]. 4.5 ml of TIPO was mixed with 12 ml of ethanol in a flask by continuous stirring. Then, 10 ml of ethanol and 3.5 ml of distilled water were added slowly, yielding a titania sol. The sol was stirred at room temperature for 2 h, followed by adding different amounts of $FeCl_3 \cdot 6H_2O$. As a result, the sol with $Fe/TiPO$ molar ratio of 1%, 5%, 10% were obtained, respectively. After the sol was stirred for another 2 h, the sol was filtered, the obtained particles were dried by vacuum extraction at room temperature for 24 h, followed by heating at 500 °C for 1 h in a muffle furnace. Finally, the Fe-doped TiO_2 nanoparticles with different doping concentrations, $TiO_2:Fe_{x\%}$ ($x = 1, 5, \text{ and } 10$), were synthesized. The pure TiO_2 was prepared by the same procedure without the addition of $FeCl_3 \cdot 6H_2O$.

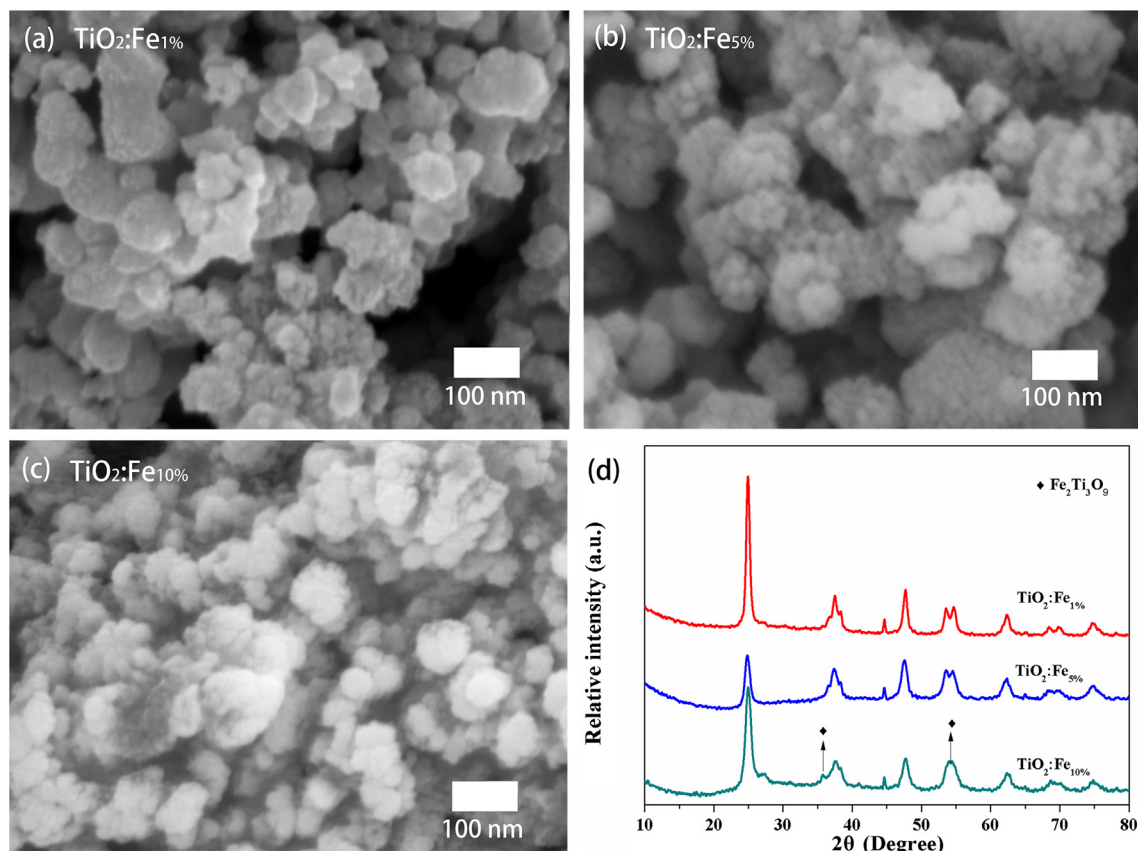


Fig. 1. The FESEM images (a, b, c) and XRD spectra (d) of the synthesized $TiO_2:Fe_{x\%}$.

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