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# A facile method to prepare a polyethylene glycol modified polysilane as a waterborne photoinitiator

Qiuhong Liang [a], Liping Zhang [b], Ying Xiong [a,**], Qingqing Wu [a], Hongding Tang [a,*]

[a] College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, PR China
[b] Guangzhou Tinci Silcone Technology Co., Ltd., Guangzhou 510760, PR China

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ABSTRACT

Developing water-soluble or waterborne polysilane photoinitiators meets the demands for environmental friendly photopolymerization applications. By employing this photoinitiated strategy, a waterborne polysilane photoinitiator polysilane-*co*-poly(polyethyleneglycol acrylate) was prepared by an efficient photodecomposition of polymethylphenylsilane in the presence of acrylate functionalized polyethyleneglycol. The prepared polymer was characterized by $^1$H NMR, $^{13}$C NMR, $^{29}$Si NMR, FT-IR, UV–vis GPC, DSC and TGA. It could disperse in water easily and form micelle. The average micelle size (10 mg/mL) was measured to be 46 nm by dynamic light scatting technique. The course of photopolymerization of acrylamide in deuterated water initiated by it was investigated by the real-time FT-IR spectroscopy. The photopolymerization kinetic data revealed that the conversion of acrylamide reached 80% and 100% after 40 and 110 s irradiation, respectively. The photopolymerization of the water solution of acrylamide, hydroxyethyl methacrylate (HEMA) and acrylic acid (AA) initiated by this polymer at air atmosphere provided successfully polymeric jelly materials in high yields.

## 1. Introduction

As the basis of numerous conventional applications such as in coatings, adhesives, inks, printing plates, optical waveguide, and microelectronics, photopolymerization is one of the most important technological processes in polymer science with a wide range of economic and ecological advantages [1,2]. A successful photopolymerization system requires the perfect formulation of the following components: an oligomer or a reactive monomer, additives, and a photoinitiator or photoinitiator system [3]. A photoinitiator or photoinitiator system can be defined as a molecule or combinations of molecules that, upon absorption of light, initiates the polymerization [4]. In spite of its lowest volume in the polymerization formulation, a photoinitiator or photoinitiator system plays an important role since it determines the photopolymerization speed and affects polymer properties such as yellowing, odor, migration, and etc. [2,5]. Many low molecular weight photoinitiators such as benzoin, acetophenone, α-hydroxy ketone, benzophenone, thioxanthone, and their derivatives have been used in photopolymerization systems due to their high initiation efficiency and good solubility in the formulation [6]. However, two apparent drawbacks such as relatively strong odor and high migration from cured films greatly limit their applications and trigger the development of polymeric photoinitiators [7–15]. Featured with chromophore on pendant or in polymer main chain, polymeric photoinitiators have shown an obvious lower odor and migration, higher absorption and efficiency than low molecular weight photoinitiators [7–15].

Polysilanes as radical photoinitiators for a variety of vinyl monomers have been demonstrated to have some special properties such as high quantum yield and good resistance to oxygen inhibition when photopolymerization [16–18]. Meanwhile, polysilane photoinitiators can be converted to cationic photoinitiators when accompanying with the ferrocenium salts or onium-type photoinitiators such as iodonium and sulfonium salts [2]. With the demand of developing waterborne photopolymerization system, the water-soluble or waterborne photoinitiators especially their polymers are distinctive [3,19–22]. The water-soluble or waterborne photoinitiators could be obtained by introducing ionic groups such as quaternary ammonium salts, carboxylic acids, sulfonates [22–26], or hydrophilic groups such as ethoxyethers and carbohydrates into oil-soluble photoiniatiators [27,28], or through inclusion chemistry such as the inclusion complex of 2-hydroxy-2-methyl-1-phenylpropan-1-one and

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[*] Corresponding author. Tel.: +86 2787164219.
[**] Corresponding author.
*E-mail addresses:* yingxiong@whu.edu.cn (Y. Xiong), chhdtang@whu.edu.cn (H. Tang).

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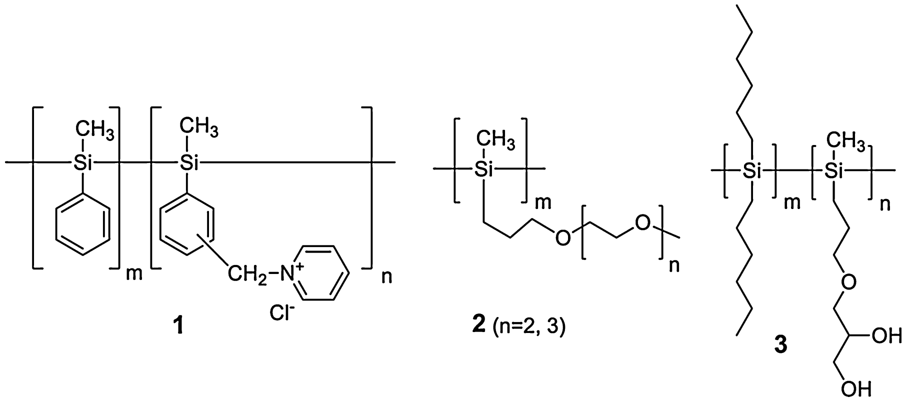


**Chart 1.** Examples of reported water-soluble polysilanes.

methylated β-cyclodextrin [21]. Conventionally, water-soluble polysilanes such as **1–3** in Chart 1, were prepared by attaching quaternary ammonium salts [29–32], ethoxyethers [33–35] and multihydroxy groups [36] with polysilanes. Some water-soluble polysilanes such as **1** can also be used as a photoinitiator to photoinitiate a series of vinyl monomers in water solution [31]. However, the preparations of water-soluble polysilane photoinitiators according to the reported procedures were complicated and accompanied with some unfavorable outcome such as a low yield of chloromethylation and serious decomposition of polysilane backbone in the synthesis of polysilane **1** [31]. Therefore, it is necessary to develop a more convenient method to prepare water-soluble (or waterborne) polysilane photoinitiators for waterborne photopolymerization.

Polymethylphenylsilane has been used as a photoinitiator for the polymerization of some functional vinyl monomers to prepare copolymers with polysilane segments in the main chain [37–39]. Recently, a polysilane-polybenzylmethacrylate (PMPS-PBzMA) was prepared by using polymethylphenylsilane (PMPS) as a polymeric photoradical initiator [40,41]. Interestingly, this PMPS-PBzMA with polysilane chain in the backbone was photobleachable and could be potentially used as optical waveguide, which may imply that the polysilane chain in PMPS-PBzMA still kept enough polysilane properties. Indeed, a polysilane and poly(methyl methacrylate) copolymer was obtained by photoinitiated polymerization of methyl methacrylate through the photolysis of PMPS and was used as a photoinitiator for styrene to prepare copolymers [42]. The preparation of this polysilane copolymer as a photoinitiator through a photoinitiated strategy could provide a more facile method to reach functionalized polysilanes such as waterborne polysilanes. To our best knowledge, this strategy has not been used to prepare waterborne polysilane photoinitiators for aqueous photopolymerizations. Herein, a waterborne polysilane photoinitiator, polymethylphenylsilane-*co*-poly(polyethyleneglycol acrylate) **6** (Scheme 1) was prepared through the photopolymerization of acrylate functionalized polyether **5**, which was photoinitiated by **4.** The photopolymerization of the water solution of acrylamide, hydroxyethyl methacrylate (HEMA) and acrylic acid (AA) initiated by polysilane **6** at air atmosphere were also investigated.

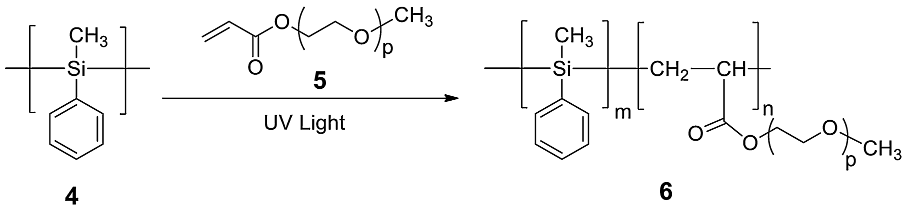
## 2. Experimental

### 2.1. Materials

Methylphenyldichlorosilane was provided by Wynca Chemical Industry Co., Ltd. Polyethyleneglycol (average molecular weight 550, MPEG-550) and acryloyl chloride were purchased from Alfa Aesar. The MPEG-550 was dried in vacuum at 65 °C before use. Triethylamine (TEA) was dried over $CaH_2$ and distilled before use. Toluene and tetrahydrofuran (THF) were dried over sodium metal and distilled before use.

### 2.2. Characterization

$^1$H NMR and $^{13}$C NMR spectra of the polymers were obtained with a Bruker Advance III 400 MHz spectrometer, $^{29}$Si NMR spectra of the polymers were obtained by employing a Bruker Advance III 500 MHz spectrometer. FT-IR spectra were recorded on a Nicolet IS10 in the region of 4000–400 $cm^{-1}$ using KBr pellets or film. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) in THF solution using a Waters 2960D Separation Module containing Waters 515 pump, HR1, HR3 and HR4 THF columns and a Waters 2414 Refractive Index Detector with a calibration curve for polystyrene standards. Differential scanning calorimetry (DSC) was performed using a Mettler Toledo DSC822e at a scan rate of 10 °C $min^{-1}$ under a nitrogen atmosphere. Thermogravimetric analysis (TGA) was carried out by Aetaram Setsys16 at a scan rate of 10 °C $min^{-1}$ under a nitrogen atmosphere. Polymer **6** (10 mg) was dispersed in 1 mL of water, and the particle size was measured by dynamic light scattering (DLS) using a Nano-ZS ZEN3600 (Malvern Instrument) at room temperature. The properties of UV absorption and UV degradation were studied by UV absorption spectroscopy (Shimadzu UV-3600 spectrometer) and scanned between 200 and 500 nm in THF or in aqueous. A high-pressure mercury lamp (Ushio



**Scheme 1.** Synthesis of polysilane 6.