



Synthesis, optical properties and stability of two σ - π conjugated polycarbosilanes with silylene-1,2-diphenyleneethylene-silylene and silylene-terephthalydene-silylene backbones via Grignard reactions

Fen Chen^{a,b}, Rui Zhou^{a,b}, Liang Liao^{a,b}, Ru Jia^{a,b}, Rong Zhao^{a,b}, Changping Fu^{a,b,c}, Rongqian Yao^{a,b,c,*}, Zude Feng^{a,b}

^a Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen 361005, China

^b Fujian Provincial Key Laboratory of Advanced Materials, Xiamen University, Xiamen 361005, China

^c Shenzhen Research Institute of Xiamen University, Shenzhen 518057, China

ARTICLE INFO

Article history:

Received 30 June 2016

Received in revised form 13 September 2016

Accepted 19 September 2016

Available online 23 September 2016

Keywords:

Polycarbosilane

Diphenyl

Photoluminescence

σ - π conjugation

Oxidation cross-linking

Ultraviolet radiation

ABSTRACT

Optical properties and stability of two novel polycarbosilane (PCS) products bearing aryl groups in the main chain synthesized by Grignard reactions were studied. 4-bromostyrene, α , α' -dibromo-*p*-xylene and dichloromethylsilane were employed as reactants to yield σ - π conjugated PCS with silylene-1,2-diphenyleneethylene-silylene backbone (PCS-SDS) and PCS with silylene-terephthalydene-silylene backbone (PCS-STs), respectively. Effects of oxidation cross-linking and ultraviolet (UV) radiation on the luminescence properties were examined. Photoluminescence (PL) spectra exhibit excellent blue light emission (maximum emission peaks at about 422 nm) compared to PCS and the intensity is exactly enhanced due to the insertion of phenyl into the conjugated main chains with Si—C bonds and the combined delocalization of the σ - σ^* transitions in Si chains and the π - π^* transitions in the benzene rings. Especially, PCS-SDS with more diphenyl and C=C groups possesses stronger emission intensity, higher quantum yield, better oxidation and UV resistance, and excellent thermal shock behavior below 400 °C in comparison with PCS and PCS-STs. Time-resolved PL spectra analysis also indicate that PCS-SDS can maintain longer fluorescence lifetime. These results prove PCS-SDS to be potentially applied to many fields, including but not limited to polymeric semiconducting materials, nonlinearoptics and organic electroluminescence devices.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Organosilicon polymers have been a subject of intensive research over the several decades owing to their excellent conductive and luminescence properties [1–6]. They have been widely used in organic electroluminescence devices, solar cells, coating and catalyst, especially as promising precursors to ceramic materials for Microelectromechanical System (MEMS) [7–12]. Organosilane polymers with different organic groups and molecular weights have been successfully synthesized by Wurtz coupling reactions, hydrosilylation polymerization or click polymerization so far [13–17]. These methods make them flexible in the molecular structure design and fabrication. In addition, it has been

demonstrated that their performances greatly depend on the properties of the organic groups bonded to silicon [18–22].

As typical organosilane polymers, polycarbosilane (PCS) with –Si–C– repeated backbone and polysilane with Si–backbone possess excellent luminescence properties owing to an σ -conjugation along the main chain [23,24]. As is well known, the optical properties and stability of PCS and polysilane can be improved by modifying their structures. So far, three main approaches have been developed. Firstly, π -conjugated groups, such as aryl, vinyl and allyl, have been introduced into the side chains to form σ - π conjugation, which can extend σ -conjugation system and avoid damage to conjugated electronic structure in the main chain. As is evident, the introduction of functional groups can dramatically change the physical and chemical properties of PCS [25–27]. Secondly, new linear PCS bearing various organic groups in the main chain has been fabricated mainly relying on the polymerization reaction of silane monomers such as dihydrosilane or trihydrosilane with unsaturated monomers. In this case, the

* Corresponding author at: Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen 361005, China.
E-mail address: rqyao@xmu.edu.cn (R. Yao).

organic groups in the backbone which have great effects on the electrochemical, optical and thermal properties play an important role in accepting σ electrons donated from Si atoms to form σ - π conjugation and become part of the chromophore [28,29]. The third way aims for hyperbranched PCS via hydrosilylation reaction of Si-containing monomers. In addition, the formation of hyperbranched PCS with excellent ultraviolet (UV)-resistant and thermal stability by introducing metal atoms into PCS is attributed to the rise of branching degree [30–33].

In our previous work, aryl-substituted polyphenylcarbosilane (PPCS) and hyperbranched metal atom-doped PCS were successfully synthesized, respectively. The attachment of phenyl side groups and introduction of metal atoms such as Al, Dy, Er and Eu can effectively improve the photoluminescence (PL) properties of PCS as well as its resistance to oxidation, UV radiation and high temperature. Moreover, the hyperbranched aluminum-containing polyphenylcarbosilane (Al-PPCS) with extended σ - π conjugation possess excellent blue light-emitting property in comparison with PCS [24,33]. As reported previously, Jitendra S. Rathore et al. have synthesized a PCS bearing aryl groups in the main chain by acyclic diene metathesis polymerization, which exhibits blue emission with high emission quantum yields. But the red shifts of these polymers are not high enough to allow their use in the more extensive luminescence wavelength region [34]. Therefore, it is significant to synthesize a new PCS bearing aryl in the main chain to enlarge the conjugation system as well as realize enough red shift in comparison with the original PCS.

On the basis of previous corresponding studies, it is considered worthwhile to obtain novel PCS bearing aryl in the main chain to form σ - π conjugation and especially strengthen the red shift. In this paper, PCS with silylene-1,2-diphenyleneethylene-silylene backbone (PCS-SDS) was synthesized using Mg powders, 4-bromostyrene and dichloromethylsilane by Grignard reactions. Similarly, PCS with silylene-terephthalidene-silylene backbone (PCS-STS) was also prepared using Mg powders, α , α' -dibromo-*p*-xylene and dichloromethylsilane by Grignard reactions. The

structure, PL properties, fluorescence lifetime and thermal stability of PCS, PCS-SDS and PCS-STS were characterized, respectively. Effects of oxidation cross-linking and UV radiation on the luminescence properties of the synthetic products were also investigated.

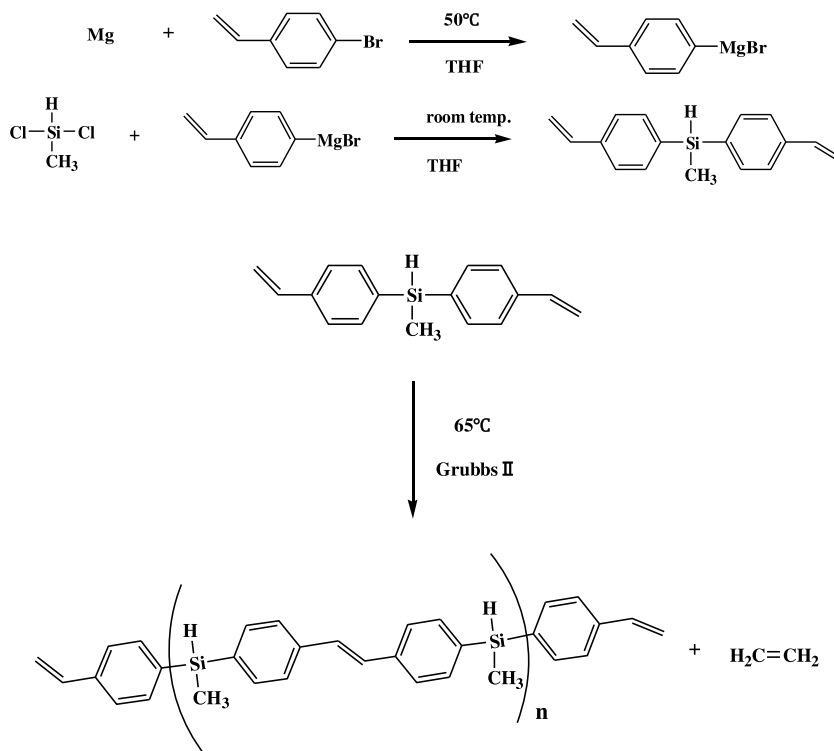
2. Experimental section

2.1. Materials and synthesis

All the chemicals were purchased from Aladdin Reagent Co., Ltd (Shanghai, China). Magnesium powder (99.9%), 4-bromostyrene (95%, containing stabilizers of 100–500 ppm TBC), α , α' -dibromo-*p*-xylene (97%), dichloromethylsilane (99%), and the second-generation Grubbs catalyst were all used as received without further purification. Based on Yajima's route [35,36], PCS in the form of transparent solid, which consists of the skeleton of alternate carbon and silicon atoms, was synthesized in our laboratory via thermal decomposition and condensation of polydimethylsilane (PDMS) polymer in an autoclave. Its atomic ratio is $\text{SiC}_{2.57}\text{H}_x\text{O}_{0.74}$ as determined by the chemical analysis, and its number average molecular weight (M_n) is 1426.

2.1.1. PCS with silylene-1,2-diphenyleneethylene-silylene backbone (PCS-SDS)

PCS-SDS was prepared by a two-step reaction process (Scheme 1). Firstly, the monomer $\{(\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4)_2\text{SiH}(\text{CH}_3)\}$ was prepared by the Grignard reaction of styrylmagnesium bromide with dichloromethylsilane. To synthesize styrylmagnesium bromide solution, 2.4 g (0.1 mol) of magnesium powder was mixed into THF (40 mL) to form a solution which was introduced into a 500 mL, three-neck flask equipped with a reflux condenser, an addition funnel, and a N_2 inlet. The mixture solution was refluxed for 30 min to activate the magnesium powder under a N_2 atmosphere at a flow rate of 30 mL/min with a ramping rate of $5^\circ\text{C}/\text{min}$ ranging from room temperature to 50°C . It was continuously



Scheme 1. Synthesis of PCS-SDS.

Download English Version:

<https://daneshyari.com/en/article/5435595>

Download Persian Version:

<https://daneshyari.com/article/5435595>

[Daneshyari.com](https://daneshyari.com)