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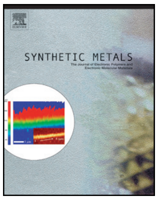

Synthesis and optical properties of σ–π conjugated aluminum-containing polyphenylcarbosilane (Al-PPCS) by hydrosilylation polymerization

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ABSTRACT

Optical properties of aryl-substituted polyphenylcarbosilane (PPCS) and aluminum-containing polyphenylcarbosilane (Al-PPCS) prepared by hydrosilylation polymerization were studied. Polycarbosilane (PCS), aluminum-containing polycarbosilane (Al-PCS) and styrene were employed as reactants to yield σ–π conjugated PPCS and Al-PPCS using chloroplatinic acid as catalyst, respectively. Phenyl was directly attached to the conjugated main chains with Si—C bonds. Effects of divinyl benzene cross-linking, oxidation curing and ultraviolet (UV) radiation on the photoluminescence (PL) properties of the samples were examined. PL spectra show strong blue light emission and the intensity of PCS is enhanced by adding the aryl groups and Al atoms. The excellent luminescent properties are attributed to the delocalization of electrons from the σ bond to π system. The hyperbranched Al-PPCS with extended σ–π conjugation has an obvious red-shifts PL, high quantum yield, excellent oxidation resistance and good UV resistance performance. Thermal analysis reveals that Al-PPCS can keep structure stability below 400 °C under an inert gas atmosphere. The Al-PPCS may have potential applications including organic electroluminescent (EL) devices.

1. Introduction

Polysilanes are a new type of σ-conjugated polymers which have attracted considerable attention because of their excellent optical properties, such as photovolatilization, nonlinear optical effects and photoconductivity [1–5]. Polysilanes are Si-backbone polymers with organic substituents attached to the main chain. The empty 3d orbitals of Si atoms cause significant delocalization of Si–Si σ-electrons along the polymer backbone. There is a strong extent of σ-conjugation throughout the main chain, where the excitonic level is observed as a sharp band in ultraviolet (UV) or near-ultraviolet (NUV) region. Therefore, polysilanes can be used as active sources for photoluminescence (PL) and electroluminescence (EL) devices [6–11]. However, most of the polysilanes only have UV emission properties which are unsuitable for their application in EL and optical devices. So the control of their electronic structures is important for such blue emission that is useful in EL applications [9–13]. In addition, the durability of organic polysilanes as optoelectronic devices is not satisfactory because of an irreversible photo-oxidation reaction.

In order to prolong the life-span and realize luminescence from devices based on polysilanes, investigation is required into method of film formation, its luminescence, chemical, thermal stability and degradation behavior, especially the durability against UV light exposure. Furthermore, it is well known that the performances and properties of polysilanes can be tuned by their electronic structures. In recent years many attempts have been made to develop effective methods for controlling the degree of σ-conjugation in polysilanes, such as by introducing functional substituents, modifying the conformation and replacing the Si atoms with foreign atoms. It was reported that introducing π-bonds into polysilanes can create σ–π conjugation copolymer with excellent photoelectricity performance [14–17]. However, these π-bonds are sensitive to radiation (such as double bonds) and result in a short service life.

As reported previously, physical properties of polysilanes are strongly influenced by the chemical structure of side groups.

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The unsaturated organic groups, can extend the conjugation length through σ–π conjugation and become part of the light-absorbing and -emitting chromophore [18–20]. Although the extent of σ–π conjugation in these polymers is generally agreed to be slight, they can lead to thermally or photoinduced charge delocalization along the polymer backbone as well as appreciable red shifts in the emission spectra. Various organosilicon polymers with photoconductive, EL, thermochromic, photorefractive, electro-optical, and non-linear optical properties can be synthesized. The polymers with well-defined fluorophores in their backbone have received considerable attention as EL materials for potential use in light-emitting diode (LED) community. Therefore, the development of new materials with appropriate blue light-emitting capabilities and the durability against UV light exposure for PL and EL devices is of both scientific and practical interest.

Our previous work has introduced a technique based on melt spinning of polymer to produce continuous freestanding polycarbosilane (PCS) films [21,22]. PCS with a backbone formed by Si and C atoms is one of the most well-known polymeric precursors to ceramic materials, such as SiC fibers, SiC films, SiC nanopowders, microporous SiC-based membranes and SiC-based microelectromechanical systems (MEMS) in harsh environments [23–27]. The electronic structure of PCS with main chain formed by repeating —Si—C— units is similar to that of polysilane and expected to be significantly different from those of homopolymers because of the large atomic orbitals (AO) energy difference between Si and C atoms. The highest occupied molecular orbital (HOMO) of PCS is formed by Si—C bond orbitals in the backbone, retaining some degree of σ-conjugation of the backbone. In addition, the electronic structure and degree of σ-conjugation can be significantly modified by properly inserting or substituting heteroatoms into the PCS backbone, and also electronic properties can be controlled and optimized possibly [28]. Therefore, in order to increase the emission intensity and improve degradation behavior, the σ-conjugated electronic structure of PCS should be extended as there is a close relationship between the delocalization level of σ-electrons and luminescence properties [29,30].

Based on the previous corresponding investigations, the introduction of metal atoms are beneficial to the PL properties, oxidation resistance, high temperature resistance and UV radiation resistance of PCS [31]. In this paper, the attempt is made to prepare hyperbranched aluminum-containing polycarbosilane (Al-PCS) with aryl groups to form σ–π conjugation copolymer, which can extend σ-conjugation system and do not cause damage to conjugated electronic structure in the main chain. Aryl groups with rigid plane structure were introduced into Al-PCS by hydrosilylation polymerization. Al-PCS and styrene were used as reactants, and chloroplatinic acid was used as catalyst. The product named aluminum-containing polyphenylcarbosilane (Al-PPCS) can be widely used as a novel preceramic polymer precursor which has carbon rich property due to its phenyl group [32–34]. Introduction of aryl groups into Al-PCS leads to H consumption through which aryl is closely bonded to Si by breaking Si—H to form Si—CH_2—CH_2—phenyl bonds in Al-PPCS. The luminescence properties of Al-PPCS were characterized and effects of divinylbenzene cross-linking, oxidation curing and UV radiation on the PL properties of the samples were also investigated.

2. Experimental

2.1. Materials and synthesis

All reagents and solvents were obtained from Sinopharm Chemical Reagent Co., Ltd. and used without further purification. PCS samples with Si–C backbone (Si: 41.03 wt%, C: 43.24 wt%, O: 1.05 wt%, $SiC_{2.5}H_xO_{0.74}$) employed in our laboratory were prepared by thermal decomposition of polydimethylsilane (PDMS) following the pioneering work of Yajima et al. [35,36]. They are transparent solid with a number average molecular weight of 1426. Aluminum-containing polycarbosilane (Al-PCS) samples (Si: 42.61 wt%, C: 36.73 wt%, O: 5.02 wt%, Al: 1.32 wt%, $SiC_{2.1}H_xO_{0.21}Al_{0.03}$) were synthesized in an autoclave at 450 °C under a N_2 atmosphere by thermolysis of a mixture of 4 g aluminum acetylacetonate [$Al(AcAc)_3$; Aldrich, 99%] with 100 g polysilacarbosilane (PSCS), which was prepared by thermolysis and condensation of PDMS. Al element was introduced into Al-PCS by cross-linking reaction in the formation of the Si—O—Al bonds during the process of synthesis. They are gold-colored solid with a number average molecular weight (M_n) of 2040.

2.1.1. Aryl-substituted polyphenylcarbosilane (PPCS) and aluminum-containing polyphenylcarbosilane (Al-PPCS)

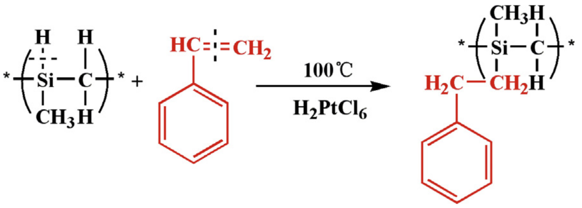
PPCS was prepared from PCS and styrene (Scheme 1). Typically, the procedure as follows: PCS (5 g, 3.51 mmol) was dissolved in xylene (30 mL, 0.25 M) to form a transparent solution which was introduced into a 1 L, three-neck flask equipped with a reflux condenser, mechanical stirrer, and a N_2 inlet. The chloroplatinic acid catalyst (0.386 mmol in 10 mL IPA) (1 mL, 0.0386 mmol) was added to the styrene (10 mL, 55 mmol) and activated for 20 min. The activated styrene solution was gradually added to the mixture of PCS and xylene under stirring in a N_2 atmosphere. After completing the addition, a highly air-sensitive, dark brown solution was obtained. This mixture solution was treated with a heating rate of 0.5 °C/min and held for 1 h at 100 °C. The solution was subsequently refluxed at 70 °C for 2 h under a N_2 atmosphere to remove the solvent and superfluous styrene. Then, the resultant organic solid was triturated into fine powder. At last, the triturated aryl-substituted PCS powder was heated at about 200 °C and held for 3 h under vacuum to remove small molecule impurities and yield a light yellow powder (3.85 g, 77%, $M_n = 1503$).

Al-PPCS was synthesized according to the above procedure using Al-PCS (5 g, 2.45 mmol), xylene (30 mL, 0.25 M), chloroplatinic acid catalyst (0.386 mmol in 10 mL IPA) (1 mL, 0.0386 mmol) and styrene (10 mL, 55 mmol) to obtain a light yellow powder (3.25 g, 65%, $M_n = 2126$) (Scheme 2).

2.1.2. Cross-linkable polycarbosilane/divinylbenzene (PCS/DVB) and aluminum-containing polycarbosilane/divinylbenzene (Al-PCS/DVB)

PCS/DVB was synthesized according to the procedure described for PPCS using PCS (5 g, 3.51 mmol), xylene (30 mL, 0.25 M), chloroplatinic acid catalyst (0.386 mmol in 10 mL IPA) (1 mL, 0.0386 mmol) and 1,2-divinylbenzene cross-linking agent (10 mL, 35 mmol) to gain a light yellow powder (3.53 g, 70.6%) (Scheme 3). The mixture solution was treated with a heating rate of 0.5 °C/min and held for 1 h at 120 °C during the cross-linking reaction.

Al-PCS/DVB was synthesized according to the above procedure described for PCS/DVB using Al-PCS (5 g, 2.45 mmol), xylene (30 mL, 0.25 M), chloroplatinic acid catalyst (0.386 mmol in 10 mL IPA) (1 mL, 0.0386 mmol) and 1,2-divinylbenzene cross-linking agent (10 mL, 35 mmol) to obtain a light yellow powder (3.06 g, 61.2%) (Scheme 4).



Scheme 1. Synthesis of PPCS.