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Preparation of polystyrene grafted silica nanoparticles by two-steps UV induced reaction

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Abstract

Polystyrene grafted silica nanoparticles (PSSNs) were prepared by the followed two steps: methacryloxypropyl silica nanoparticles (MPSNs) were modified with the monomer-iniferter, 4-vinylbenzyl *N*,*N*-diethyldithiocarbamate (VBDC) under UV irradiation. Then the VBDC modified silica nanoparticles (VBDCSNs) were used as iniferter for the surface-initiated (SI) controlled/"living" radical polymerization of styrene. A percentage of grafting (PG%) of 315.7% was achieved with a conversion of styrene of about 35% after 18 h UV irradiation.

Keywords: Polystyrene grafted silica nanoparticles; Monomer-iniferter; Surface-initiated; Controlled/"living" radical polymerization; UV irradiation

1. Introduction

Grafting polymer brushes onto solid surfaces has attracted intensive interest in recent years because of potential applications in colloidal stabilization [1], lithography [2], biocompatibility [3], electronic devices [4], and nanocomposite materials [5]. As compared to chemisorption and physisorption of preformed polymers [6,7], "one-pot" method [8], macromonomer method [9] and macro-chain transfer agent method [10], much attention is being focused on densely grafted polymer brushes through surface-initiated polymerization (SIP), in which chain growth is promoted from initiators already attached to the surface [11]. This is mainly because in the former approach, initially grafted chains (at the beginning of adsorption) sterically shield remaining active sites on surfaces, resulting in limited graft density and thickness of polymer brushes [12]. The advantage of SIP is that high-density polymer brushes are accessible where the average distance between grafting points is much smaller than the radius of gyration (R_g). A wide variety of polymerization methods have been applied toward SIP protocols on surfaces including free radical polymerization [13], anionic polymerization [14], atomic transfer radical polymerization (ATRP) [15–17], and polymerizations by 2,2,6,6-tetramethyl-1-piperidyloxy (TEMPO) [18].

In the present work, we report the preparation of polystyrene grafted silica nanoparticles (PSSNs) with a two-step photo-induced reaction.

2. Experimental

2.1. Materials and reagents

Silica nanoparticles used was MN1P obtained from Zhoushan Mingri Nano-materials Co. Ltd., Zhejiang, China. The surface area and particle size were 640 $m^2 g^{-1}$ and 10 nm, respectively. It was dried in vacuum at 110 °C for 48 h before use. γ-Methacryloxypropyltriethoxysilane (MPTES) (Gaizhou Chemical Industrial Co. Ltd., Liaoning, China) was used as received. 4-Vinyl benzyl chloride (VBC) is analytical reagent and used without any treatment. Styrene was purified by vacuum distillation. Sodium *N*,*N*-diethyl dithiocarbamate and other reagents used were all analytical grade reagents.

2.2. Preparation of VBDC

The monomer-iniferter, 4-vinylbenzyl *N*,*N*-diethyldithiocarbamate (VBDC), was synthesized from the reaction of 4-vinyl benzyl chloride (VBC) with sodium diethyldithiocarbamate as reported previously [19]; mp: 56.5–57.5 °C; IR (KBr): 915, 985, 1415 cm^{-1} ($CH{=}CH_2$), 1210,1485 cm^{-1}

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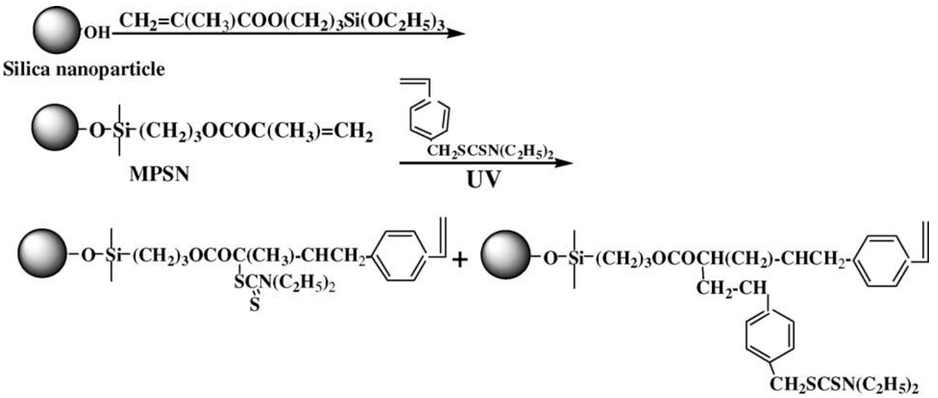


Scheme 1. Preparation of VBDCSNs.

(CS–N); EA found (%): C, 63.56; H, 6.95; N, 5.15; S, 24.34.

2.3. Preparation of VBDCSNs

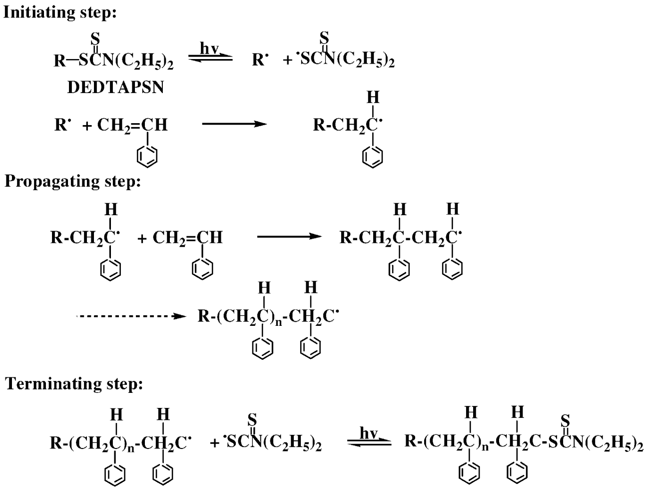
Methacryloxylpropyl silica nanoparticles (MPSNs) were achieved by the self-assembly of MPTES on the surfaces of the silica nanoparticles as described previously [20]. γ-Methacryloxypropyl groups content was 1.03 m mol g^{-1} MPSNs. The 4-vinylbenzyl *N*,*N*-diethyldithiocarbamate modified silica nanoparticles (VBDCSNs) were carried out at ambient temperature (20 °C) using a 300 W UV lamp at a distance of 10 cm. One gram of MPSNs and 1.0 g VBDC were dispersed in 50 mL toluene with ultrasonic vibrations for 10 min. After the mixture was placed under the UV lamp for 3 h. The mixture was centrifuged (1×10^4 rpm for 30 min) and washed with methanol for several times for remove the free VBDC monomer and oligomer.

2.4. Preparation of PSSNs

The surface-initiated (SI) controlled/“living” radical polymerization of styrene from VBDCSNs was also carried out at ambient temperature (15 °C) using a 300 W UV lamp at a distance of 10 cm. One gram VBDCSNs was dispersed in 20.0 mL mixture of toluene and styrene (volume ratio: 1:1) with ultrasonic vibrations for 10 min. Then the mixture was placed under the UV lamp for irradiation. After polymerization for a given time, the polystyrene grafted silica nanoparticles (PSSNs) were separated by three cycles of being centrifuged (1×10^4 rpm for 30 min)/dissolved in toluene, dried in vacuum at 40 °C, weighed, and the monomer conversion was calculated.

Table 1
Elemental analysis results of the PSSNs

Samples	Polymerizing time (h)	EA results (%)			
		C	H	N	S
VBDCSNs	0	9.87	1.48	0.11	0.54
PSSNs 1#	3	39.50	2.97	0.07	0.35
PSSNs 2#	6	53.16	3.67	0.08	0.26
PSSNs 3#	9	61.07	4.33	0.04	0.21
PSSNs 4#	12	65.78	4.92	0.04	0.16
PSSNs 5#	15	69.77	5.14	0.03	0.15
PSSNs 6#	18	72.48	5.56	0.02	0.13



Scheme 2. The mechanism of the photo-induced controlled/“living” radical polymerization of styrene under UV irradiation.

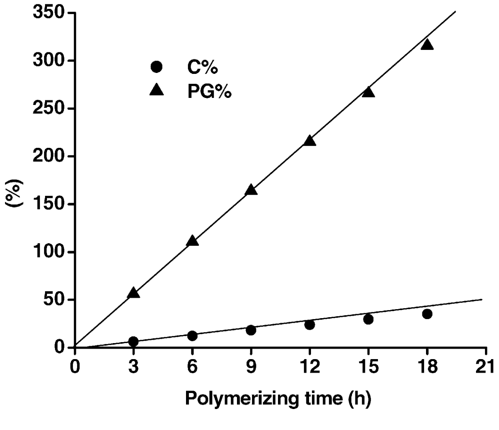


Fig. 1. Photopolymerization of styrene from VBDCSNs.

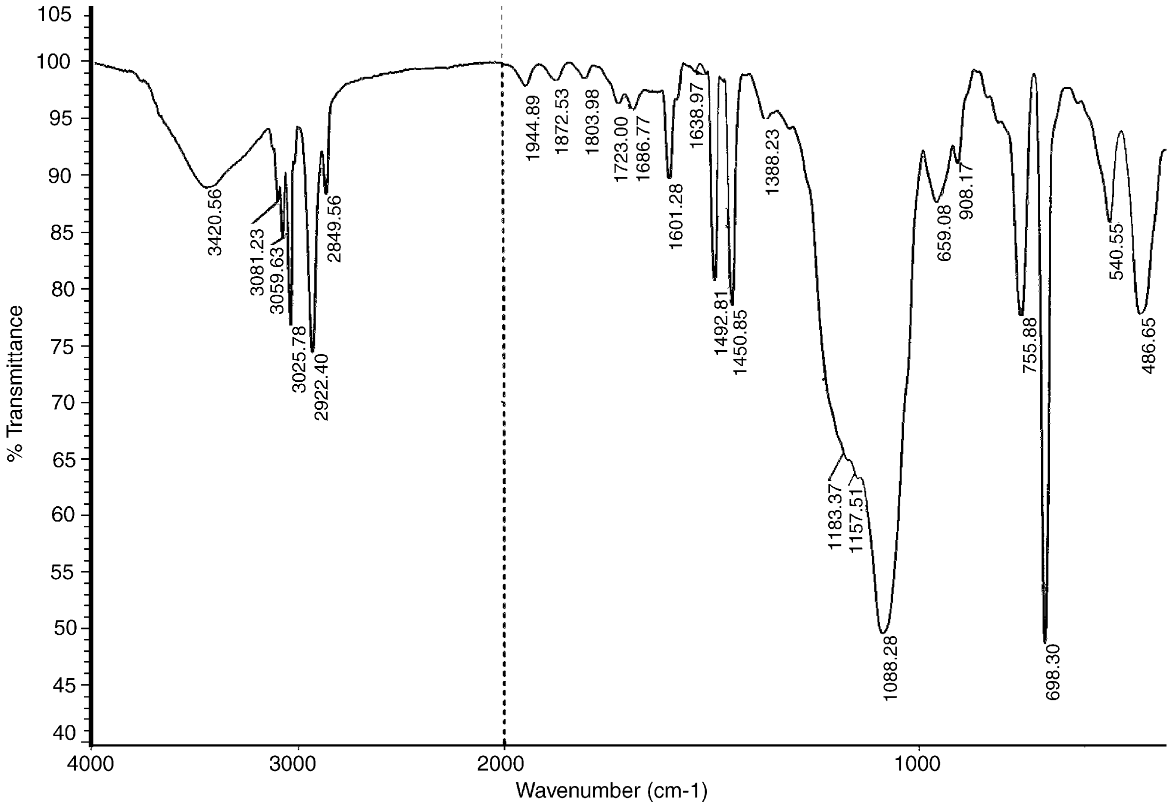


Fig. 2. FT-IR spectra of PSSNs.

3. Results and discussions

Photoiniferter-modified silica nanoparticles, VBDCSNs, was prepared through the UV induced reaction of VBDC and MPSNs as shown in Scheme 1. The *N*,*N*-diethyldithiocarbamyl group content of the macro-photoiniferter was 0.08 m mol g^{-1}, calculated from the sulfur elemental analysis of VBDCSNs (Table 1). Compared with the γ-methacryloxypropyl groups content of MPSNs (1.03 m mol g^{-1}), it was very small. This maybe due to the big space hindrance of VBDC and it is difficult to being polymerized.

The mechanism of the surface-initiated (SI) controlled/“living” radical polymerization of styrene from VBDCSNs was illustrated in Scheme 2 [16]. The *N*,*N*-diethyldithiocarbamyl group was used to initiate the radical polymerization of styrene on the surface of silica nanoparticles to form an outer polymer shell around the inorganic silica core. The iniferter photochemically dissociates into a carbon-centred radical $R^{\bullet}$ and a sulfur-centred radical $Et2NSCS^{\bullet}$. The $R^{\bullet}$ radical is reactive and initiates polymerization; the $Et2NSCS^{\bullet}$ radical, with low reactivity, mainly reacts with growing radicals $RM_n^{\bullet}$ to form dormant covalent species, which can again photochemically dissociate.

According to the above mechanism of polymerization with VBDCSNs photoiniferter, the immobilized silica nanoparticles bearing *N*,*N*-diethyldithiocarbamyl structure can serve as a photoiniferter and the polymerization should display characteristics of a living radical polymerization. The percentage of grafting (PG%) (the weight ratio of the grafted polystyrene and the VBDCSNs charged) and the conversions of styrene (the weight ratio of the grafted polystyrene and the styrene monomer used) with different UV irradiation time were calculated from the elemental analyses results (Table 1) shown in Fig. 1. They all increased linear with increasing of the polymerization time and reached 276.3% with a conversion of styrene of about 35% after a UV irradiation time of 18 h. Both of them are nearly a straight line. It was resulted from the low density of *N*,*N*-diethyldithiocarbamyl groups on the surfaces of the photoiniferter and there would be less effect of the space hindrance in the surface-initiated polymerization of styrene, although the PG% and C% were low after long times of UV irradiation.

The FTIR spectrum of the polystyrene grafted silica nanoparticles (PSSNs) was shown in Fig. 2. The vibration bands corresponding to both diethyldithiocarbamyl group (1601 cm^{-1}), PS (3003, 3026, 3060, 3081, 3105, 755 and 698 cm^{-1}) and silica (1088, 540 and 467 cm^{-1}) were all found. It indicated that polystyrene had been successfully grafted onto the surface of silica nanoparticles by the proposed UV surface-initiated (SI) controlled/“living” radical polymerization at ambient temperature.

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