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Quantification of surface-anchored RAFT chain transfer agent on silica particles

Zongqiang Duan[a,b,1], Zhenyuan Qu[b,1], Fenglin Hu[b], Yunxia Yang[a], Guorong Chen[a], Hong Xu[b,*]

[a] Key Laboratory for Ultrafine Materials of Ministry of Education, School of Material Science and Engineering, East China University of Science and Technology, Shanghai 200237, PR China
[b] School of Biomedical Engineering, Med-X Research Institute, Shanghai Jiao Tong University, Shanghai, 200030, PR China

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ABSTRACT

Surface-initiated RAFT polymerization has received much attention in the fabrication of spherical brushes. The grafting density of surface-anchored RAFT chain transfer agents (SA-RAFT CTA) exerts great influence on the properties of the resulting spherical brushes. In this paper, we proposed a modified measurement approach named fitting method to determine the grafting density of SA-RAFT CTA by means of UV–vis spectrometry using about 100-nm silica particles (SiPs) as model materials. On the basis of an in-depth investigation on the UV absorption and scattering characteristics of SiPs, the background absorption of SiPs in RAFT CTA modified SiPs (SiP@RAFT) was accurately identified by fitting method and the error introduced by the scattering interference of SiPs was greatly suppressed. With such improvement, the present method exhibits a much higher accuracy and sensitivity (the detection limit is 2.6 μmol/g), which makes it an ideal method for SA-RAFT CTA quantification, especially for particles with a relatively large size. The present method was successfully applied in the study of RAFT CTA immobilization kinetics and the synthesis of spherical poly(tert-butyl ester) brushes (SiP@P(t-BA)) with tunable brush thickness.

Introduction

Reversible addition-fragmentation chain transfer (RAFT) polymerization has been proved to be one of the most promising living radical polymerization (LRP) techniques and successfully applied in the tailored design of polymers with various architectures [1]. Recently, much attention has been directed to the fabrication of spherical polyelectrolyte brushes using surface-initiated RAFT polymerization (SI-RAFT) from particles to achieve a good control over the brush structure [2]. As a general SI-RAFT process, RAFT chain transfer agent (RAFT CTA) is firstly anchored onto the particles, followed by SI-RAFT to form the brush layer. Hence the grafting density of RAFT CTA is very crucial to the SI-RAFT process, exerting great influence on the polymerization kinetics, molecular weight, molecular weight distribution (polydispersity) and grafting density of the brush layer [3,4]. The accurate quantification of surface-anchored RAFT CTA (SA-RAFT CTA), then, is of vital significance to obtain the desired brush structure in a controlled manner.

A few methods have been used for the quantitative determination of SA-RAFT CTA on particles. Thermogravity analysis (TGA) was employed in many works as a general method to estimate the amount of SA-RAFT CTA [5–9]. However, it suffers from the problem of poor specificity and accuracy due to the fact that TGA only provides information about total weight loss. An accurate attribution to the weight loss region of SA-RAFT CTA is hardly available, and side-reactions or impurities absorbed on the particles may greatly contribute to the error of quantification. An error of 0.5%∼1 wt. % corresponds to an error of ca. 25–50 μmol/g SA-RAFT CTA (assuming that SA-RAFT CTA has a molecular weight of 200 g/mol), which is hardly acceptable given the fact that the total amount of SA-RAFT CTA usually falls into 10–100 μmol/g order-of-magnitude. In addition, TGA is not applicable to polymeric particles, which will be burnt out together with the surface organics. Thus TGA can only be regarded as a quasi-quantitative measurement. Elemental analysis (EA) is another frequently used method [10–14]. The amount of SA-RAFT CTA can be identified by quantification of the characteristic sulfur element, which generates a more accurate result in comparison with TGA. EA usually has a detection limit of 0.03 mg for sulfur element, corresponding to 23 μmol/g and 16 μmol/g for dithioester and trithioester RAFT CTA, respectively (assuming that 20 mg of samples are used in a single test). When the grafting

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* Corresponding author. Tel.: +86 21 62933743; fax: +86 21 62932907.
E-mail address: xuhong@sjtu.edu.cn (H. Xu).

[1] These authors contributed equally to this work.

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density of RAFT CTA is even lower, great amounts of samples are needed to render a reliable result.

Still another useful quantitative method is based on UV–nis spectrometry taking advantage of the strong characteristic absorption of thiocarbonyl group, which is inherently present in all RAFT CTA. The UV–vis adsorption properties of RAFT CTA has been extensively studied in solution [15] and applied in end-group analysis of polymers [16]. Fukuda's and Benicewicz's groups further used UV-Vis spectrometry to determine the SA-RAFT CTA on 14 and 20 nm colloidal silica particles (SiPs) [3,4]. And the latter reports a grafting density of 0.15–0.68 CTA/nm^2. This method is simple, low-cost, sensitive and even more reliable than EA because the intensity of UV adsorption is directly correlated with the amount of characteristic thiocarbonyl groups in RAFT CTA (sulfur element in other forms will not contribute to the adsorption). In the strict sense, as we know, Lambert–Beer's law is only applicable to homogeneous, non-scattering systems. Thus the quantification of SA-RAFT CTA using UV–vis spectrometry is faced with the interference from particles, in which scattering of particles in UV–vis spectrum is a major problem. With the increase of particles size, the scattering problem will be more prominent, accompanied by a lowered grafting amount of SA RAFT CTA due to the lowered specific surface area, leading to a low signal-to-noise ratio in UV–vis spectrometry. A close examination on the reliability, sensitivity and optimized measurement condition to minimize interference from particles is quite necessary before this method can be extended to larger particle systems with an enhanced accuracy for the determination of SA-RAFT CTA.

In this paper, we conducted a detailed investigation on the measurement using SiPs as model particles and extended UV–vis spectrometry of SA-RAFT CTA to particles with a larger size. With the aim of minimizing interference from particles, we studied the scattering property of SiPs before and after RAFT CTA modification (SiP@RAFT) and proposed a modified measurement approach. This approach was further employed to study the kinetics of RAFT CTA immobilization reaction. SiP@P(t-BA) spherical brushes with different polymer grafting densities was also synthesized under the guidance of this approach to study the effect of SA-RAFT CTA immobilization density on RAFT polymerization.

Experimental

Materials and instrumentation

Materials

SiPs were synthesized by stöber method and their sizes were tuned by adjusting the concentration of water and ammonia [17]. The RAFT CTA was also synthesized by our laboratory. The synthesis process was described in our previous work [18]. Modification of RAFT CTA on the SiPs was conducted in ethanol at 70 °C and its grafting density was tuned by controlling the concentration of RAFT CTA and the reaction time. All the reagents used in this study were obtained from China National Medicines Group Shanghai Chemical Reagents Company and used as received.

Instrumentation

UV–vis spectrum was recorded by a Unicam UV300 UV-vis spectrometer. The hydrodynamic diameter (D_h) and dispersity of particles was studied by dynamic light scattering (DLS) using a Malvern Nano ZS particle size analyzer. Thermogravimetric analysis (TGA) of SiP@P(t-BA) spherical brushes was performed on a Netzsch (TG 209 F1 Iris) thermogravimetric analyzer in air at a heating rate of 10 °C/min. The number-average molecular weight of P(t-BA) was obtained by gel permeation chromatography (Waters, USA) equipped with a differential refractive index detector and a multiangle light scattering detector (Wyatt Technology Corp., USA) using THF as the eluent.

Methods

Fitting method

SiP@RAFT dispersed in ethanol with predetermined concentration (mg/mL) was subjected to UV–vis spectrometry. The absorbance of SiP@RAFT at ten different wavelengths (260, 265, 270, 308, 355, 360, 365, 370, 380, and 390 nm) were measured and the nine measurement points except that of 308 nm were used to fit the background absorption curve of SiPs using an exponential function. The 308-nm absorbance (A_{308}) of SiPs in SiP@RAFT was identified from the fitting function. The grafting amount of SA-RAFT CTA, named N (μmol/g) is calculated by the following equation:

$$N = \frac{A_{308SiP@RAFT} - A_{308\,SiPs}}{\varepsilon_{308} \cdot l \cdot C} \times 10^6 \qquad (1)$$

where $A_{308SiP@RAFT}$ is the absorbance of SiP@RAFT at 308 nm, $A_{308SiPs}$ is the background absorbance of SiPs at 308 nm identified by fitting method. ε_{308} (L·mol^{-1}·cm^{-1}) is the molar absorption coefficient of the RAFT CTA. l (cm) is the optical length, which is 1 cm in this article. C (mg/mL) is the concentration of SiP@RAFT.

One-point method

Instead of measuring absorbance of SiP@RAFT at ten difference wavelengths, only two wavelengths (308 and 360 nm) were measured. The ratio of SiPs absorbance at 360 nm to that at 308 nm was determined to be 0.673 ± 0.017, which is quite stable for SiPs with different size. Hence the A_{308} of SiPs in SiP@RAFT is obtained by dividing the 360-nm absorbance (A_{360}) of SiP@RAFT by the factor of 0.673. The grafting amount of SA-RAFT CTA is calculated by the following equation:

$$N = \frac{A_{308SiP@RAFT} - \frac{A_{360SiP@RAFT}}{0.673}}{\varepsilon_{308} \cdot l \cdot C} \times 10^6 \qquad (2)$$

Subtractive method (comparison method)

In this method, the A_{308} of the original SiPs was regarded as the background in SiP@RAFT and subtracted [19]. In other words, $A_{308SiPs}$ in Eq. (1) is the A_{308} of original SiPs. This method was employed as the comparison method.

Synthesis of SiP@P(t-BA) spherical brushes with different grafting densities

Three SiP@RAFT particles with different grafting densities of SA-RAFT CTA were synthesized by adjusting the adding concentration of RAFT CTA and the reaction time. The grafting densities were determined to be 0.75, 0.32, and 0.10 CTA/nm^2 by the fitting method.

SiP@P(t-BA) spherical brushes with different grafting densities (named as SiP@P(t-BA)-HD, SiP@P(t-BA)-MD, and SiP@P(t-BA)-LD for brushes with high, medium, and low densities, respectively) were synthesized using the above-mentioned three SiP@RAFT particles via surface initiated RAFT (SI-RAFT) polymerization. 200 mg of SiP@RAFT particles were transferred into 4.2 mL toluene and mixed with 7.8 mL t-BA in a dry schlenk tube. Free RAFT CTA, benzyl dodecyl carbonotrithioate, was added to help control the polymerization and ratio of monomer to RAFT CTA (including free RAFT CTA and SA-RAFT CTA) was set as 150. Finally, 7.36 mg of AIBN was added into the mixture. After four cycles of freeze-pump-thaw, the system was sealed up and placed into an oil bath thermostat at 70 °C for 3 h. Then the polymerization was quenched by putting into an ice bath and opening to the air. The product was diluted by toluene and centrifuged to obtain SiP@P(t-BA) spherical brushes, which