Dyes and Pigments 160 (2019) 572–578

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Mechanistic investigation on fluorescence instability of AIE polymeric nanoparticles with a susceptible AIEgen prepared in miniemulsions

Xiaoqin Liang[a], Yaxin Hu[a], Junjie Lou[a], Zhihai Cao[a,*], Lin Liu[a], Yijia Wang[a], Zujin Zhao[b,**], Dongming Qi[a], Qinmin Cui[c,***]

[a] Key Laboratory of Advanced Textile Materials and Manufacturing Technology and Engineering Research Center for Eco-Dyeing & Finishing of Textiles, Ministry of Education, Zhejiang Sci-Tech University, Hangzhou, 310018, China
[b] Center for Aggregation-Induced Emission, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou, 510640, China
[c] School of Pharmacy, Hangzhou Medical College, 481 Binwen Road, Hangzhou, 310053, China

ARTICLE INFO

Keywords:
Fluorescence stability
Aggregation-induced emission
Hydrolysis
Miniemulsion polymerization
AIE polymeric nanoparticles

ABSTRACT

Fluorescence stability is a key index for application of aggregation-induced emission (AIE) polymeric nanoparticles (NPs) as fluorescent probes. In this work, the temperature-dependent fluorescence stability of AIE polystyrene (PSt) NPs with a susceptible AIE luminogens (1-methyl-1,2,3,4,5-pentaphenylsilole, MPPS), which was named as PSt/MPPS NPs, was thoroughly investigated. The PSt/MPPS NPs in aqueous emulsions showed an abnormally fast fluorescence loss at the temperatures close to or above the glass transition temperature of the matrix polymer. The poor fluorescence stability of PSt/MPPS NPs at elevated temperatures could be ascribed to the continuous hydrolysis of MPPS. Firstly, the MPPS molecules at the surface of NPs undergo hydrolysis. At elevated temperatures, the incorporated MPPS inside the NPs can freely diffuse to the particle/water interface to undergo hydrolysis under the drive of MPPS concentration difference between the interior and surface of NPs, leading to an almost complete fluorescence quenching. Based on the fluorescence loss mechanism of the PSt/MPPS NPs, several effective strategies were designed to improve fluorescence stability of AIE polymer/MPPS NPs, for example through using matrix polymers with a relatively less hydrophobicity or a higher glass transition temperature to replace PSt, or fabrication of a less hydrophobic polymer shell on the PSt/MPPS NPs.

1. Introduction

Since proposed by Tang et al., in 2001, aggregation-induced emission (AIE) luminogens (AIEgens) have been extensively investigated due to their unique emission mechanism and wide applications in biology, disease diagnostics, optoelectronic devices, sensors, and advanced coatings [1–8]. For biological applications, it is a commonly-used strategy to incorporate AIEgens in a nanoscale polymeric matrix to fabricate AIE polymeric nanoparticles (NPs) [9–11]. Compared with nano-aggregates of pristine AIEgens, AIE polymeric NPs may embody better aqueous dispersibility, more tunable brightness, more controllable particle size, and more flexible surface functionalization [12–14]. Thus, the AIE polymeric NPs may display good biocompatibility, high-quality cell imaging, and targeting ability to specific cells or tissues [15,16].

In recent years, many innovative fabrication techniques, such as solvent evaporation technique [17], self-assembly of amphiphilic copolymers with AIEgens [18,19], flash nanoprecipitation of block copolymers with AIEgens [20], surface functionalization of NPs with AIEgens [21], semi-continuous polymerization [22], and water-borne heterophase polymerization techniques, such as emulsion and miniemulsion polymerization techniques [23–26], have been devised to prepare versatile AIE polymeric NPs. In water-borne miniemulsion polymerization systems, many hydrophobic monomer droplets are homogenously dispersed in an aqueous continuous phase [27]. The polymeric NPs are formed mainly through monomer droplet nucleation, and each monomer droplet can be regarded as one separated nanoreactor [27]. Versatile functional NPs could be conveniently prepared through *in situ* encapsulation of functional compounds by polymers during the miniemulsion polymerization process [28,29]. In our previous work, AIE polymeric NPs were prepared through miniemulsion copolymerization of common monomers, like styrene (St) and methyl

* Corresponding author.
** Corresponding author.
*** Corresponding author.
E-mail addresses: zhcao@zstu.edu.cn (Z. Cao), mszjzhao@scut.edu.cn (Z. Zhao), cuiqm@hmc.edu.cn (Q. Cui).

https://doi.org/10.1016/j.dyepig.2018.08.051
Received 5 August 2018; Received in revised form 26 August 2018; Accepted 27 August 2018
Available online 30 August 2018
0143-7208/

methacrylate (MMA), and a silole-based AIE functional monomer 1-allyl-1-methyl-2,3,4,5,-tetraphenylsilole (AMTPS) [23,24]. The photoluminescence (PL) intensity of AIE polymeric NPs could be accurately tuned by the AMTPS content. The synthesized AIE poly (methyl methacrylate) (PMMA) NPs displaying high brightness, low cytotoxicity, and efficient cellar uptake, are of high potential in biological applications. It is well accepted that the fluorescence stability at various circumstances is an important index for AIE probes. In our previous work, the fluorescence stability of AIE PMMA NPs under continuous UV light irradiation was evaluated [23]. However, for AIE polymeric NPs with susceptible AIEgens, like silole-based AIEgens, their fluorescence stability may also been influenced by many external factors, such as temperature, type of the dispersed media and matrix polymers, and pH value of the dispersed media [30].

In this work, AIE polymeric NPs were prepared through miniemulsion polymerization using 1-methyl-1,2,3,4,5-pentaphenylsilole (MPPS) as the model susceptible AIEgen. The temperature-dependent fluorescence stability of polystyrene (PSt)/MPPS NPs was thoroughly investigated. Although the MPPS molecules were encapsulated in the PSt matrix, the PSt/MPPS NPs in aqueous emulsions displayed an abnormally faster fluorescence loss than the pristine MPPS particles at elevated temperatures. A possible fluorescence loss mechanism of the PSt/MPPS NPs based on the continuous hydrolysis of MPPS was proposed. On the basis of this mechanism, the fluorescence stability of AIE polymeric NPs with a susceptible AIEgen was successfully enhanced by using matrix polymers with a less hydrophobicity or a higher glass transition temperature (T_g) to replace PSt, or fabrication of a less hydrophobic polymeric shell on the PSt/MPPS NPs to suppress the continuous hydrolysis of MPPS.

2. Experimental section

2.1. Materials

MPPS was synthesized according to the Curtis method [31]. ^{1}H NMR, UV–vis absorption spectrum, and PL spectra of MPPS in the mixed THF/water solvent with various water fractions are provided in supporting information (Fig. S1 and S2). MMA (AR, Tianjin Kermel Chemical Reagent Co., Ltd.) and St (AR, Tianjin Yongda Chemical Reagent Co., Ltd.) were purified through reduced distillation, and stored in a refrigerator before use. Butyl methacrylate (BMA, 99%, Shanghai Aladdin Chemistry Co., Ltd.) was purified through passing an aluminum oxide column. Hexadecane (HD, 99%, Acros Organics), isopar M (a C12−C14 isoparaffinic mixture, Exxon Mobil), sodium dodecyl sulfate (SDS, CP, Shanghai Aladdin Chemistry Co., Ltd.), potassium persulfate (KPS, AR, Shanghai Aladdin Chemistry Co., Ltd.), toluene (AR, Zhejiang Sanying Chemical Reagent Co., Ltd.), and ethanol (AR, Hangzhou Gaojing Fine Chemical Co., Ltd.) were used as received. Tetrahydrofuran (THF, 99%, Sinopharm Chemical Reagent Co., Ltd.) was purified through distillation in the presence of sodium benzophenone ketyl immediately prior to use. Self-made deionized water was used in all experiments.

2.2. Preparation of AIE polymeric NPs

A series of MPPS-doped polymeric NPs, including PSt/MPPS NPs, PMMA/MPPS NPs, and poly (butyl methacrylate) (PBMA)/MPPS NPs were prepared through miniemulsion polymerization. Firstly, 0.05 g MPPS was dissolved in a mixed solution of monomer (10 g) and HD (0.6 g) to form a hydrophobic solution, which was used as the oil phase. Secondly, 0.2 g SDS was dissolved in 125 g deionized water to form an aqueous solution, which was used as the water phase. Thirdly, both solutions were mixed and preemulsified with a magnetic agitation of 700 rpm at 40 °C for 15 min to obtain a crude emulsion. Subsequently, the crude emulsion was sonicated at 400 W for 9 min by using a pulse mode (work 12 s, break 6 s) to form a monomer miniemulsion. After addition of KPS (0.05 g), the monomer miniemulsion was poured into a 250 mL four-necked reactor, and the reactor was kept in a preheated oil bath at 70 °C. The polymerization ran for 3 h under a magnetic agitation of 400 rpm in a nitrogen atmosphere to obtain various polymer/MPPS NPs.

2.3. Fluorescence stability of polymer/MPPS NPs at various temperatures

Ten gram of the original polymer/MPPS NP emulsions were used for each temperature-dependent fluorescence stability measurement. The polymer/MPPS NP emulsions were heated at various temperatures. A small amount of samples were periodically withdrawn in the heating process for fluorescence measurements. The typical PL spectra of PSt/MPPS NP emulsion heated at 70 °C for various time lengths are shown in Fig. S3. The peak PL intensity was used to evaluate the time-dependent fluorescence loss of polymer/MPPS NPs at various temperatures.

2.4. Fluorescence stability of MPPS NPs in water

MPPS (0.01 g) was dissolved in 2 g ethanol, and then mixed with 25 g deionized water. The mixed solution was equally divided into 4 parts, and they were put into oil baths preheated at 30 °C, 50 °C, 60 °C, and 70 °C, respectively. The samples were periodically withdrawn, and their PL spectra were recorded on a Hitachi F-4600 spectrofluorometer. The peak PL intensity was used to evaluate the time-dependent fluorescence loss of MPPS in water at various temperatures.

2.5. Preparation and fluorescence stability of PSt/MPPS blended films

Firstly, MPPS and PSt were completely dissolved in THF. Afterwards, uniform thin PSt/MPPS films were fabricated by spin-coating and evaporation of THF. The PL spectra of the PSt/MPPS films heated at 70 °C for various time lengths were recorded on the Hitachi F-4600 fluorescence spectrophotometer. The peak PL intensity was used to evaluate the time-dependent fluorescence loss of the PSt/MPPS blended films.

2.6. Preparation and fluorescence stability of PSt/MPPS NP emulsion in isopar M

The solid sample of PSt/MPPS NPs was obtained through drying the aqueous emulsion of PSt/MPPS NPs at 45 °C for 3 h by a rotary evaporator. Isopar M was added to the PSt/MPPS solid sample, and then the dispersion was stirred at room temperature until it became a uniform milky-white emulsion. For evaluation of the fluorescence stability of the PSt/MPPS NP emulsion in isopar M, the emulsion was heated in an oil bath at 70 °C for 19 h under magnetic agitation of 400 rpm, and the PL spectrum of the heated powder sample collected from the emulsion was recorded on the Hitachi F-4600 fluorescence spectrophotometer.

2.7. Preparation and fluorescence stability of core–shell PMMA@PSt/MPPS NPs

The core PSt/MPPS NPs were prepared as follows: 0.05 g MPPS was dissolved in 7 g St and 0.6 g HD to form an oil solution; 0.2 g SDS was dissolved in 125 g water to form an aqueous solution; the monomer miniemulsion was prepared with the same conditions of pre-emulsification and sonication as the preparation of other polymer/MPPS NPs; 0.05 g KPS was added into the monomer miniemulsion to start the reaction; the polymerization ran at 70 °C; After 2 h, 3 g MMA was dropwise added into the polymerization system, and the polymerization was continued to run for another 3 h to obtain PMMA@PSt/MPPS NPs.

The emulsion of PMMA@PSt/MPPS NPs was heated at 70 °C for