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UV light-initiated RAFT polymerization induced self-assembly

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5 Unlike the conventional polymerization induced self-assembly (PISA) triggered by thermal stimuli, reversible addition-fragmentation chain transfer (RAFT) PISA initiated by UV light with a friendly and easily manipulated way as a new strategy is exploited to prepare polymeric micelles at room temperature.

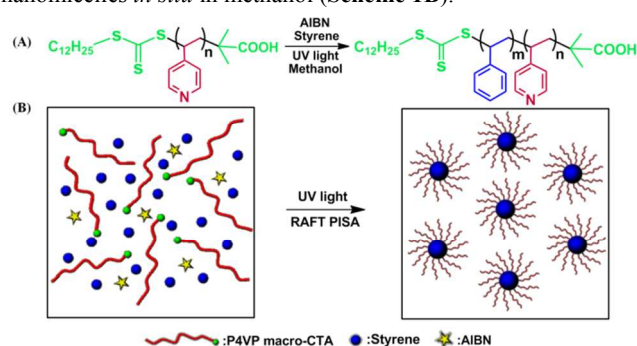
The self-assembly of block copolymers in selective solvent has been regarded as a powerful protocol to fabricate polymeric nanostructures (e.g., micelles, worms and vesicles),¹ which has attracted a great deal of attention due to their potential application in many fields, such as drug delivery, catalysis and bioimaging. The traditional self-assembly processes (e.g., direct dissolution, dialysis, film rehydration)² are usually required multiple steps and operated time consuming in very low concentration (<1%), which prevents its further commercialization. The recent emerging strategy of polymerization induced self-assembly (PISA)³ based on controlled radical polymerization (CRP) can achieve the preparation of polymeric nanostructures with high solids content in one-pot polymerization. PISA thus provides a powerful possibility to prepare the polymeric nano-materials for large scale in the purpose of commercial applications.

As one of the most popular methods for PISA, reversible addition-fragmentation chain transfer (RAFT)⁴ mediated PISA is suitable and convenient for direct preparation of polymeric nanostructures. Significant progress has been made by RAFT-mediated PISA both in emulsion and dispersion systems. For examples, Pan and coworkers^{5,6} reported the PISA of styrene (St) by using poly (4-vinylpyridine) (P4VP) macro-RAFT agent in one-pot polymerization at 80°C. Subsequently, Charleux,^{7,8} Armes⁹ and Lowe¹⁰ extended the RAFT-mediated PISA to the polymerization of various functional polymer monomers with different macro-RAFT agents. Armes and coworkers¹¹ investigated the PISA of 2-hydroxypropyl methacrylate (HPMA) by using hydrophilic poly (glycerol monomethacrylate) (PGMA) macro-RAFT agent in concentrated aqueous solution at 70 °C. All above mentioned PISA process usually require higher thermal stimuli to induce the polymerization.

Unlike thermal stimuli, light is a friendly and easily manipulated resource,¹² which can conduct the polymerization process at low temperature (usually at room temperature).¹³⁻¹⁵ Recently, the research of photo-controlled living radical polymerization (photo-CRP) are mainly focused on the preparation of well-defined polymers, such as homopolymer,¹⁶ block copolymers,¹⁷ and graft copolymers.¹⁸ Among all of the studied photo-CRP methods, the photo-RAFT polymerization has proven to be an extremely useful technique for a variety of monomers at various conditions.¹⁹⁻²¹ While many efforts have been achieved to prepare copolymers in solution polymerization

by photo-RAFT, there is still no report about light induced RAFT PISA. Since RAFT has some distinctive features such as the universal adaptation of monomers and the mild polymerization conditions, therefore, it is of significant importance to exploit light induced RAFT PISA as an alternative strategy for the fabrication of polymeric nanostructures.

In this communication, we reported a new RAFT PISA method initiated by UV light to prepare polymeric micelles in one step polymerization process at room temperature (Scheme 1). In order to compare with thermal induced RAFT PISA directly, a similar recipe^{5,6} was used to investigate the UV light initiated RAFT PISA. It was conducted by using P4VP macromolecular chain transfer agent (macro-CTA) with an end-capped reactive trithiocarbonate group as chain extender, styrene as monomer, 2,2'-azobis(isobutyronitrile) (AIBN) as photoinitiator (Scheme 1A). As the polystyrene (PS) chains grow, the P4VP-*b*-PS block copolymers undergo spontaneous self-assembly to form polymeric nanomicelles *in situ* in methanol (Scheme 1B).



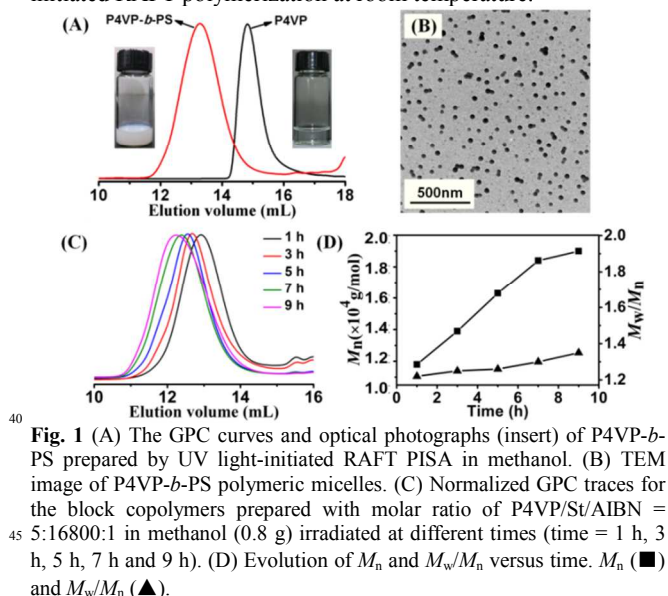
Scheme 1 (A) Synthesis of the P4VP-*b*-PS block copolymers by UV light-initiated RAFT PISA at room temperature. (B) Formation of polymeric micelles by UV light-initiated RAFT PISA in methanol.

It has been reported that UV light can induce polymerization through the photochemical activation of trithiocarbonate compounds.^{22,23} However, the rate of the polymerization by just using the photolysis of trithiocarbonate was very slowly.²⁴ Furthermore, the photochemical decomposition of the trithiocarbonate moieties under UV radiation can unavoidably lead to permanently premature termination, thus affecting the living character at long irradiation time.²⁵ The addition of photoinitiator can remarkably suppress the retardation effect in RAFT process, thus significantly shortening the initialization period and accelerating overall RAFT process at room temperature.²⁶ In that case, the photoinitiator added into the system could generate primary free radicals to initiate the polymerization, so the trithiocarbonate only played a main role of RAFT CTA in the photopolymerization. Here, we select AIBN as photoinitiator in the polymerization.²⁷ The photolysis of AIBN

was studied by UV-vis spectra (Fig. S1) and ^1H NMR spectra (Fig. S2) under the UV lamp ($\lambda_{\text{max}} = 365$ nm). The photolysis half-life ($t_{1/2}$) of AIBN was around 0.5 h in d_7 -methanol, determined by the plot of the relative concentration of AIBN at $\delta = 1.70$ ppm to time (Fig. S3).

Fig. 1A shows a typical example of the successful polymerization of UV light-initiated RAFT PISA at room temperature. After the UV irradiation for 3 h, the color of the polymerization solution was changed from transparent into milky, indicating the successful chain extension of P4VP macro-CTA. This was further confirmed by gel permeation chromatography (GPC) measurement. The results showed that the molecular weight (M_n) was increased from 6500 to 12600 g/mol, which was consistent with the data from ^1H NMR (Fig. S4). Transmission electron microscope (TEM) was used to analyze the morphologies of the obtained aggregates created by UV induced RAFT PISA. It is obvious to see that uniform spherical nanostructures with an average size of 30 nm (Fig. 1B) are obtained. The striking feature of the developed UV light-initiated RAFT PISA is that the uniform spherical micelles can be prepared not only *in situ* in one step polymerization at room temperature, but also with high solids content.

The polymerization kinetics of the UV light-initiated RAFT PISA was further systemically investigated via GPC (Fig. 1C). As shown in Fig. 1D, it is clear to see that the molecular weights are gradually increased with the polymerization time under UV irradiation. Furthermore, the results indicated that the M_n increased linearly at early stage (less than 7 h of UV irradiation) and almost maintained unchanged after 7 h of UV irradiation. The *in situ* ^1H NMR spectroscopy (Fig. S5) was also used to monitor the polymerization kinetics by controlling the reaction in d_7 -methanol, showing a similar evolution of the molecular weight with GPC. Compared with thermal dispersion polymerization, the UV light initiated RAFT polymerization of styrene has very low monomer conversion and much slower polymerization rate. This is due to styrene is not a high activity monomer for UV light-initiated RAFT polymerization at room temperature.²⁶



The characteristic of PISA is able to tune the sizes of polymeric nanostructures precisely in one step polymerization.³ In the present study, it was also found that the sizes of polymeric micelles could be tuned by changing the St content in UV light-initiated RAFT PISA process. TEM images in Fig. 2A-C shows

the average sizes of the obtained polymeric micelles were about 35, 40 and 60 nm, corresponding to the St content of 0.46 g, 0.91 g and 1.82 g, respectively. This controlled trend of polymeric micelles size was also confirmed by dynamic light scattering (DLS) (Fig. 2D). The GPC curves (Fig. 2E) further show that the molecular weight increased by adding higher styrene content in the reaction system, which resulted in the bigger sizes of micelles (see the details of M_n and PDI etc. in Table S1). This is because the higher content of St can maintain the growth rate even after the microphase separation of P4VP-*b*-PS polymeric micelles.⁶

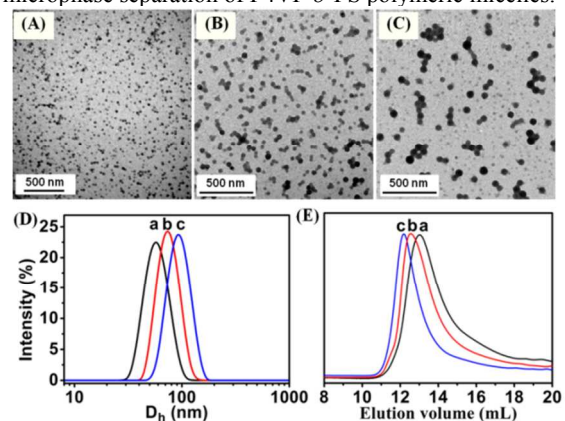


Fig. 2 TEM images of P4VP-*b*-PS micelles formed at (A) 0.46 g St, (B) 0.91 g St, (C) 1.82 g St. (D) DLS results for polymeric spherical micelles in A-C. (E) GPC traces for the block copolymers from A-C. Experimental conditions: UV light intensity: $I_{365} = 2.50$ mW cm^{-2} , irradiation time: 9 h, 25 $^{\circ}\text{C}$.

From previous discussion in Fig. 1C-D, there was almost no more increase of the molecular weight after the micelles were formed at 7 h. Further investigation was carried out to find that the formed polymeric micelles via the UV light-initiated RAFT PISA could achieve the secondary polymerization by heating at 80 $^{\circ}\text{C}$. The color of polymeric micelles changed from milky to pink after heating (Fig. 3A). TEM images in Fig. 3B and 3C showed that the sizes of polymeric micelles increased to 150 nm after heating from previous 40 nm micelles prepared by the UV light-induced RAFT PISA. Moreover, the GPC (Fig. 3D) and ^1H NMR results (Fig. S6) confirmed the increase of molecular weights of the formed block copolymers, indicating the successful secondary polymerization. The possible reason is that a certain amount of AIBN residuals are encapsulated in spherical micelles, which cannot be irradiated by UV light^{28, 29} to trigger the polymerization. Furthermore, the successful thermal polymerization also indicated that the trithiocarbonate moieties in the system still had living character for further polymerization.

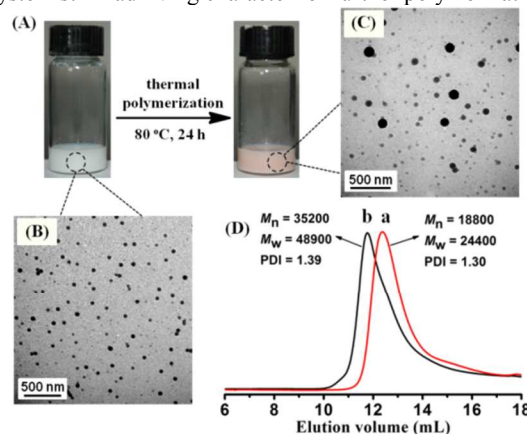


Fig. 3 (A) Optical photographs of the UV light-initiated RAFT PISA for 9

h (left) and the secondary polymerization by heating at 80 °C for another 24 h (right). TEM images of the P4VP-*b*-PS assemblies obtained (B) before and (C) after the secondary polymerization by heating. (D) GPC traces for the prepared block copolymers (a) before and (b) after the secondary polymerization. Experimental conditions: the molar ratio of P4VP/St/AIBN = 5:16800:1 in methanol (0.8 g).

In summary, inspired by the convenience of photo-CRP and based on the conventional RAFT PISA induced by thermal stimuli. It can be carried out under mild conditions to prepare polymeric micelles with high solids content at room temperature. The size of the polymeric spherical micelles could be adjusted through the increase of monomer content or the secondary polymerization by conventional RAFT dispersion polymerization triggered with thermal stimuli. It should be noted that thermal induced RAFT PISA has evolved into a stage where production of higher order and adjustable morphologies, it is still a challenge for UV light induced RAFT PISA to control the morphology evolution. Further investigation in selecting suitable photo-initiator and monomer etc. during our new strategy is being carried out. There is a great possibility that the facile UV light-initiated RAFT PISA method can be extended to a variety of monomers or other CRP methods. We believe the UV light induced RAFT PISA triggered by UV light with a friendly and easily manipulated way should be developed into a powerful alternative strategy to achieve various polymer nanomaterials in large scale which will make it useful for both academia and industry applications.

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Notes and references

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TOC

Reversible addition-fragmentation chain transfer (RAFT) polymerization induced self-assembly (PISA) initiated by UV light as a new strategy is exploited to prepare polymeric nanomicelles at room temperature.

