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Regular Article

A step-wise self-assembly approach in preparation of multi-responsive poly(styrene-*co*-methyl methacrylate) nanoparticles containing spiropyran

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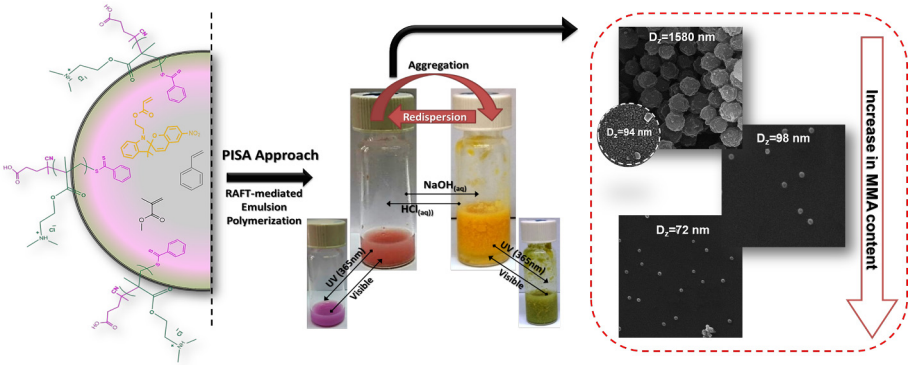
GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Surfactant-free emulsion polymerization has become favorable due to circumventing instability issues reasonably. Incorporation of an appropriate hydrophilic macroRAFT, could provide controlled in-situ self-assembly via copolymerization with hydrophobic monomers into polymer particles. So far, this approach has mostly been studied in dispersion systems and further studies are needed in emulsions. Beside the corresponding mechanistic studies, the prepared latex particles would potentially exhibit smart behaviors by choosing stimuli-responsive monomers.

Experiments: Poly(styrene-*co*-methyl methacrylate) latexes were prepared by utilizing pH-responsive polydimethylaminoethyl methacrylate as the hydrophilic segment through polymerization induced self-assembly (PISA). A systematic study on the effect of MMA amount, role of smart spiropyran ethylacrylate (SPEA) comonomer and the synthesized macroRAFT for inducing efficient assembly has been performed comparatively for the first time.

Findings: SEM and DLS analyses showed the effect of MMA content on the obtaining of spherical particles with bimodal or monodisperse size distributions in both series of samples. Kinetic studies through conversion measurements along with GPC analysis revealed that the incorporation of MMA and SPEA strongly affected the efficiency of in-situ self-assembly, particle formation and RAFT-controllability on molecular weights. Ultimately, acido/basochromism, pH-responsivity and UV-responsivity of the prepared latexes were verified and the results showed their facile and fast multi-responsivity.

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1. Introduction

Surfactant-free emulsion polymerization (SFEP) techniques are highly desirable due to some problems such as surfactant migration, sensitivity to different chemical, physical or mechanical conditions and environmental issues in the latexes prepared by using conventional surfactants [1,2]. It would be possible to design copolymer chains with pre-determined structures with the ability of self-stabilization by involving reversible deactivation radical polymerization (RDRP) processes such as reversible addition fragmentation radical transfer (RAFT), nitroxide mediated (NMP) or atom transfer (ATRP) radical polymerizations [3]. In RAFT-mediated cases, hydrophilic chains are prepared in a former step as the macroRAFT through solution polymerization. Afterward, it will be extended from the reactive chain-end with a hydrophobic segment as long as it becomes capable of micellization in the continuous phase (mostly water or alcohol) and continues until termination to give a dispersion [4,5]. This approach is entitled as polymerization induced self-assembly (PISA) [6,7]. If the incorporated macroRAFT is chosen in a way that it holds a specific functionality, the corresponding latex would mimic this potential activity. Considering the capability of stimuli-responsivity, this field addresses a breakthrough in raising applicability of these latexes in various fields such as biomedical applications, paints and coatings, drug delivery and sensors [8]. Stimuli-responsivity can be triggered by pH, light, temperature, CO_2 and other physical, chemical or even mechanical stimulants [9].

Among the stimuli-responsive polymers, guanidine -, amidine- and tertiary amine-containing groups like poly(diethylaminoethyl methacrylate) (PDEAEMA) or poly(dimethylaminoethyl methacrylate) (PDMAEMA) are able to reversibly absorb/desorb protons in acidic/basic media [10,11]. Consequently, they would have different polarities and solubility in response to different pH conditions [12]. Localizing such pH-responsive polymers on the surface of nanoparticles would provide sufficient charge density for latex stabilization, when they are positively charged. Polystyrene (PS) and poly(methyl methacrylate) (PMMA) latexes have been previously prepared through surfactant-free miniemulsion polymerization by using a dithioester-capped PDMAEMA as the macroRAFT [13]. SFEP of styrene has also been reported by using PDEAEMAH$^+$Cl$^-$ macroRAFT [14]. There is another report on the electro-sterically stabilized PS latexes by using PDMAEMAH$^+$Cl$^-$ macroRAFT, polyethylene glycol (PEG)-macroRAFT and PEG-b-PDMAEMAH$^+$Cl$^-$ and their stability has been compared [15]. In another attempt, partial hydrolysis of PDMAEMA to methacrylic acid (MAA) was carried out and the obtained poly(DMAEMAH$^+$Cl$^-$-co-MAA) was employed as an appropriate stabilizer for polymerization of MMA through PISA approach [16]. Furthermore, switching "on" and "off" their surface activities by means of variations in pH would induce redispersibility to the corresponding latex nanoparticles [17–19]. This is highly demanded in practice, due to the lowering of transportation costs and issues [20,21].

Incorporating another smart component would prompt multi-responsivity to the obtained polymer chains for obtaining advanced materials. Spiropyran (SP) is a well-known photochromic compound and has found vast applications in various research fields, such as targeted drug delivery and cell imaging, optical data storage, gas/pH-sensors, biosensors, metal ion identification, anti-counterfeiting papers, pH/polarity indicators [22]. C—O bond in the spirocarbon dissociates to form conjugated zwitterionic mercocyanine (MC) isomer by UV irradiation (365 nm) and returns to the pyran ring by visible light or heat [23]. The spirocarbon is also susceptible to dissociation and re-bonding by several triggers such as solvent polarity, pH or temperature [24,25]. This isomerization can be well-controlled by its incorporation into a polymer matrix or nanoparticle. Having nano-scaled particles containing SP has been proved to be essential for obtaining efficient photochromic responsivity to provide adequate transparency to the incident beam and suppression of unwanted light scattering [26]. SP can be grafted onto the polymer chains via its functional groups [27]. However, the most popular methods for preparation of these nanoparticles are emulsion or miniemulsion polymerization systems [28–32].

There are growing number of investigations on SP-based polymeric latex particles and their optimizations [33–35]. However, combination of SFEP, RAFT technique and PISA process would be a fascinating method in preparation of latexes bearing SP groups. A PEG-based macroRAFT was prepared and used as the modulator to manipulate the polymerization of polyspiropyran methacrylate (PSPMA) to obtain PEG-b-PSPMA [36]. This amphiphilic copolymer could self-assemble into micelles which are able to be disrupted by UV irradiation and being regenerated by irradiation with visible light. Spherical micelles were obtained in a work which consisted of PS cores embedded with a photo-responsive benzoxa-diazole derivative and also thermo-responsive poly(N-isopropyl acrylamide) (PNIPAAm) and SPMA as coronas [37]. Then, they were embedded with a pH-responsive rhodamine-based monomer as a dye with efficient multi-responsivity through RAFT polymerization. PNIPAAm-b-sodium [2-(acrylamido)-2-methylpropane sulfonate] tagged with a SP dimer at the PNIPAAm end was synthesized by RAFT polymerization to give multi-responsive micelles [38]. It was found that the block copolymer was responsive to four different triggers, *i.e.* light, temperature, metal ion and pH. Beside these studies on the preparation of stable micelles, photochromic polymeric vesicles composed of the amphiphilic poly(4-vinylpyridine-*co*-SPMA)-b-PS copolymer were prepared via PISA process of styrene in methanol by means of a SPMA-based RAFT agent with stimuli-responsivity [39].

After 20 years from the first report of RDRP in the aqueous dispersions [40], this subject still suffers from some problems. Hitherto some techniques have been developed and examined [41]. However and as mentioned above, there are only a few studies on SFEP and more specifically on PISA process for preparing photochromic latexes. Toward these developments and better elucidation of the process, this work represents a mechanistic approach on the RAFT-mediated PISA process for preparation of P(St-*co*-MMA) along with incorporation of spiropyranethyl acrylate (SPEA) comonomer to induce multi-responsivity to the corresponding latexes. In this work, PDMAEMA-macroRAFT (PDM-macroRAFT) was prepared firstly through RAFT-mediated solution polymerization. Its employment as the hydrophilic block for preparation of an amphiphilic P(St-*co*-MMA) copolymer with capability of in-situ self-assembly was examined next. This structure was expected to show pH-responsivity for obtaining redispersible latexes. By considering this facile approach, pH- and photo-responsive P(St-*co*-MMA) latexes containing SPEA were then prepared. Mechanism of particle formation, efficiency of RAFT-mediated polymerization and also the role of comonomer ratios were investigated from kinetic studies. Finally, multi-responsivity of the obtained latexes was examined to confirm the existence and performance of the stimuli-responsive moieties in the polymer nanoparticles.

2. Materials and methods

2.1. Materials

2-(Dimethylaminoethyl) methacrylate (DMAEMA), styrene (St) and methyl methacrylate (MMA) were provided from Merck Chemical Co. (Germany) and used as received and without further purification. SPEA was synthesized based on our previous report