RAFT-Photomediated PISA in Dispersion: Mechanism, Optical Properties and Application in Templated Synthesis

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Diblock copolymer nanoparticles were prepared without initiator by visible-light photopolymerization-induced self-assembly ("photo-PISA") in dispersion. Both copolymer blocks were synthesized via an original photomediated reversible deactivation radical polymerization mechanism combining reversible addition-fragmentation chain transfer (RAFT) and reversible photolysis of the C-S bond of the chain-transfer agent (CTA). The photosensitive CTA was a commercially available trithiocarbonate, namely cyanomethyl dodecyl trithiocarbonate. The first hydrophilic poly(hydroxyethyl acrylate) block was synthesized in solution, then used as a macro-CTA for the dispersion polymerization of styrene in methanol/water. Spherical nanoparticles with a narrow size distribution and an average diameter of 20-40 nm were achieved. The copolymers were characterized by size-exclusion chromatography (SEC) in DMF, which confirmed the control of the reaction, with relatively narrow molecular weight distributions ($M_w/M_n \leq 1.30$). Two regimes can be discerned in the RAFT-mediated dispersion photo-PISA: a slow particle nucleation (4-15 % conv.) followed by particle growth. A steady number of particles was obtained when steric stabilization was adequate. Study of the optical properties by UV-Vis spectrophotometry enabled to separate the respective contributions of absorption and scattering during the PISA process. Finally, we demonstrated that the copolymer nanoparticles could act as soft templates for the synthesis of mesoporous carbon materials.

Introduction

Over the last decade, polymerization-induced self-assembly (PISA) has emerged as a versatile method for the preparation of well-defined block copolymer nanoparticles with various morphologies.¹ In a PISA mechanism, self-assembly occurs during the synthesis itself of the amphiphilic diblock copolymer, when the first solvophilic block is chain-extended with the second solvophobic one.² Reaching a critical chain-length for this latter block results in the spontaneous copolymer self-assembly. The solvophilic block acting as a steric stabilizer is generally prepared via solution polymerization, while the insoluble block can be formed via two different methods: aqueous *emulsion* polymerization involving insoluble monomers,³⁻⁵ or *dispersion* polymerization, using on the contrary, soluble monomers.⁶

Scheme 1 Overview of the photomediated controlled radical polymerization mechanism combining RAFT with the reversible photolysis of the chain-transfer agent.

There are two main advantages of PISA over more conventional post-polymerization self-assembly techniques:⁷⁻⁹ (i) higher solids content (10 -50 wt% instead of < 1 wt%);¹⁰ and (ii) reduced processing and purification steps.¹¹

Therefore, nano-objects derived from PISA have attracted much attention for a diverse range of applications, including enzyme catalysis,¹² drug delivery,^{3,13} nanostructured films,¹⁴ stimuli-responsive smart nanomaterials¹⁵ etc. With the exception of recent works resorting to ring-opening metathesis¹⁶ or non-controlled¹⁷ mechanisms, the fast development of PISA has been mostly driven by reversible-deactivation radical polymerizations. Also referred to as

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Fig. 1 Synthesis of poly(hydroxyethyl acrylate) macro-CTA via photomediated RAFT polymerization in 1,4-dioxane. Subsequent chain extension via dispersion photo-PISA of styrene in a methanol/water mixture.

controlled radical polymerizations (CRPs), these mechanisms have made possible to synthesize a broad range of diblock copolymer structures. Among the different reported CRPs, reversible addition–fragmentation chain transfer (RAFT, **Scheme 1**) utilizing thiocarbonylthio compounds as chain-transfer agents (CTA) is by far the most widely used in PISA, owing to its versatility in terms of compatible monomers and experimental procedures.⁹

RAFT-mediated PISA has been developed mostly using thermal initiators, but the alternative use of radiation-mediated processes grouped under the term “photo-PISA”, can be an even more advantageous route.¹⁸ A major asset is the possibility to perform PISA over a wide temperature range. For example, ambient temperature contributes to reducing energy consumption or making the process safer. In addition, the use of low temperatures has proved beneficial for the synthesis of polymer nanoparticles encapsulating thermally sensitive proteins,¹⁹ possessing CO₂- or thermo-responsive properties,^{20–22} and bearing reactive functional groups.²³ A second advantage of photo-PISA is to drive high-throughput synthesis. To maximize the number of tests run in parallel, Tan et al. demonstrated for example that photo-PISA could be performed in multi-well open plates through an enzyme (glucose oxidase) reacting with dissolved oxygen.²⁴

Exploiting the different photo-induced RAFT mechanisms,²⁵ three photo-PISA approaches have been already reported in the literature. The most common strategy consists simply in using a photoinitiator^{26–37} rather than a thermal initiator. In order to avoid non desired absorption by the RAFT agent, near UV^{35,36} or visible irradiation³⁷ is usually preferred. In 2014, a second approach was proposed by Boyer and co-workers, who demonstrated that visible photoredox catalysts such as Ir(ppy)₃ and [Ru(bpy)₃]Cl₂ can be used to activate the RAFT agent via a photo-induced electron transfer.^{38–41} At the center of the current study is a third approach based on the reversible β -cleavage of the excited state, formed under irradiation, of the thiocarbonylthio compound (**Scheme 1**), which yields an initiating alkyl radical and a thiyl radical. As result, the CTA acts also as a photoinitiator. Another distinctive feature of this mechanism over its photoinitiated homologue is the temporal control of polymerization. Because the RAFT agent photoactivation becomes reversible, it is possible to (re)initiate or to terminate reversibly the propagating chains by switching *on* or *off* the light source. The photochemical reactivity of thiocarbonylthio compounds has been known for a long time.^{42,43} However, its interest for photomediated polymerization has been recently revived thanks to the

discovery that photolysis can occur not only under UV irradiation but also visible light. In this latter case, the weak absorption corresponding to the $n \rightarrow \pi^*$ transition is exploited instead of the main and dramatically more intense $\pi \rightarrow \pi^*$ band.^{44,45} Using visible light, a better control of RAFT-mediated polymerizations was reported in solution, possibly as a result of minimized side/termination reactions involving the thiyl radicals.^{36,43,44,46–48} Although this route obviates the need of additional photoinitiator or photocatalyst, it is surprisingly the least developed in photo-PISA. There has been only two reports on RAFT-mediated photo-PISA relying on the reversible photolysis of a CTA, namely 4-cyano-4-((dodecylsulfanylthiocarbonyl)sulfanyl)pentanoic acid, under visible light at 460 nm. In these studies, the dispersion polymerization of benzyl methacrylate⁴⁶ and hydroxypropyl methacrylate⁴⁹ was performed in presence of a solvophilic macro-CTA based on poly(oligo(ethylene oxide)).

Following a similar methodology, new spherical and narrowly distributed diblock copolymer nanoparticles (20 – 40 nm) were synthesized by RAFT dispersion polymerization of styrene (St) at 35 °C and 20 % w/w solids using a poly(hydroxyethyl acrylate) (PHEA) macro-CTA as steric stabilizer block (**Fig. 1**). Both solvophilic PHEA block and solvophobic polystyrene (PS) block were obtained via photomediated RAFT polymerization by leveraging the reversible β -fragmentation of the commercial *S*-cyanomethyl-*S*-dodecyltrithiocarbonate (TTC) RAFT CTA under blue light ($\lambda_{\text{max}} = 472$ nm). Emphasis was made on two domains poorly investigated so far in photo-PISA: the mechanism of particle formation/growth, as well as the characterization of optical properties throughout the dispersion polymerization. Finally, we showed that the resultant PHEA-*b*-PS nanoparticles can be utilized as template in the synthesis of mesoporous carbon materials. Interconnected and tuneable mesopores were achieved in the size range of 20–30 nm, a domain generally inaccessible with conventional liquid crystal mesophases.

Experimental section

Materials

Hydroxyethyl acrylate (HEA; Tokyo Chemical Industry (TCI); >96%) was purified by passing through a basic alumina column (Sigma-Aldrich) prior to use. Styrene (St; Sigma-Aldrich ; $\geq 99\%$) and 1,4-dioxane (Sigma-Aldrich; 99.5%) were distilled under reduced pressure over CaH₂ prior to use. Methanol (Fischer Chemical; $\geq 99\%$), *S*-cyanomethyl-*S*-dodecyltrithiocarbonate

(TTC; Sigma-Aldrich; 98%), phloroglucinol (Sigma-Aldrich; $\geq 99\%$), glyoxylic acid (Sigma-Aldrich; $\geq 99\%$) and diethyl ether (Sigma-Aldrich; $\geq 99\%$) were used as received.

Synthesis

Photomediated RAFT polymerization of HEA in solution (ex. PHEA₂₅-TTC). In a typical synthesis, HEA (4.04 g, 34 mmol), TTC (0.396 g, 1.2 mmol) and dioxane (12.16 g) were charged into a Schlenk tube equipped with a stirring bar. The mixture was degassed by three freeze–pump–thaw cycles before being placed under nitrogen. The tube was then placed in a pre-heated oil bath at 25 °C and irradiated during 5 h in an immersion type photoreactor containing a blue LED spot light ($\lambda = 472$ nm, 547 mW cm⁻²) (Fig. S1). Aliquots were regularly withdrawn to determine the conversion by ¹H NMR analysis (0.1 mL dissolved in 0.5 mL of D₂O). After 5 h (HEA conversion of 58 %), the polymer was recovered by precipitation into 200 mL of diethyl ether, before being dried under vacuum overnight to give ~1.5 g of purified PHEA. The macro-CTA was then characterized by SEC in THF ($M_n = 6.36 \cdot 10^3$ g mol⁻¹, $M_w/M_n = 1.26$).

Synthesis of PHEA-PS diblock copolymer particles via photomediated dispersion PISA of St (ex. PHEA₂₅-PS₁₁₈). In a typical synthesis, PHEA₂₅-TTC (0.266 g, 0.082 mmol), St (1.721 g, 16.5 mmol) and a methanol/water mixture (8.18 g/0.43 g, 95/5 w/w %) were charged into a Schlenk tube equipped with a stirring bar. The mixture was degassed by three freeze–pump–thaw cycles before being placed under nitrogen. The tube was then placed in a pre-heated oil bath at 35 °C and irradiated during 70 h in an immersion type photoreactor ($\lambda = 472$ nm, 547 mW cm⁻²). In the kinetic study, the mean degree of polymerization of the PS block was systematically varied by adjusting the irradiation time. The syntheses involving PHEA macro-CTA of different lengths were performed at the same monomer/solvent weight ratio of 1/3. Three aliquots of 0.1 mL were regularly withdrawn during reaction. The first one was used for ¹H NMR analysis (after dissolution in 0.5 mL of CDCl₃) to determine St conversion. The second one was employed for SEC measurements to determine polymer molecular weights. Finally, DLS and TEM measurements were carried out using the third aliquot (see next section for details).

Synthesis of mesoporous carbon materials. Phloroglucinol (0.205 g, 1.63 mmol) and glyoxylic acid monohydrate (0.152 g, 2.05 mmol) were dissolved under stirring at room temperature in methanol (2.96 g). This solution was then added to a non-purified PHEA₂₅-PS₁₁₈ copolymer dispersion (4.96 g, mass of copolymer = 0.62 g). The obtained turbid solution was transferred into smooth glass dishes and left at room temperature for about 6 h in order to evaporate methanol solution and the non-reacted St. Subsequently, a thermal consolidation of the phenolic resin was performed at 60 °C overnight to increase the cross-linking density of the phenolic resin framework. The resultant material was pyrolysed at 600 °C under inert atmosphere (Ar) for 2 h.

Characterizations

Size exclusion chromatography (SEC-THF). Accurate molecular weights of macro-CTAs were determined by SEC in THF at 35 °C. Samples with precise concentrations around 1–3 mg mL⁻¹ were prepared and filtered (PTFE membrane; 0.20 μ m) before injection. The flow rate was 1.0 mL min⁻¹. The following Agilent 1260 Infinity series setup was used: a G1310B isocratic pump; a G1322A degasser; a G1329B auto-sampler; a G1316A thermostated column compartment equipped with a set of Polymer Laboratories ResiPore columns (nominal particle size: 3 μ m; porosity: 2 μ m) composed of a guard column (50 $\times$ 7.5 mm) and two columns (300 $\times$ 7.5 mm); a G1314B variable wavelength detector; a G7800A multidetector suite equipped with a MDS refractive index detector and a MDS viscometer detector. Universal calibration was performed using a set of EasiVial polystyrene (PS-M) standards. Agilent GPC/SEC software and multi-detector upgrade were used to determine molar mass values and distributions.

Size exclusion chromatography (SEC-DMF). Molecular weights of PHEA-PS copolymers were determined by SEC in DMF with additive of 0.01 M LiBr at 50 °C. For sample preparation, an aliquot was precipitated in 2 mL of diethyl ether under intense stirring, then the copolymer collected after filtration was dried and dissolved in DMF. Solutions of samples with precise concentrations around 1–3 mg mL⁻¹ were then prepared and filtered (PTFE membrane; 0.20 μ m) before injection. The flow rate was 0.9 mL min⁻¹. The following Agilent 1260 Infinity series setup was used: a G1311A isocratic pump; a G1322A degasser; a G1313A auto-sampler; a G1316A thermostated column compartment equipped with a set of Polymer Laboratories ResiPore columns (nominal particle size: 3 μ m; porosity: 2 μ m) composed of a guard column (50 $\times$ 7.5 mm) and two columns (300 $\times$ 7.5 mm); a G1314B variable wavelength detector; a G7800A multidetector suite equipped with a MDS refractive index detector. Relative calibration was performed using a set of EasiVial poly(methyl methacrylate) (PM) standards. Agilent GPC/SEC software and multi-detector upgrade were used to determine molar mass values and distributions.

Nuclear magnetic resonance (NMR). ¹H spectra were recorded in D₂O (homopolymers) or CDCl₃ (diblock copolymer) at 300 MHz on a Varian Mercury spectrometer.

Dynamic light scattering (DLS). Hydrodynamic diameter of diblock copolymer nano-objects were determined using a VASCO nanoparticle size analyzer (Cordouan technologies) with a 15 mW laser operating at a wavelength of 658 nm. The scattered light is detected at an angle of 135°. Prior to measurements, samples were diluted 20-fold.

Transmission electron microscopy (TEM). The TEM images of copolymer nanoparticles and carbon mesoporous materials were obtained with a JEOL ARM-200F instrument working at 200 kV. Latex samples were diluted 200 times, cast onto the TEM grid, and dried overnight at room temperature.

UV-Spectroscopy. UV-Vis spectra were obtained using a JascoV730 UV/Vis/NIR spectrophotometer. The selected range of wavelengths was 280–800 nm.

LED lamp. The emission spectrum and irradiance of the LED were determined using a Field Max II (COHERENT) optical

spectrum analyzer and a Power Max PM10 powermeter at a distance of 1 cm.

Details on *nitrogen adsorption measurements* are available in the Electronic Supplementary Information (ESI).

Results and discussion

I. Synthesis of PHEA macro-CTA by photomediated RAFT polymerization in solution

In order to synthesize nano-objects based on amphiphilic diblock copolymers, a series of hydrophilic macro-CTAs was first synthesized by photomediated RAFT polymerization of hydroxyethyl acrylate (HEA) in 1,4-dioxane at ambient temperature (25°C). The initiator-free synthesis was carried out under blue light irradiation (provided by a 472 nm LED) and using the trithiocarbonate TTC as RAFT CTA (Fig. 1). TTC was selected because of its β -photocleavage ability at this wavelength⁴⁷ and the fact that relatively unstable primary alkyl radicals can be produced. A short radical lifetime drives fast radical recombination allowing therefore to minimize degradation reactions.⁴⁸ Fig. 2a shows a typical kinetic profile for the synthesis of PHEA₅₈-TTC. The determination of the conversion of HEA by ¹H NMR (Fig. S2) evidenced a pseudo first order kinetics, in agreement with a constant concentration of propagating species during the polymerization. A conversion of 58 % was achieved within 5 h of irradiation. The SEC traces revealed narrow dispersities (Fig. 2b) over the reaction, suggesting a controlled mechanism. In addition, the linear relationship between the measured molecular weights and conversions (Fig. 2c) fully supported a well-controlled RAFT synthesis. Following the same procedure, other PHEA macro-CTAs exhibiting different chain lengths ($DP_n = 25, 52$ and 82) were successfully synthesized (see complete data in Table S1 of ESI).

II. Synthesis of PHEA-PS by photomediated RAFT dispersion polymerization of styrene

II.1 Kinetic study

Fig. 2 Visible light photomediated polymerization of HEA in solution during the synthesis of PHEA₅₈-TTC. (a) Polymerization kinetics, conversion measured by ¹H NMR; (b) SEC chromatograms (RI detector) in THF; (c) Number-average molecular weight (M_n) and dispersity ($D = M_w/M_n$) with conversion; dashed line: theoretical molecular weight calculated with conversion. Experimental conditions: HEA : TTC = 100 : 1; [HEA]₀ = 2.97 M in dioxane, blue LED (547 mW cm⁻², 25 °C).

Fig. 3 Series of photographs showing the evolution of the reaction medium during the photomediated RAFT dispersion polymerization of St (synthesis of PHEA₂₅-PS_m diblock copolymer particles).

The PHEA macro-CTAs discussed above were then chain-extended with St at 35 °C in a methanol/water mixture (95/5 % w/w) using a similar photomediated RAFT approach ($\lambda = 472$ nm), and in absence of any external photoinitiator. Consistently with a PISA process in dispersion, the reaction medium progressively turned turbid as polymerization proceeded (see pictures of the reaction medium taken at different reaction times in **Fig. 3**). As depicted in **Fig. 4a**, the polymerization rate was slow and a monomer conversion of approximately 60 % was achieved after 70 h. Note that even conventional RAFT alcoholic dispersion polymerizations of St carried out at higher temperatures ($T \geq 70$ °C) is known to suffer from significantly incomplete conversion;^{50,51} a problem somehow mitigated by the addition of water.⁵² In our case, the slow polymerization can be mostly ascribed to the dramatic effect of temperature on the propagation rate constant of St ($k_p = 132 \text{ L mol}^{-1} \text{ s}^{-1}$ at $T = 35$ °C vs $k_p = 482 \text{ L mol}^{-1} \text{ s}^{-1}$ at 70 °C).⁵³ Two distinct *intervals* (I, II) corresponding to different rate behaviors were observed in the $\ln([M]_0/[M])$ versus time plot of **Fig. 4a**. This substantially differs from the first step of solution polymerization where a single linear regime was obtained (**Fig. 2a**). Irrespective of the initiation method employed, this dual rate behavior was reported by many authors in RAFT dispersion polymerization,^{26,31} and was interpreted broadly as the transformation from a “homogeneous” to “heterogeneous” polymerization. In *Interval I*, lasting typically 30–40 h, the reaction rate was extremely slow (15 % after 30 h). As can be seen in **Fig. 3** ($t = 0 - 30$ h), the medium was macroscopically homogeneous at the beginning, then slightly scattering at the end ($t = 30$ h). This suggests that this first regime includes not only the solution polymerization of the PHEA₂₅-PS_n-TTC diblock copolymer chains but also the formation of micellar particle by self-assembly (particle nucleation). Starting after 35 h, *interval II* was marked by a significant increase of the polymerization rate (2 times greater). Meanwhile, the medium became increasingly scattering (**Fig. 3**, $t = 47$ –70 h), most likely because of the gradual increase of particle (micelle) diameter (see TEM and DLS size data in **Fig. 4a**). The acceleration of St conversion translates the change of polymerization site from continuous phase to copolymer particles. The particles become favored as the main reaction site since, firstly, most copolymer chains have precipitated, and secondly, the monomer concentration

Fig. 4 (a) Polymerization kinetics for the synthesis of a PHEA₂₅-PS₁₁₈ copolymer. Conversion measured by ¹H NMR (**Fig. S2**). Evolution of particle size determined by DLS and TEM. (b) SEC chromatograms in DMF at 50 °C (RI detector) of PHEA₂₅-TTC and PHEA₂₅-PS_m diblock copolymers synthesized via photomediated RAFT polymerization in dispersion. (c) Evolution of M_n and dispersity index with monomer conversion; dashed line: theoretical molecular weight calculated with conversion. Experimental conditions: PHEA₂₅-TTC:St = 1:200; [PHEA₂₅-TTC]₀ = 7.68 mM in methanol/water mixture (95/5 w/w %), blue LED (547 mW cm⁻², 35 °C).

in particles $[M]_p$ is higher to the one in solution $[M]_s$. The high local monomer concentration within the particle core, similar to bulk monomer concentration, drives a higher propagation rate in this second interval. To support this assumption, a control experiment of PS extension performed in solution (**Fig. S3**) showed only a single and slow regime reaching only 30 % conv. after 70 h under irradiation. As polymerization proceeds, the monomer diffuses from the continuous phase into the polymer particles to replace that which has been reacted. An equilibrium (saturation) monomer concentration is thus maintained in the particles, accounting for the steady

polymerization rate observed. Because the reaction is stopped before completion, there is no hypothetical *interval III* where monomer depletion within the particles could cause a decrease of reaction rate.

The kinetic study was completed by SEC analysis in DMF as function of irradiation time, clearly evidencing the efficient re-initiation of the RAFT chain-ends and propagation of the chains (Fig. 4b). Narrow dispersities were measured ($\bar{D} \sim 1.1$), accordingly with a controlled mechanism. The controlled character was definitely confirmed by the linear relationship between the measured molecular weights and conversions (Fig. 4c). We thus demonstrate the versatility and broad applicability of the photomediated PISA synthesis by showing that the photolysis of the RAFT chain-end can be exploited to synthesize successively the solvophilic (PHEA) and solvophobic (PS) blocks.

II.2 Colloidal study

Fig. 5 TEM images of PHEA₂₅-PS_m samples taken at different times during dispersion PISA of St.

Fig. 5 shows a series of representative TEM images obtained from samples withdrawn at different intervals during the dispersion photopolymerization of St starting from PHEA₂₅-TTC macro-CTA. After 47 h of irradiation, spherical and narrowly distributed nanoparticles with increasing mean diameters were observed. Particle nucleation is assumed to take place earlier, but at shorter times, the PS block is likely too short to drive a high enough glass transition temperature necessary to preserve the integrity of the particles under the TEM beam. In agreement with this assumption, the samples taken before 30 h showed a coalesced structure. After 47 h of irradiation, narrow particle size distributions (PDI = 1.05) were obtained,

irrespective of the samples, with a mean diameter increasing from 22.5 nm for PHEA₂₅-PS₆₈ (47 h) to 31.6 nm for PHEA₂₅-PS₁₁₈ (70 h) as detailed in **Table 1**. As a result, varying irradiation time proved to be a suitable means of controlling particle size in the size range 20–40 nm. DLS studies (**Fig. 4a**) confirmed the particle growth as a function of time at a rate similar to that of the TEM data. As expected, substantially larger mean particle diameters (+ 20 nm) were measured by DLS (intensity-average diameters) that takes into account the solvation of the PHEA layer on the nanoparticle surface and the swelling of the polymer particles by residual monomer. It is also worth mentioning that these diblock copolymer nanoparticles invariably possess a spherical morphology whatever the length of the PS chains. The causes do not lie in the specificities of the mechanism (RAFT agent photolysis, low temperature) but rather in the choices made as regards DP of the stabilizer and core-forming blocks. Other trials, which go beyond the framework of this study, showed that utilizing a relatively short PHEA block and targeting sufficiently high DP for the PS block enabled to access higher-order morphologies, as extensively reported in literature.¹¹ An example leading to vesicles is reported in Supporting Information (**Fig. S4**).

III Progress of RAFT-mediated dispersion photo-PISA

Although the synthesis of diblock copolymer nanoparticles during RAFT dispersion polymerization is well documented,²⁶ only a few studies addressed the issues of nucleation process and the way particles grow.⁵⁴ The fact that our system displays slow kinetics of polymerization and a single uniform spherical morphology provides a simplified and appropriate framework to explore these mechanistic points.

III.1 Micellization

A conventional dispersion polymerization⁶ starts from a homogeneous solution.⁴⁶ Given that PHEA₂₅-TTC contains both a lyophilic group (PHEA block) and a lyophobic moiety ($-SC_{12}H_{25}$ as $-Z$ group of the RAFT agent), one might legitimately wonder about its capacity to form micelles initially in the alcoholic reaction medium. **Fig. 6a** displays the evolution of surface tension σ as a function of PHEA₂₅-TTC concentration for measurements performed in MeOH/H₂O (95/5, w/w %), containing also St to reproduce reaction medium. No significant surface tension reduction was observed in the concentration range 0 – 10⁻² mol L⁻¹, proving the absence of surface activity under our reaction conditions. By contrast, surface tension reduction was demonstrated in water in which PHEA₂₅-TTC has probably a lower affinity (72 mN m⁻¹ in pure water vs 52.5 mN m⁻¹ at 10⁻³ mol L⁻¹). As a conclusion, micelles were not present at the beginning, and polymerization of St undoubtedly took place in solution initially. This accounts from the slow polymerization in *Interval I* since the monomer concentration was low. To detect when nucleation (micellization) starts, we used a DLS-based method originally developed to determine the critical micellar concentration of amphiphilic diblock copolymers formed in solution.⁵⁵ Our hypothesis is that the onset of micellization (beginning of particle nucleation) should be marked by a sudden increase in

the intensity of scattered light (I_s). **Fig. 6b** shows the evolution of scattered

Table 1. Colloidal data of PHEA₂₅-PS_m particles formed by dispersion photo-PISA at two different temperatures (35 and 55 °C).

Time h	<i>m</i> (PS degree of polymerization)	<i>D_p</i> nm	<i>PDI</i>	<i>N_p</i> L ⁻¹	<i>N_{agg}</i>	<i>S_{agg}</i> nm ²
PHEA ₂₅ -PS _m (35 °C)						
47	68	22.5 ± 0.4	1.03	1.31·10 ¹⁹	368	4.3
50	76	22.6 ± 0.3	1.04	1.26·10 ¹⁹	353	4.6
54	78	24.8 ± 0.5	1.05	1.01·10 ¹⁹	456	4.3
70	118	31.6 ± 0.4	1.05	6.74·10 ¹⁸	686	4.6
PHEA ₂₅ -PS _m (55 °C)						
24	76	24.0±0.3	1.03	1.13·10 ¹⁹	410	4.4
47	160	41.2±0.6	1.03	4.00·10 ¹⁸	1160	4.6
54	160	41.8±0.5	1.02	3.85·10 ¹⁸	1200	4.6
70	160	42.1±0.6	1.04	3.75·10 ¹⁸	1230	4.5

D_p – Diameter of particles determined by TEM. *N_p* – Number of particles per liter of the reaction mixture. *PDI* – Dispersity index. ⁵⁶ *N_{agg}* – Number of RAFT chain-ends per particle. *S_{agg}* – Area occupied by 1 RAFT chain-end function on the surface of the particles.

Fig. 6 (a) Surface tension of a MeOH:H₂O (95/5, w/w %) mixture for different concentrations of PHEA₂₅-TTC as determined by the Wilhelmy plate method. The typical concentration of macro-CTA used in photomediated RAFT polymerization in dispersion is 7.68 mM. (b) Scattered intensity (mcps–mega counts per second, at low concentration is proportional to particles concentration) determined by DLS technique from aliquots withdrawn during photo-PISA via RAFT polymerization in dispersion.

III.2 Particles growth

To elaborate the mechanism of photo-PISA, several colloidal data were determined quantitatively: *particles number* (*N_p*, concentration of polymer particles in units of number of particles per liter), *mean aggregation number* (*N_{agg}*, i.e. the number of block copolymer chains in a single nanoparticle), *surface area stabilized by a copolymer chain* (*S_{agg}*). **Table 1** summarizes their evolution for different mean DP (*m*) of the PS core-forming block (details on calculation are provided in ESI). These data were obtained from a combination of TEM and ¹H NMR spectroscopy analysis for the dispersion polymerization of the PHEA₂₅ macro-CTA. Because TEM particle size values were accessible from *Interval II*, only the mechanism of particle growth could be examined in detail.

Between 47 and 70 h, the particle size increase (from 22.5 nm to 31.6 nm) was accompanied by a 2-fold decrease in *N_p* (from 1.3·10¹⁹ L⁻¹ to 6.7·10¹⁸ L⁻¹) and larger *N_{agg}* (from 368 to 686). In this case, the steric stabilization of PHEA₂₅ block is likely to be insufficient to withstand the growth of the PS core and the resultant increase of particle surface area. In accordance with this hypothesis, *S_{agg}* was found to be relatively constant (~4.3–4.6 nm²), regardless of PS chain length or particle size. Such mechanism where particle growth requires the incorporation of new copolymer chains to stabilize the newly formed surface area was already reported by the groups of Zhang and Armes.^{54,57} This trend was exacerbated when the reaction was carried at 55 °C instead of 35 °C (Table 1), which resulted in larger particle diameters (42.1 nm). In this case, the drop of *N_p* was even more pronounced because the larger DP of PS (160 instead of 118) can drive the incorporation more polymer chains. Another plausible explanation is that a higher temperature causes more particles coalescence.

Table 2. Colloidal data of PHEA₅₂-PS_m and PHEA₈₅-PS_m particles formed by dispersion photo-PISA.

Time h	<i>m</i> (PS degree of polymerization)	<i>D_p</i> nm	<i>PDI</i>	<i>N_p</i> L ⁻¹	<i>N_{agg}</i>	<i>S_{agg}</i> nm ²
PHEA ₅₂ -PS _m (35°C)						
47	48	20.3±0.4	1.03	1.90·10 ¹⁹	244	5.3
54	52	21.0±0.4	1.03	1.78·10 ¹⁹	260	5.3
70	110	24.0±0.4	1.03	1.80·10 ¹⁹	257	7.0
PHEA ₈₅ -PS _m (35°C)						
47	78	21.0±0.4	1.06	2.76·10 ¹⁹	168	8.3
54	92	20.0±0.4	1.06	3.45·10 ¹⁹	134	9.4
70	114	20.5±0.5	1.08	3.57·10 ¹⁹	130	10.2

D_p – Diameter of particles determined by TEM. *N_p* – Number of particles per liter of the reaction mixture. *PDI* – Dispersity index.⁵⁶ *N_{agg}* – Number of RAFT chain-ends per particle. *S_{agg}* – Area occupied by 1 RAFT chain-end function on the surface of the particles.

Scheme 2. Schematic representation of photo-PISA mechanism. (*N_p* is the number of particles per liter of the reaction mixture).

Table 2 provides similar colloidal characteristics for PISA syntheses performed with PHEA₅₂-TTC and PHEA₈₅-TTC. In both instances, *N_p* and *N_{agg}* remain unchanged during the polymerization. Consistently, the area occupied by PHEA blocks on the particle surface is larger for longer blocks and tends to increase with conversion. This result can be understood on the basis of the stronger steric stabilization of longer solvophilic blocks, which makes possible particle growth without the need for additional copolymer chains in the particle. This indicates that the observed increase in particle size in this case is simply the result of the growth of the PS core.

III.3 General mechanism of particle nucleation/growth

Two intervals (*I*, *II*) can be discerned in the RAFT-mediated dispersion photo-PISA presented in **Scheme 2**. *Particle nucleation* occurs in *Interval I*. The main mechanism for the formation of polymer particles is homogeneous nucleation involving the self-assembly of solution-polymerized copolymer chains. As revealed by DLS analysis, nucleation begins as early as 8 h (only 6–8 St units), making monomer partitioning inside the PS core-forming block of the micelles possible. Nevertheless, the polymerization remains slow due to a low number of particles. A long nucleation period occurs with particle number increasing slowly with time, and the medium becoming more turbid. Its duration varies only in the conversion range 4–15 % (DP of St increasing from 6 to 30), but

it runs between 8 and 35 h because of the slow propagation of St in solution. At the end of *Interval I*, nucleation stops and no new particles are generated (but *N_p* is not necessarily constant). In *interval II*, polymerization proceeds in the polymer particles, and the system undergoes change of reaction kinetics. The high number of polymer particles swollen by monomer drives both a constant and higher polymerization rate. A steady-state number of particles can be preserved when steric stabilization is adequate (PHEA₅₂ and PHEA₈₅). With shorter PHEA stabilizers (PHEA₂₅), the particle diameter increase requires the addition of new copolymer chains through possibly two ways: particle coalescence or migration of individual chains from one particle to another. The occurrence of this second mechanism was evidenced by a simple experiment where a shot of divinylbenzene acting as a cross-linker (3 w % with respect to St) was added to the PHEA₂₅-PS₁₁₈ latex. Gelation was observed within 24 h of irradiation, and clear indications of cross-linking between particles were evidenced by TEM (**Fig. S5**). Conversely, in the absence of exchange of copolymer chains between particles, cross-linking would be limited to PS core, thus preventing gelation.

IV Optical properties

Despite its impact on polymerization progress, very few studies on photo-PISA address the issue of optical properties.⁵⁵ In regular transmission, the apparent absorbance A_λ of a diluted diblock copolymer latex may be expressed as:

$$A_\lambda = E_\lambda l = (K_\lambda + S_\lambda) l \quad (1)$$

where

E_λ : extinction coefficient [cm⁻¹]
 K_λ : absorption coefficient [cm⁻¹]
 S_λ : scattering coefficient [cm⁻¹]
 l : optical path length [cm]

Fig. 7a shows a series of absorption spectra of PHEA₂₅-TTC macro-CTA in the range 300 – 400 nm taken throughout St dispersion polymerization. They clearly show that the extinction coefficient E_λ is the combined result of both

Fig. 7 (a) UV-Vis absorption spectra of PHEA₂₅-TTC macro-CTA in the range 300 - 400 nm throughout St dispersion polymerization. (b) Fitted scattering coefficient (S_λ^{Fit}) at 500 nm versus particles average diameter (D_p). (c) Estimated absorption coefficient K_λ^{TTC} of PHEA₂₅-PS_m during dispersion photo-PISA.

absorption and light scattering as soon as particles are formed ($t > 47$ h). The λ_{max} (310 nm) of the absorption band of the π, π^* -transition of TTC-based RAFT agent is clearly visible in all spectra, while scattering contribution increases during irradiation. In the selected spectral range > 280 nm, only the RAFT agent absorbs (St, PS and PHEA have a negligible absorption above 300 nm). Consequently, the eq. 1 can be simplified as:

$$E_\lambda = K_\lambda^{TTC} + S_\lambda \quad (2)$$

The challenge is the quantitative differentiation of both absorption K_λ^{TTC} (cm⁻¹) and scattering S_λ (cm⁻¹) coefficients. Because there is no absorption between 500 nm and 800 nm

($K_\lambda^{TTC} = 0$), in this range, E_λ is thus simply equal to S_λ (eq. 2). Given the small droplet diameters (less than 0.1 times the wavelength), Rayleigh theory applies and the experimentally determined S_λ may be proportional to the inverse of the wavelength to the power four. In agreement with this hypothesis, a range of simple fitting plots $S_\lambda^{Fit} = k\lambda^{-4}$ showing an excellent agreement with the experimental S_λ plots could be built (Fig. S6). The validity of our fitting was also supported by the linear correlation between S_λ^{Fit} and the intensity-average diameters of particles (D_p) to the power six predicted by the Rayleigh theory (Fig. 7b). The final step consisted in using the calculated S_λ^{Fit} data in the 280-500 nm range to estimate separately the absorption coefficient $K_\lambda^{TTC} = E_\lambda - S_\lambda^{Fit}$. Fig. 7c shows the K_λ^{TTC} values during the dispersion polymerization. Clearly, a decrease of K_λ^{TTC} within the time of reaction can be observed. An analogous study performed in solution revealed a similar trend, suggesting that the change in the microenvironment of the RAFT agent, from solution to particles, was not accountable (Fig. S3). As emphasized by Qiao and co-workers, a more likely reason is the partial photolytic degradation of RAFT agent.^{48,58} Up to 12% of photodegradation was determined after 15 hours of irradiation by these authors. In our case, longer irradiation (70 h) together with higher irradiance (547 mW cm⁻²) explain the higher extent of degradation.

V Template synthesis of mesoporous carbon materials

The PHEA-PS spherical nanoparticles described above were utilized as template for the synthesis of three-dimensional mesoporous carbons, i.e. with pores ranging from 2 to 50 nm. Intensive research currently takes place on these materials due to their high technological potential in fields such as adsorption,⁵⁹ catalysis⁶⁰ or sensors.⁶¹ Generally, only macroporous structures (> 50 nm) can be synthesized using latex templates.⁶⁰ With the exception of microemulsion polymerization,⁶² most polymerization processes in dispersed system giving birth to polymer particles are not appropriate, because the accessible sizes are larger than 50 nm under standard synthesis conditions. More suitable templates to elaborate mesoporous carbons include rather colloidal (or mesoporous) silica as well as block copolymer mesophases.⁴⁵ Unlike these conventional approaches, we propose photo-PISA-derived particles as highly suitable soft template because of several unique features: access to spherical nanosized particles with diameters < 50 nm, size uniformity (PDI = 1.04) and tunability (see Table 1).⁵⁹

In a typical synthesis, the as-synthesized copolymer nanoparticles PHEA₂₅-PS₁₁₈ ($D_p = 31.6$ nm) were dispersed in a phloroglucinol/glyoxylic acid mixture without any sign of colloidal destabilization. Subsequently, a copolymer/phenolic resin hybrid including a template content of 62 wt% was created after solvent evaporation (see precise conditions in

Fig. 8 TEM pictures of mesoporous carbon materials synthesized with three different templates: PHEA₂₅-PS₁₁₈ (a), PHEA₂₅-PS₁₆₀ (b) and Pluronic F127 (c). In all instances, a steady molar ratio phloroglucinol:glyoxylic acid:template = 1:1:0.019 was chosen.

the experimental section). Finally, pyrolysis enabled in a single step to carbonize the phenolic resin and degrade the copolymer nanoparticles. As can be seen in **Fig. 8** (image **a**), which shows a typical TEM image after carbonization, the structure consists of randomly distributed interconnected spherical mesopores. The size of these pores (22.0 nm) was rather uniform, which results from the narrow size distribution of the initial colloidal particles. Control experiment without nanoparticles led to a system devoid of mesopores. Remarkably, the size of the pores could be manipulated by changing the diameter of the copolymer particles. For example, the PHEA₂₅-PS₁₆₀ latex ($D_p = 41.6$ nm, Table 1) possessing a higher DP of the core-forming block led to an average mesopore size of 29 nm (**Fig. 8**, image **b**). For these two samples, the BET (Brunauer-Emmett-Teller theory) surface area was found to be 691 and 702 m² g⁻¹, respectively (see nitrogen adsorption/desorption isotherms in **Fig. S7**). The BJH (Barrett-Joyner-Halenda theory) cumulative pore volumes (corresponding to pores > 2 nm) were also high: 1.01 (PHEA₂₅-PS₁₁₈) and 1.23 cm³ g⁻¹ (PHEA₂₅-PS₁₆₀). For comparison, a third mesoporous carbon (**Fig. 8**, image **c**) was prepared using as template a conventional lyotropic mesophase formed by the self-assembly of an amphiphilic triblock copolymer (poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide), Pluronic F127).⁶³ Due to size limitation of liquid crystal phases, much smaller mesopores (7 nm) were created. In addition, lower volumes (0.49 cm³ g⁻¹) were obtained for a BET surface area which remained similar (689 m² g⁻¹). Despite the absence of ordered structure and their cost, PISA-derived particles appear as an excellent template for the synthesis of uniform nanoscale porous carbons with large mesopores.

Conclusions

Well-defined spherical nanoparticles were prepared by an original approach combining PISA in dispersion with a photomediated RAFT mechanism under visible-light irradiation. PHEAs were first synthesized in solution before being used as macro-CTAs for a subsequent chain-extension with St in dispersion. Besides the confirmation of the control of the polymerization, the kinetic studies evidenced two distinct regimes related to particle nucleation and particle growth. In the second interval, the high number of particles swollen by monomer resulted in much faster polymerization rate. UV-visible measurements revealed that absorption due to the TTC functions decreased during a first phase of the polymerization, before reaching a constant value, suggesting that a partial degradation of the terminal functions could first occur in the early stage of reaction. Complementary investigations are carried out for a better understanding of this observation. As expected, it was possible to modify particle size by playing on the respective lengths of the solvophilic and solvophobic blocks. Interestingly, photo-PISA could be conducted at ambient or lower temperatures than the ones commonly used in conventional PISA. This wider range of possible experimental conditions is expected to broaden the scope of PISA to new applications, involving for instance

thermally sensitive compounds. The temporal control of the polymerization is undoubtedly a supplementary advantage, which could lead to more finely controlled or even adaptable morphologies. Finally, it has been demonstrated that PISA-derived particles appear as excellent template for the synthesis of uniform nanoscale porous carbons with large mesopores size, difficult to achieve with block copolymer mesophases.

Conflicts of interest

There are no conflicts to declare.

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