



# Atom transfer radical polymerization in dispersed media with low-ppm catalyst loading

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## ARTICLE INFO

### Keywords:

Atom transfer radical polymerization (ATRP)  
Dispersed media polymerizations  
Emulsion polymerization  
Pickering emulsion  
Polymer latexes

## ABSTRACT

Polymerizations in aqueous dispersed media benefit from good heat transfer, low viscosity, low content of volatile compounds, and established industrial use. Over the past two decades, the implementation of ATRP in dispersed media highlighted the possibility of achieving improved livingness and producing a variety of macromolecular architectures. With the introduction of several methods for activator regeneration in ATRP, catalyst loading has been greatly diminished, and the reaction setup has been simplified. The availability of ATRP techniques employing low-ppm (part per million) catalyst loadings enabled to access an even larger variety of polymer architectures and functional polymer particles, which have been applied for molecular recognition, drug delivery, bio-quantification, and advanced coatings. This minireview presents innovative synthetic approaches, polymer architectures, and relevant applications, as well as the challenges that remain to be overcome to promote the industrialization of ATRP in dispersed media.

## 1. Introduction

Polymerizations in aqueous heterogeneous media are characterized by good heat transfer, low amount of volatile organic solvents, low viscosity, and low toxicity [1], making them advantageous for commercial applications [2]. Moreover, conducting radical polymerizations in heterogeneous systems promotes easier access to high molecular weight (MW) polymers, because radical segregation and compartmentalization limit radical termination events [3–6]. In these dispersed and segregated systems, the small polymerization loci perform as “nano-reactors” [7] that enable the preparation of various nanoobjects. Polymerizations in microemulsion, miniemulsion, emulsion, and dispersion have been used to prepare polymer-based nanoparticles with various morphologies (e.g., core-shell, microcapsules, and multilayered particles), which have found applications in catalysis, coatings, and in the biomedical and diagnostic fields [1,8–11].

Reversible-deactivation radical polymerizations (RDRPs) are robust and versatile techniques for the synthesis of polymers with predetermined MW and low dispersity ( $D$ ), starting from a wide range of

monomers [12,13]. Among RDRP techniques, atom transfer radical polymerization (ATRP) [14–18], reversible addition-fragmentation chain-transfer (RAFT) polymerization [19], nitroxide-mediated polymerization (NMP) [20], and organotellurium mediated polymerization (TERP) [21] have been successfully developed in both homogeneous and heterogeneous media [22–29]. While limited advances in NMP in dispersed media were reported over the past 15 years [26], progress in TERP and particularly RAFT polymerization in dispersed media predominantly focused on exploiting the self-assembly of amphiphilic polymer chains prepared through emulsion polymerization processes, to produce nanoobjects with controllable morphologies. On the other hand, the implementation of ATRP in dispersed media has considerably advanced in the past 15 years, driven by the development of novel polymerization components and strategies to mediate ATRP systems [30], giving access to a broader range of building blocks and polymer architectures. In contrast to other RDRPs that require a stoichiometric amount of chain transfer or trapping agents, ATRP is a catalytic process, and the continuous evolution in catalyst design has enabled to prepare polymers with minimal catalyst contamination, which can additionally

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<https://doi.org/10.1016/j.polymer.2023.125913>

Received 18 February 2023; Received in revised form 25 March 2023; Accepted 29 March 2023

Available online 2 April 2023

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be removed through various methods (see below).

ATRP is based on radical generation by the “activator” form of a catalyst, which is typically a Cu complex with a polydentate amine ligand (L) in its lower oxidation state, i.e.,  $\text{Cu}^{\text{I}}/\text{L}$  (Scheme 1). The  $\text{Cu}^{\text{I}}/\text{L}$  complex activates an alkyl halide initiator ( $\text{R-X}$ ) or dormant chain end ( $\text{P}_n\text{-X}$ ) via an inner sphere electron transfer (ISET) process, forming a propagating radical and a higher oxidation state, “deactivator” complex,  $\text{X-Cu}^{\text{II}}/\text{L}$  [31–33]. The high concentration of dormant species minimizes the fraction of terminated chains, in contrast to conventional radical polymerization. The fast initiation and rapid activation-deactivation equilibrium ensure that all chains grow concurrently, resulting in polymers with low dispersity and high chain-end functionality [34].

To compensate for the accumulation of  $\text{Cu}^{\text{II}}$  deactivator, which is generated by unavoidable radical termination, traditional ATRP methods required high concentration of Cu species. However, this caused issues related to catalyst solubility and removal. In the past decade, the loading of Cu catalysts was drastically decreased from over 10,000 parts per million (ppm, expressed as molar concentration relative to the monomer) to hundreds or less ppm, by implementing a variety of methods for the continuous regeneration of the  $\text{Cu}^{\text{I}}/\text{L}$  activator. These methods include the addition of a reducing agent in the polymerization system, as in activators re-generated by electron transfer (ARGET) ATRP [35,36], the addition of a thermal radical initiator as in initiators for continuous activator regeneration (ICAR) ATRP [37], and the use of metallic Cu in supplemental activator and reducing agent (SARA) ATRP [38–40], as well as the use of external stimuli such as electrical current, light, and ultrasounds in electrochemically mediated ATRP (eATRP) [41,42], photoATRP [43,44], and mechanoATRP, respectively [45,46]. These techniques are collectively called “ATRP with activator regeneration” or “low-ppm ATRP”, and they can provide polymeric materials with complex architectures, including decorated nanoparticles, networks and gels [15]. The residual small amount of catalyst could be left in the product, or removed by column filtration, electrodeposition, or other purification techniques [47–50], achieving a sufficiently low Cu contamination for most applications.

During the past 15 years, low-ppm ATRP methods have been successfully implemented in dispersed media. Most initial works were carried out in miniemulsion, due to the advantage of conducting polymerizations in a “mini-bulk” environment, with minimal migration of polymerization components into the continuous phase. More recently, ATRP was expanded to *ab initio* emulsion, thanks to an improved understanding and engineering of catalyst location during the heterogeneous polymerization process.

This minireview describes the development of low-ppm ATRP in dispersed media. The outline and structure of this minireview is presented in Scheme 2. Section 2 provides relevant background on the topics of polymerization in dispersed media and low-ppm ATRP. Section 3 discusses synthetic strategies involving engineered polymerization

components, particularly surfactants and catalysts, as well as the different external stimuli that were used to trigger ATRP in (mini) emulsion systems. The unique features resulting from the combination of heterogeneous polymerizations and low-ppm ATRP enabled to prepare a broad variety of well-defined polymer architectures, which are presented in Section 4. Finally, relevant applications are reviewed in Section 5, while conclusions and perspectives are provided in Section 6.

## 2. Background

### 2.1. Types of dispersed media polymerizations

Heterogeneous polymerization processes involve multiphase systems where the starting monomer(s) and/or the resulting polymer are dispersed in an immiscible liquid. Typically, dispersed media are generated by using a surfactant and an external force to form a kinetically and hydrodynamically stable mixture, although the dispersion can also be thermodynamically stable in some cases. The dispersed droplets have a spherical shape, which enables to minimize the surface-to-volume ratio, and thus the surface energy [51]. Typically, oil-in-water (O/W) systems are employed, where “oil” refers to any water-insoluble liquid (monomer/polymer), and water is the continuous phase. Water-in-oil (W/O) systems are also possible.

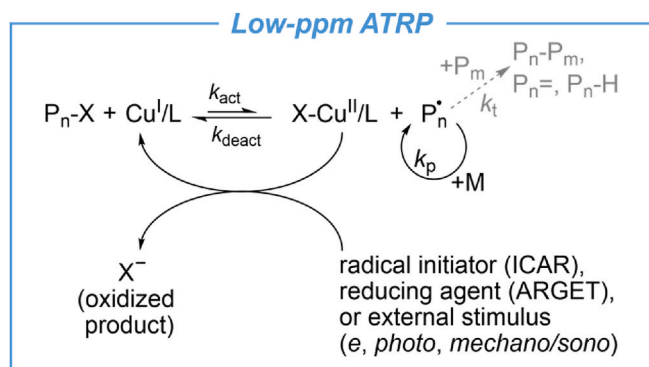
Heterogeneous polymerizations are generally categorized as suspension, emulsion, miniemulsion, microemulsion, dispersion, or precipitation [51]. However, the nomenclature and definitions are sometimes ambiguous in the literature. In this review, the different techniques of polymerization in dispersed media are distinguished by considering four features: (i) the initial state of the polymerization mixture; (ii) the kinetics of polymerization; (iii) the mechanism of particle formation; and (iv) the size of the final polymer particles. The following paragraphs describe the most relevant features of the different heterogeneous polymerization techniques, which are then summarized in Table 1.

**Suspension polymerization.** To perform a suspension polymerization, the initiator is first dissolved in the monomer phase, which is then dispersed in the aqueous phase to form droplets. Water is a nonsolvent for both the monomer and the polymer. The mixture is stirred in the presence of a droplet stabilizer or suspension agent, such as poly(vinyl alcohol). Via thermal polymerization, the monomer droplets are converted directly to polymer microbeads with no significant size change. Suspension polymerization is typically used to produce polymer beads with a size of 20  $\mu\text{m}$  - 2 mm [51].

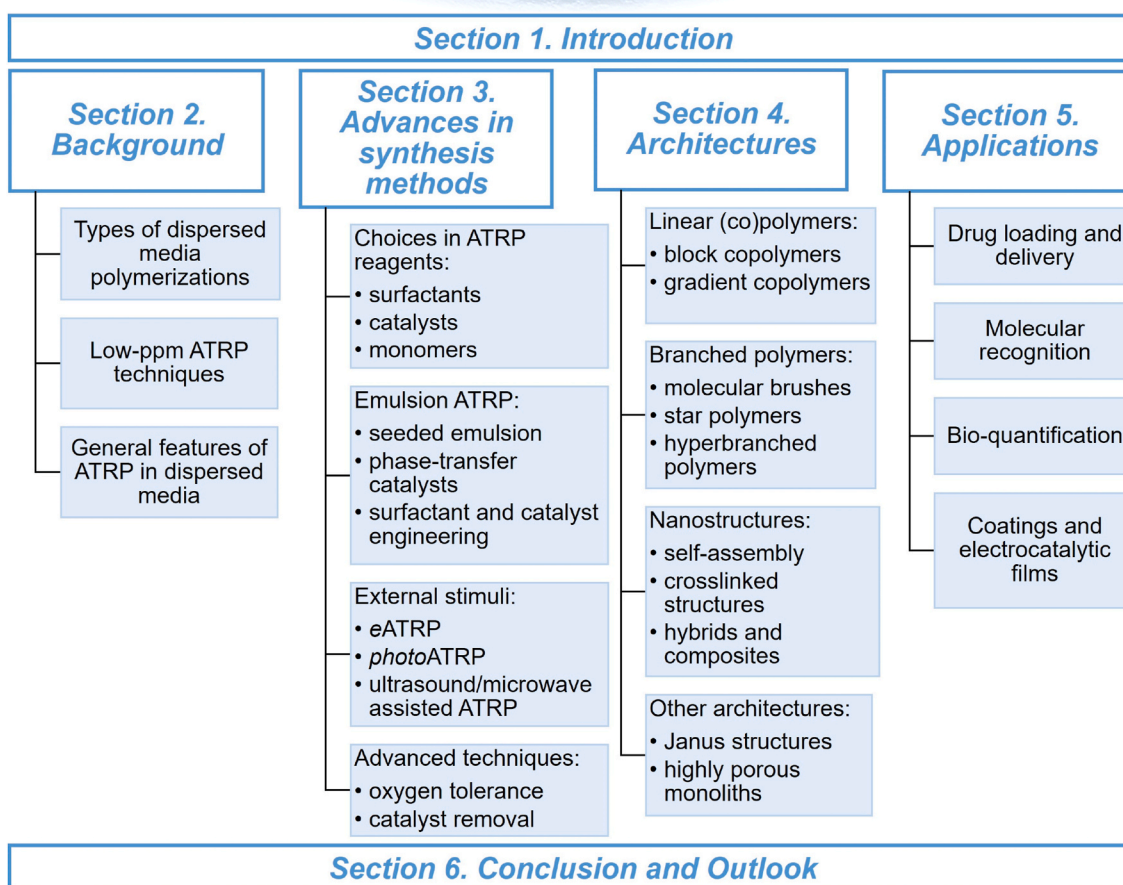
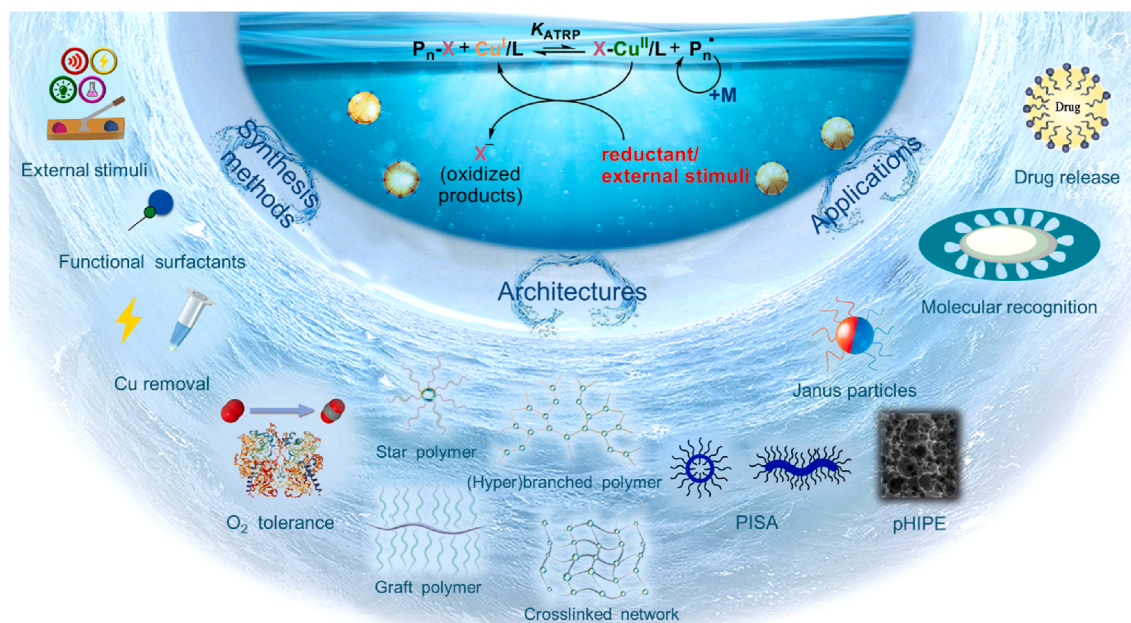
**Precipitation polymerization.** This technique starts from a homogeneous solution of monomer, initiator, and stabilizers; the system quickly turns into a heterogeneous one, because the generated polymer is not soluble in the reaction medium beyond a critical MW. For example, in the polymerization of polyacrylonitrile (PAN), the polymer is insoluble in its own monomer (acrylonitrile), therefore it precipitates after reaching a critical chain length. After the first phase of particles nucleation, the monomer swells the particles, so the polymerization continues in the droplets/colloids. The polymer particles have a size in the range of 1–15  $\mu\text{m}$  [22].

**Dispersion polymerization.** This method is a subclass of precipitation polymerizations, with final particle dimension <10  $\mu\text{m}$ , i.e., colloidal dimensions. The smaller particle size of a dispersion polymerizations is achieved by applying more effective dispersing agents in larger amounts than in typical precipitation polymerizations.

**Emulsion polymerization.** A traditional emulsion polymerization system, also known as *ab initio* emulsion polymerization system, consists of a hydrophobic monomer, a water-soluble initiator, a surfactant, and water. At the beginning of the polymerization, a large portion of the monomer resides in large, surfactant-stabilized monomer reservoirs ( $> 1 \mu\text{m}$ ), and only a small fraction of monomer molecules is in water and in surfactant-formed micelles (<10 nm). The initiator molecules are decomposed in water, where they initiate the growth of oligomeric



**Scheme 1.** Mechanism of low-ppm ATRP, i.e., ATRP with activator regeneration ( $k_{\text{act}}$  = activation rate constant,  $k_{\text{deact}}$  = deactivation rate constant,  $k_p$  = propagation rate constant,  $k_t$  = termination rate constant, M = monomer).



Scheme 2. Graphical and schematic outline of this minireview.

radicals. Upon reaching a critical chain length, the hydrophobic oligomeric radicals enter the micelles rather than the monomer droplets, due to the much higher surface area of the smaller and numerous micelles relative to the larger but fewer monomer droplets. The monomer molecules diffuse from the reservoirs into the aqueous phase, and enter the micelles to propagate the radical chains, resulting in the formation and growth of polymer particles (Scheme 3). The final polymer particle size is 50–500 nm [52].

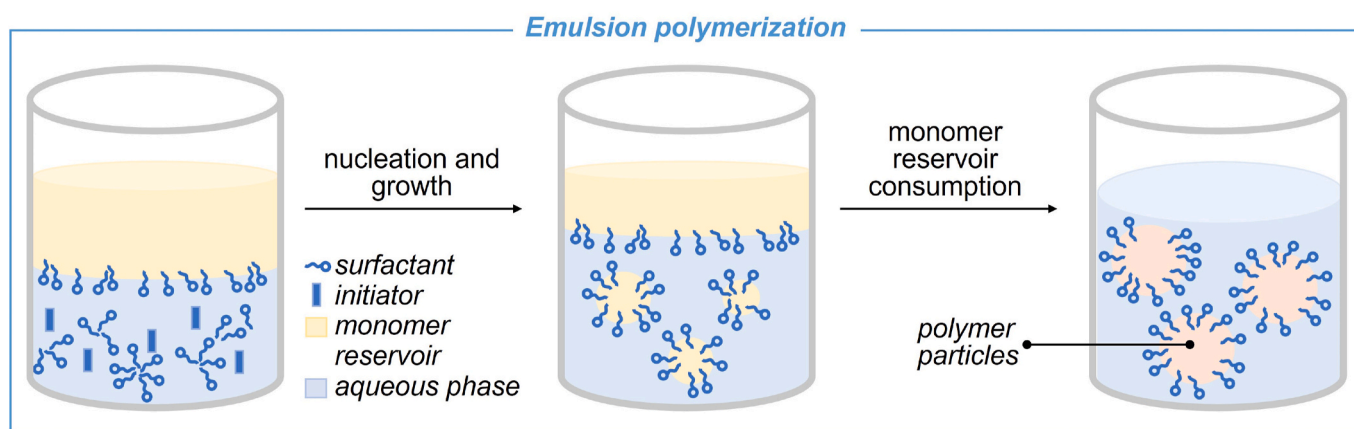
**Miniemulsion polymerization.** Before polymerization, the hydrophobic monomer, oil-soluble initiator, and a hydrocarbon co-stabilizer form a macroscopic organic phase, while the surfactant is dissolved in a macroscopic aqueous phase (Scheme 4). The miniemulsion is generated by a vigorous homogenization process, such as by employing probe ultrasonication or a microfluidizer. The monomer droplets have a size of 50–500 nm, and they are stabilized by the surfactant and the co-stabilizer, which strongly limit the mass transfer of monomer during

**Table 1**  
Polymerizations in different dispersed media.

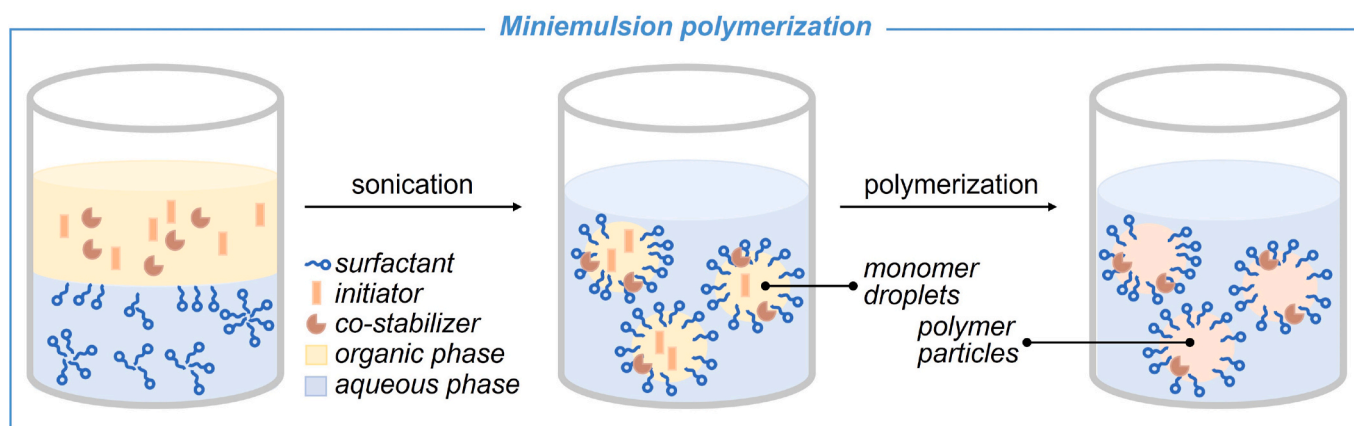
Type of dispersed media	Monomer solubility in the continuous phase	Dispersing force and/or agent	Initiator location	Initial size of the dispersed phase	Kinetics	Typical polymer particle size
<b>Suspension</b>	Insoluble or scarcely soluble	Stirring + suspension agent	Oil phase	20 $\mu\text{m}$ –2 mm	Direct conversion of monomer droplets	20 $\mu\text{m}$ –2 mm
<b>Precipitation</b>	Soluble	Stirring + stabilizers	Solution	–	Nucleation and precipitation	1–15 $\mu\text{m}$
<b>Dispersion</b>	Soluble	Stirring + stabilizers	Solution	–	Nucleation and precipitation	0.1–10 $\mu\text{m}$
<b>Emulsion</b>	Insoluble or scarcely soluble	Surfactant above CMC <sup>a</sup>	Aqueous phase	>0.1 mm <sup>b</sup>	Nucleation, monomer diffusion, and particle growth	50–500 nm
<b>Miniemulsion</b>	Insoluble or scarcely soluble	High shearing force + surfactant above CMC + co-stabilizer	Oil phase	50–500 nm	Direct conversion of monomer droplets	50–500 nm
<b>Micro-emulsion</b>	Insoluble or scarcely soluble	Stirring + surfactant(s) in large quantity	Oil phase	10–50 nm	Direct conversion of monomer phase	10–50 nm

<sup>a</sup> CMC: critical micelle concentration.

<sup>b</sup> a small fraction of monomer is located in 5–10 nm micelles and in water.



**Scheme 3.** Schematic mechanism of oil-in-water emulsion polymerization.



**Scheme 4.** Schematic illustration of a polymerization process within an O/W miniemulsion.

the polymerization. Thus, the polymerization proceeds in each droplet like in a “mini-bulk” polymerization and, as a result, the size of the final polymer particles is similar to that of the initial monomer droplets [53].

**Microemulsion polymerization.** By using a large amount of an appropriate surfactant, the interfacial tension of a dispersed media can be ultra-low, leading to particle size <50 nm, and an optically transparent and thermodynamically stable system with high interfacial area. This system is termed microemulsion [54], and the polymerization proceeds similarly to a miniemulsion system.

Other specialty configurations of polymerization in dispersed media are possible, some of which are described in the following paragraphs.

**Self-assembled non-spherical nanoparticles.** Molecules of

polymeric surfactants can self-assemble into structures that are not necessarily globular, resulting in a combination of spherical micelles, cylindrical micelles, vesicles, and even bicontinuous planar interfaces. Polymerization occurring inside these particles can lead to the formation of non-spherical latex particles [55].

**Pickering emulsion.** A Pickering emulsion is an emulsion that is stabilized by solid particles (for example colloidal silica or proteins) which adsorb onto the interface between the water and oil phases.

**High Internal Phase Emulsions (HIPes).** Typically, for any polymerization mechanism, the volume percentage of the internal (i.e., dispersed) phase is 55% or less. Higher content of internal phase often results in very high viscosity. In fact, the maximum volume percentage

occupied by uniform, non-deformable spheres packed in the most effective way is 74%. High internal phase emulsions (HIPEs) represent a special case where the internal (droplet) phase exceeds 74% of the total volume of the system. HIPEs are generally stabilized by large amounts of surfactants. Because of its high-volume fraction, the dispersed phase forms non-uniform interconnected spheres or polyhedral shapes. In such systems, the continuous phase is loaded with the monomer(s) and crosslinker(s), and polymerized to yield, upon purification, a highly porous material with interconnecting voids, which is called polyHIPE or pHIPE (Scheme 5A). This emulsion templated method is convenient for the synthesis of porous polymers, as it can provide a wide variety of highly interconnected, highly porous monolithic systems (Scheme 5B) [56–58].

## 2.2. Low-ppm ATRP techniques

The equilibrium constant of ATRP,  $K_{\text{ATRP}}$ , is expressed by Equation (1), where  $P_n^*$  and  $P_n-X$  are, respectively, the active and dormant chains.

$$K_{\text{ATRP}} = \frac{[P_n^*][X - \text{Cu}^{\text{II}}/\text{L}]}{[P_n - X][\text{Cu}^{\text{I}}/\text{L}]} \quad (1)$$

Thus, the rate of ATRP polymerization,  $R_p$ , can be expressed by Equation (2) (where M is the monomer, and  $k_p$  is its propagation rate constant), and it depends on the relative amount of  $\text{Cu}^{\text{I}}/\text{L}$  activator and  $X-\text{Cu}^{\text{II}}/\text{L}$  deactivator.

$$R_p = k_p[M][P_n^*] = k_p K_{\text{ATRP}}[M][P_n - X] \frac{[\text{Cu}^{\text{I}}/\text{L}]}{[X - \text{Cu}^{\text{II}}/\text{L}]} \quad (2)$$

The dispersity  $D = M_w/M_n$  of the resulting polymer decreases by increasing the equilibrium concentration of the  $X-\text{Cu}^{\text{II}}/\text{L}$  deactivator, according to Equation (3), where  $DP_n$  is the degree of polymerization,  $k_{\text{deact}}$  is the deactivation rate constant, and  $p$  is the conversion.

$$\frac{M_w}{M_n} = 1 + \frac{1}{DP_n} + \left( \frac{k_p[\text{RX}]_0}{k_{\text{deact}}[X - \text{Cu}^{\text{II}}/\text{L}]} \right) \left( \frac{2}{p} - 1 \right) \quad (3)$$

In low-ppm ATRP techniques, the polymerization kinetics follows the steady-state in radical concentration [30,59]. Thus,  $R_p$  is expressed by Equation (4), whereby the numerator corresponds to the rate of  $\text{Cu}^{\text{I}}/\text{L}$  (re)generation.

$$R_p = k_p[M][P_n^*] = k_p[M] \sqrt{\frac{R_{\text{Cu}^{\text{I}}/\text{L regeneration}}}{k_t}} \quad (4)$$

In ARGET ATRP, the  $\text{Cu}^{\text{I}}/\text{L}$  activator is (re)generated by means of a chemical reducing agent, such as the water-soluble ascorbic acid (AsAc) or oil-soluble  $\text{Sn}^{\text{II}}\text{R}_2$  compounds [35,36]. The rate of polymerization depends on the amount or feeding rate of the reducing agent. In ICAR

ATRP, a thermal radical initiator such as the water-soluble 2,2'-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044) or the oil-soluble azobisisobutyronitrile (AIBN) are employed to exploit their slow thermal decomposition to induce the reduction of the  $X-\text{Cu}^{\text{II}}/\text{L}$  deactivator [30]. The slow decomposition of the thermal radical initiator can cause the generation of a small fraction of new chains, thus ICAR ATRP can be non-ideal for the synthesis of well-defined block copolymers. SARA ATRP uses zero-valent copper as both supplemental activator and reducing agent [39,60], and the rate of polymerization is affected by the ratio of the surface area of  $\text{Cu}^0$  and the volume of the reaction. Metallic Cu can be reused for multiple polymerizations or can be periodically lifted from the reaction mixture to achieve temporal control [61].

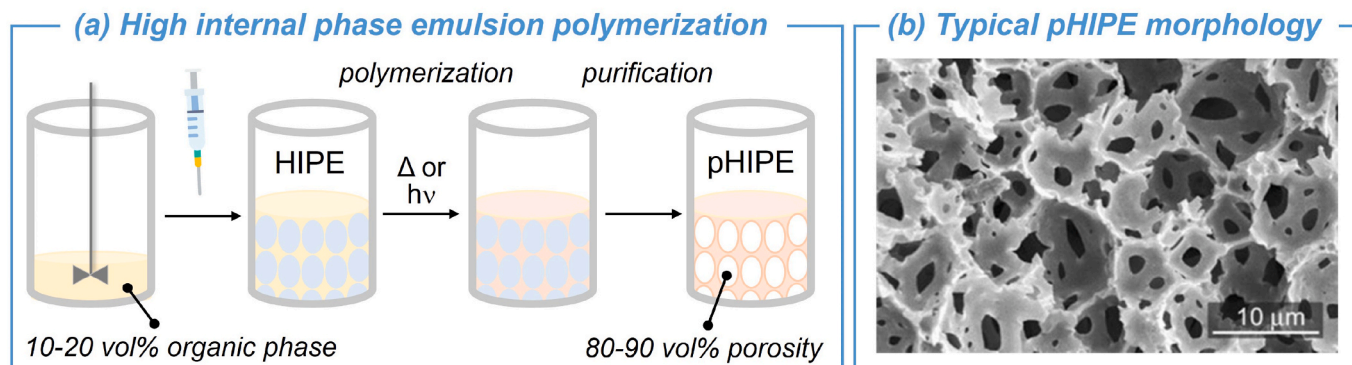
Electrochemically mediated ATRP (eATRP) takes advantage of an applied current or voltage to continuously reduce  $\text{Cu}^{\text{II}}$  species [41]. No external chemicals are needed in eATRP. Since the rate of polymerization is affected by the ratio of  $\text{Cu}^{\text{I}}$  and  $\text{Cu}^{\text{II}}$  species, it can be tuned by the applied potential, according to the Nernst equation [59]. Temporal control over polymerization can also be achieved by adjusting the applied potential or current. eATRP was recently scaled up to a pilot scale [62].

In photoATRP, UV or visible light promotes the photo-excitation of  $X-\text{Cu}^{\text{II}}/\text{L}$  complexes followed by the reduction of excited  $X-\text{Cu}^{\text{II}}/\text{L}^*$  to  $\text{Cu}^{\text{I}}/\text{L}$  in the presence of an electron-donor species, typically an aliphatic amine, which can be an excess of ligand [43,44]. Thus, the rate of polymerization is influenced by the ratio of ligand (or other electron donor) to copper. Similar to eATRP, the use of light as an external stimulus enabled temporal control over the polymerization. PhotoATRP can also be performed by employing other metal photocatalysts, which typically operate in the absence of an electron donor, as well as organocatalysts, such as phenothiazines, phenazines, and phenoxazines [63,64]. A procedure for scale up of photoATRP has also been recently disclosed [65].

MechanoATRP and sonoATRP employ ultrasounds to (re)generate the activator. In the first technique, the sonication of piezoelectric materials induces an electron transfer to the  $\text{Cu}^{\text{II}}$  species [45,46], while in the second case, the application of ultrasound in aqueous media produces hydroxyl radicals from water molecules [66]. The hydroxyl radicals react with monomer or with alcoholic solvent, forming carbon based radicals that start the propagation.

## 2.3. General features of ATRP in dispersed media

The implementation of ATRP in dispersed media requires the partitioning of each species among the aqueous and organic phases prior, throughout, and at the end of the polymerization. In a typical free radical polymerization in dispersed media the only components are the monomer and radical initiator, besides the surfactant and/or eventual



**Scheme 5.** (a) Schematic illustration of HIPE formation and pHIPE synthesis within a water-in-oil HIPE; (b) typical SEM of porous pHIPE structure. Reproduced with permission from Ref. [57].

co-surfactant, (co)stabilizers or dispersing agents (Table 1). Conversely, a low-ppm ATRP requires an alkyl halide initiator, the catalyst, i.e., a Cu-halide salt and the ligand, and either a reducing agent, a thermal radical initiator, metallic Cu, or an external trigger. All these elements should be located in the appropriate phase (water, oil, or their interphase) at any stage of the polymerization. For instance, at the onset of a miniemulsion ATRP, the catalyst and RX must reside in the surfactant-stabilized monomer droplets, and they should remain in the hydrophobic phase for the whole duration of the process. An eventual reducing agent or thermal radical initiator should also reach the hydrophobic phase, and the eventual external stimulus must be conveyed to the hydrophobic phase. Therefore, the design of low-ppm ATRP systems in dispersed media necessitates tuning the hydrophilicity of the catalyst, RX and eventual reductants, as well as appropriately selecting the surfactant and/or stabilizers. Low-ppm ATRP techniques have been effectively performed in various types of dispersed media by carefully designing the catalytic systems, as it will be explained in Section 3.

An important advantage provided by the use of heterogeneous media is the possibility to reduce or suppress bi-radical termination events. In homogeneous ATRP, bi-radical termination is unavoidable and can result in decreased rate of polymerization, low chain-end functionality, and even gelation if a branching point exists. In dispersed media, radicals located in different particles are unable to terminate with each other (segregation effect), which is particularly relevant for the design of complex polymer architecture [3]. On the other hand, the confined space effect can result in enhanced reaction rate between two radicals located in the same particle as the particle size decreases. However, compartmentalization in dispersed media ATRP also enhances the rate of deactivation. Thus, depending on the catalytic system, lower polymerization rates and improved control were observed for particle volumes below a threshold value [7,67]. The latter is dependent on the particular system, and it generally increases with increasing the targeted degree of polymerization, i.e., decreasing the amount of initiating molecules (and thus of growing radicals) confined within each particle [67].

In dispersed media, each droplet acts as a “nanoreactor”, allowing the preparation of nanoobjects that cannot be easily prepared in other media, including crosslinked nanoparticles, nanocapsules, and core-crosslinked hairy nanoparticles. In Pickering emulsion system, Janus platelets with either a polymer grafted on a single side or different polymers on each side were synthesized. By adding the monomer and crosslinker to the continuous phase, porous polymer monoliths could be fabricated. The different polymer architectures prepared by low-ppm ATRP in dispersed media will be presented in Section 4, whereas their most relevant applications will be discussed in Section 5.

### 3. Advances in synthesis methods

#### 3.1. Choices in ATRP reagents

##### 3.1.1. Surfactants and initiators

Seminal ATRP in dispersed media with high loading of Cu catalyst generally employed non-ionic or cationic surfactants, which stabilized the latex without interfering with the cationic Cu complexes and thus with the ATRP equilibrium [68,69]. In contrast, anionic surfactants can interact with the Cu complexes used as catalysts, modifying their stability and catalytic activity [22]. The introduction of low-ppm ATRP methods was concomitant to the engineering of the surfactant, resulting in the use of anionic, ionic liquid, and reactive surfactants.

The most important drawback of conventional surfactants is their tendency to remain in the final polymer, negatively affecting its electric, photonic, and surface properties. In conventional emulsion free radical polymerization, this issue was overcome by designing soap-free emulsion systems. In such systems, traditional surfactants are replaced by initiator or monomer molecules capable of anchoring onto the surface of the latex particles, leading to improved colloidal stability and the

absence of surfactant leaching from the produced latexes. This immobilization strategy eliminates the need for surfactant removal after polymerization. In ATRP, soap-free emulsion polymerizations were developed by exploiting the concept of “reactive surfactant” [70], which is a multifunctional molecule that combines the function of a surfactant with an initiator, monomer, or catalyst/ligand [71,72].

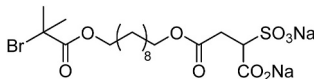
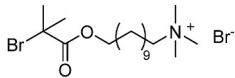
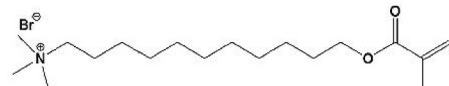
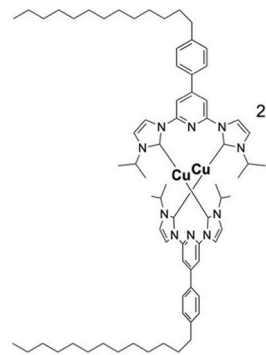
For example, hydrophilic or amphiphilic macroinitiators prepared by RDRP were employed as reactive surfactants to simultaneously initiate polymerizations and stabilize micelles, forming amphiphilic polymers that behave as macro-emulsifiers (Table 2). In fact, poly(ethylene oxide) homopolymer with terminal  $\alpha$ -bromoisobutyrate moiety (PEO-Br), and poly(ethylene oxide)-*b*-polystyrene (PEO-*b*-PSt-Br) block copolymer made by ATRP were used as macroinitiators and stabilizers in mini-emulsion AGET ATRP of butyl acrylate (BA), generating polymer latexes with narrow particle size distribution [73].

Besides macroinitiator surfactants, small-molecule surfactants can be used to initiate an ATRP. When a polymerization initiating site is introduced in surfactant molecules the resulting construct is termed an “inisurf”, i.e., initiator-surfactant [74]. Both anionic [75,76], and cationic [77,78] inisurfs were employed for ATRP in dispersed media. Dextran derivatives bearing a phenoxy hydrophobic group were modified to introduce  $\alpha$ -bromoisobutyrate sites for ATRP initiation, forming a multifunctional inisurf. Nanoparticles with hydrophobic cores and hydrophilic shells were formed during polymerization [9]. By grafting polymer from the inisurf, a “sterically-stabilized latex” was obtained, which was particularly resistant toward destabilization induced by high shear force, electrolyte addition, and freeze-thaw.

The various types of reactive surfactants provided latexes with increased stability and eliminated the need for removing the surfactant after polymerization. Alternatively, surfactant monomers have been employed, that copolymerized within the main chain. Unsaturated molecules such as a methacrylic ester [79] or a cardanol ether [80], were covalently attached to a tetraalkylammonium cationic surfactant, forming surfactant-monomers exhibiting drastically decreased CMC values and enhanced stabilization capabilities.

A complementary strategy consists of incorporating multidentate nitrogen groups into the surfactant to form a surfactant-ligand (SL). In *ab*

**Table 2**  
Categories of reactive and engineered surfactants employed in dispersed media ATRP.

Type	Structure	ref
Surfactant-initiator		[75]
		[77]
Surfactant-monomer		[79]
Surfactant-ligand		[82]

*initio* emulsion ATRP, a SL “locked” the Cu<sup>II</sup> on the surface of the droplet, eliminating the escape of Cu<sup>II</sup> to water [81,82]. However, the immobilization of the catalyst on the surface of polymerizing droplets can restrict its diffusion rate and result in decreased degree of control. The addition of conventional ligand, dNbp (4,4'-dinonyl-2,2'-bipyridine), narrowed the molecular weight distribution [83].

Ionic liquid surfactants represent a useful alternative to conventional ionic or neutral surfactants as they can be easily separated and reused. *N*-tetradecyl-*N*-methyl-2-pyrrolidonium bromide was employed in microemulsion AGET ATRP of methyl methacrylate (MMA). The ionic liquid surfactant had low toxicity and was recycled and reused for up to 5 times [84].

Besides ionic liquids, insoluble solids that could be partially wetted by both phases could significantly decrease the surface energy and stabilize the emulsion, giving, in this case, a so called Pickering emulsion [85]. An example of Pickering agent is cellulose nanocrystals (CNCs), which have been used for a *photo*ATRP catalyzed by Eosin Y [86]. CNCs could be recycled and reused for Pickering emulsion polymerization multiple times. CNCs modified with  $\alpha$ -bromoisobutyrate moieties could also stabilize inverted (W/O) or double (W/O/W) emulsions, and surface initiated ATRP (SI-ATRP) occurred from the surface of the CNCs. Thus, capsules, filled beads, and microporous polymers were directly prepared [87]. Similarly, silica nanoparticles modified with  $\alpha$ -bromoisobutyrate groups stabilized Pickering emulsions and acted as initiators in SI-ATRP [88,89]. Biphasic grafting from both the aqueous and organic phase resulted in Janus particles, since the *in situ* formation of amphiphilic particles restricted their own rotation [90].

Common anionic surfactants were previously considered incompatible with ATRP, since they could displace the halide ion from the X-Cu<sup>II</sup>/L deactivator, forming a Cu<sup>II</sup> species that cannot deactivate radicals [22, 91]. However, the detrimental displacement of X<sup>-</sup> was minimized by adding an excess of bromide ions in miniemulsion ATRP systems. This has opened up the possibility of employing inexpensive, effective, and readily-available surfactants, such as sodium dodecyl sulfate (SDS), instead of more costly, neutral surfactants, e.g., Brij 98, that were previously used in miniemulsion ATRP [91].

### 3.1.2. Catalysts

Catalysts are selected according to the type of dispersed media. In miniemulsion polymerizations, the hydrophobicity of the catalyst influenced the partition of the activator and deactivator between the organic and aqueous phases, thus affecting the rate of polymerization and degree of control [92]. The prevalent strategy toward well-controlled ATRP in miniemulsion involved the design of ligands for sufficiently hydrophobic Cu catalysts that resided within hydrophobic monomer droplets, where the polymerization proceeds [93]. Therefore, highly hydrophobic and highly active catalysts bearing hydrophobic alkyl chains in the polydentate amine were synthesized and effectively employed in low-ppm amounts in miniemulsion ATRP [94,95]. Only recently, the need for designing specific, hydrophobic ligands was overcome by demonstrating that the commercially available tris (2-pyridylmethyl)amine (TPMA) is a suitable ligand for miniemulsion ATRP when used in combination with an anionic surfactant, such as SDS.

Interestingly, the strong interaction between dodecyl sulfate ions (DS<sup>-</sup>), and Cu-based ATRP catalysts was later exploited to identify a Cu complex that, in the presence of SDS, could lead to enhanced polymerization control. The interaction between SDS and Cu/TPMA formed a catalyst that was conveniently partitioned between aqueous phase, surface of hydrophobic monomer/polymer droplets, and inside the hydrophobic droplets to better control the polymerization within the hydrophobic phase. The presence of SDS affected the localization of hydrophilic Cu/TPMA that would have been otherwise present almost exclusively in the water phase. It was demonstrated that in miniemulsion systems composed of BA droplets stabilized by SDS, only 4% of Cu/TPMA was located in the continuous aqueous phase, while most of it

(95%) was located at the interface of the droplets. Moreover, a small portion of Cu complex (1%), formed ion-pairs with DS<sup>-</sup> capable of entering the polymerizing particles (Scheme 6). This small amount of hydrophobic ion pair has high mobility inside the particle and can effectively deactivate growing radicals. Thus, the interaction between DS<sup>-</sup> and Cu/TPMA provided an “intelligent” catalyst that could control radical propagation from the interface and the inside of hydrophobic droplets [96]. In addition, after polymerization, a simple dilution of the system with water followed by centrifugation induced the migration of the hydrophilic Cu/TPMA back to the water phase, recovering polymers with residual Cu content as low as 0.3 ppm [97].

Beyond Cu-catalyzed systems, Fe catalysts, including *N,N*-butyldithiocarbamate ferrum [98,99], Fe/*N,N,N',N'*-tetramethyl-1,2-ethanediamine [99,100], and Fe/ethylene diamine tetraacetic acid [101], were employed for ATRP in dispersed media, either in miniemulsion or microemulsion systems. Metal-free ATRP employing 10-phenylphenothiazine as a photocatalyst was successful in microemulsion ATRP [102].

### 3.1.3. Monomers

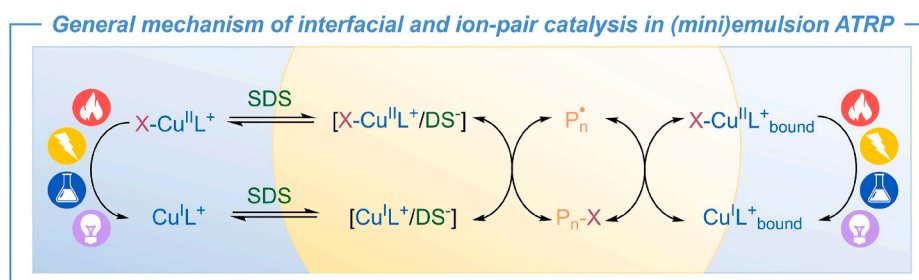
The monomers used in oil-in-water dispersed media ATRP are generally hydrophobic. A slight change in hydrophobicity (or hydrophilicity) results in different polymerization rates and control. The hydrophilicity of molecules, including monomers, is typically quantified by considering its partition coefficient (logP) in an octanol-water mixture. In emulsion ATRP, the monomer diffuses to the micelles under moderate stirring, thus, the solubility of the monomer affects the rate of diffusion, which in turn impacts the rate of polymerization and consequently the degree of control. Emulsion ATRPs of MMA, ethyl methacrylate (EMA), butyl methacrylate (BMA) and lauryl methacrylate (LMA) were carried out. Monomers with lower logP values, i.e., more hydrophilic monomers, revealed faster rate of polymerization yet lower degree of control. Additionally, more hydrophilic monomers and polymers migrated between the droplets, leading to reduced colloidal stability [103]. On the other hand, the most hydrophobic monomer, LMA, showed negligible conversion because it could not diffuse through water to reach polymerizing micelles [104].

Hydrophilic monomers were polymerized in inverse emulsion systems, i.e., water-in-oil emulsions. For example, oligo(ethylene glycol) methyl ether methacrylate (OEOMA) was polymerized in inverse miniemulsion and inverse microemulsion ATRP, forming well-defined brush-like structures [105–107].

ATRP is a versatile technique that enables the polymerization of monomers bearing various functional groups. For instance, glycidyl methacrylate (GMA) [108] and 2,2,3,3,4,4,4-heptafluorobutyl acrylate were polymerized in *ab initio* emulsion ATRP, with keeping intact the epoxy and fluorine functionalities, respectively [109].

## 3.2. Emulsion ATRP

As discussed in Section 2.1, traditional emulsion polymerization requires an aqueous initiation and nucleation phase, followed by polymerization within hydrophobic particles. Thus, in emulsion ATRP the Cu complex should “follow” the radicals from the aqueous phase to the organic phase to control the entire dynamic ATRP process. Thus, the partition of the catalysts is critical. However, several common ATRP catalysts are highly hydrophilic, resulting in the deactivating species, X-Cu<sup>II</sup>/L, leaving the oil phase, negatively affecting control over the polymerization. At the same time, specifically designed hydrophobic catalysts also performed poorly because they mostly resided in the monomer reservoir and therefore could not control the polymerization in the aqueous phase. During the past decade, three main approaches were developed to perform well-controlled emulsion ATRP: (i) a microemulsion (or miniemulsion) “seed” approach, (ii) the use of a phase-transfer catalyst, and (iii) the engineering of the surfactant and ATRP catalyst.



**Scheme 6.** Mechanism of Cu/TPMA-SDS ion-pair and interfacial catalysis in miniemulsion ATRP.

### 3.2.1. Seeded emulsion

The seeded emulsion approach enabled to “bypass” the aqueous initiation and nucleation phase by introducing an initial microemulsion (or miniemulsion) step (Scheme 7a) [110,111]. Thus, first microemulsion (or miniemulsion) ATRP was performed using a tiny amount of monomer with the aim of encapsulating the hydrophobic catalyst complex into the polymer particles. Then, the latter served as “seeds” that were swelled by the addition of a large batch of monomer, during which the catalyst remained located in the particles. This two-step approach yielded well-controlled polymers and relatively uniform latex particles. Moreover, it could be further used to form a variety of structures, including block copolymers, hairy nanoparticles [112], and onion-like structures [113,114], as it will be described in Section 4. Seeded emulsion polymerization tend to have particle size with low batch-to-batch variability.

### 3.2.2. Phase-transfer catalyst

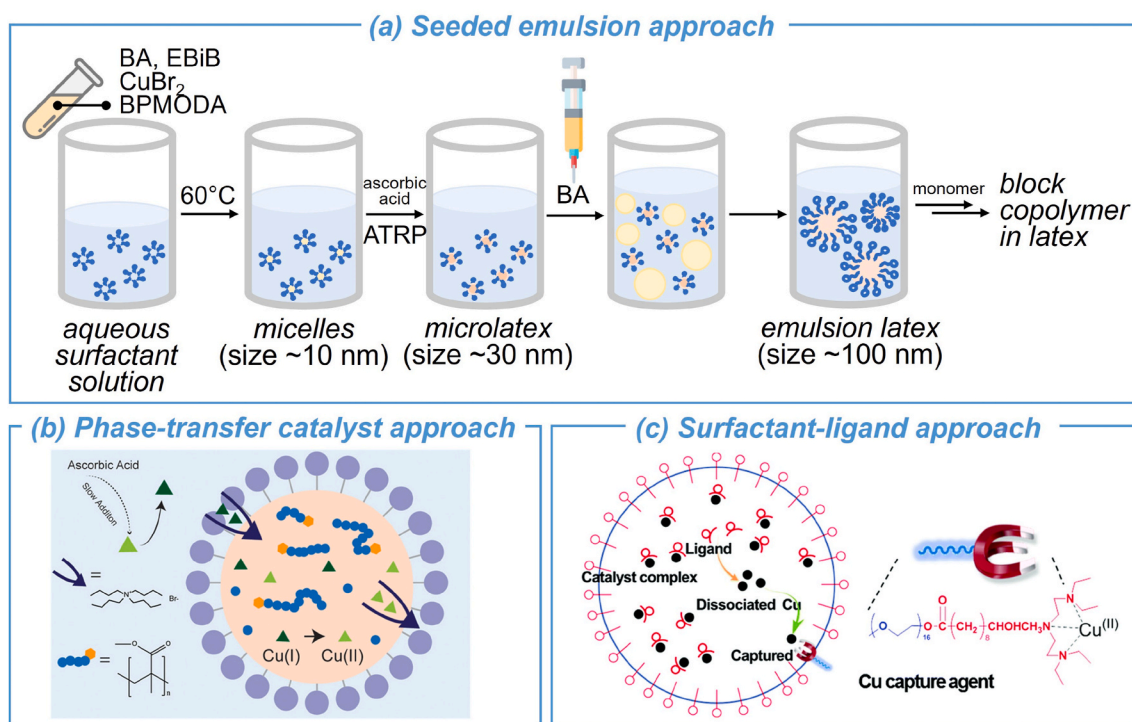
Similar to the case of miniemulsion polymerizations, highly hydrophobic ligands were employed in emulsion systems to limit the escape of Cu<sup>II</sup> deactivators from growing polymer particles. However, a large fraction of these hydrophobic catalysts resided in the oil phase rather than in the micelles during the first stage of the process, leading to a miniemulsion-like mechanism and poor polymerization control in the

initial nucleation stage. The location of the catalyst could be modulated by using phase transfer catalysts in combination with shuttle molecules. Shuttle molecules were polar organic molecules, such as acetone, that was mixed with water to aid the solubility of several components in the continuous aqueous phase in an emulsion/miniemulsion ATRP [115]. Phase-transfer catalysts, typically organic ions, were used to transport the catalysts within the phases. For example, tetrabutylammonium bromide, TBAB, was shown to favor the mobility of the catalyst as well as the initiator and halide ions to the hydrophobic polymerizing particles (Scheme 7b) [115].

### 3.2.3. Surfactant and catalyst engineering

To localize the catalyst within the micelles and surfactant-stabilized hydrophobic particles, a surfactant-ligand (SL) compound was specifically designed. The SL comprised a multidentate amine-based ligand for Cu centers, attached to an hydrophobic moiety (Scheme 7c) [83]. However, the diffusion of Cu<sup>II</sup> species coordinated to the SL was relatively slow, likely due to the steric hindrance within the SL. Thus, the addition of a hydrophobic catalyst (e.g., CuBr<sub>2</sub>/dNbp) was needed to promote sufficiently fast diffusion within the micelles.

In a complex medium such as an emulsion, the key for excellent polymerization control is the presence of a dynamic catalyst that can react with propagating radicals throughout the life of a polymer chain, i.



**Scheme 7.** Examples of different approaches to emulsion ATRP: (a) seeded emulsion; (b) hydrophobic catalyst + phase transfer catalyst (reprinted with permission from Ref. [115]); (c) surfactant-ligand (reprinted with permission from Ref. [83]).



e., from aqueous nucleation to hydrophobic propagation inside monomer droplets. A simpler and scalable approach consists of exploiting the combination of interfacial and ion-pair catalysis provided by the Cu/TPMA-SDS system described in Section 3.1 to achieve ATRP in true *ab initio* emulsion [27]. The hydrophilicity of Cu/TPMA and the use of a hydrophilic alkyl halide initiator enabled initiation of the polymerization within the aqueous phase, which then seeded SDS-micelles (Scheme 8). The much higher total surface area of the micelles relative to the monomer reservoir caused the Cu/L complexes interacting with the surfactant to preferably reside on the surface or within the micelles. The anionic surfactant acted as a shuttle for the catalyst, promoting the localization of the catalyst at the interface of the hydrophobic particles, and to a lower extent inside the particles. This emulsion ATRP technique is facile, scalable, and it was successfully adapted to *photo*ATRP [104]. Note that in this emulsion ATRP technique, pre-partitioning of catalyst and initiator was prevented by avoiding pre-mixing of the oil and water phases prior to starting the polymerization (Scheme 8) [27]. A pre-emulsified monomer could potentially be fed as monomer reservoir, but this is not been tested yet.

### 3.3. ATRP in dispersed media under external stimuli

Prior to the development of low-ppm ATRP techniques, normal, reverse, simultaneous reverse and normal initiation (SR&NI), and activator generated by electron transfer (AGET) ATRP, were performed in various dispersed media using high loadings of Cu complexes. Low-ppm techniques such as ICAR and ARGET ATRP enabled to reduce the loading of Cu in dispersed media polymerization to hundreds of ppm. ATRP techniques based on external stimuli [116] such as light, electrical current/potential and ultrasound opened new possibilities for low-ppm ATRP in dispersed media, providing additional tuning of the polymerization rate and features by simple manipulation of the external stimulus.

#### 3.3.1. eATRP

The main challenge hindering the implementation of eATRP in miniemulsion systems was identified as the physical disconnection of the working electrode (*i.e.*, the electrode that provides the electrons for the reduction of Cu<sup>II</sup> species) from the organic phase [117]. The electrode was instead in contact with the continuous aqueous phase. This hampered the regeneration of the hydrophobic catalysts generally employed in miniemulsion ATRP that dissolved in the organic phase. In fact, due to its “mini-bulk” feature, the mass transport in miniemulsion

polymerizations is negligible. To solve this issue, a dual-catalyst approach was developed, whereby a water-soluble catalyst Cu<sup>II</sup>/L<sub>aq</sub> and a hydrophobic catalyst Cu<sup>II</sup>/L<sub>org</sub> were used at the same time, so that the first could shuttle the external stimulus from the working electrode to the droplets’ interface, while the second was controlling the ATRP equilibrium inside the hydrophobic phase (Scheme 9). By comparing several combinations of Cu<sup>II</sup>/L<sub>aq</sub> and Cu<sup>II</sup>/L<sub>org</sub>, it was determined that the hydrophilicity/hydrophobicity of the catalysts played a more important role on polymerization control relative to the activity of the catalysts (*i.e.* its standard reduction potential). Later, the development of the catalytic system based on Cu/TPMA interacting with SDS enabled to simplify miniemulsion eATRP by eliminating the need for a dual-catalyst system [96].

An electrochemically mediated ATRP approach was also used to prepare molecularly imprinted polymer (MIP) nanoparticles, through a precipitation polymerization system. eATRP of 4-vinylphenylboronic acid in the presence of ethylene glycol dimethacrylate (EGDMA) as crosslinker and sialic acid as template was conducted in water/methanol (1/4 v/v), catalyzed by Cu/TPMA. By tuning the applied potential, the polymerization yielded nanoparticles with hydrodynamic diameter ranging from 160 to 330 nm, capable of recognizing the sialic acid template [118].

#### 3.3.2. PhotoATRP

The possibility to perform polymerizations in dispersed media through light irradiation could offer improved reaction efficiency, lower energy consumption, and increased safety [119]. However, photochemistry in dispersed-phase polymerizations is challenging because of the limited light penetration in turbid (mini)emulsion systems. Light absorption and scattering phenomena in miniemulsion photopolymerizations have been extensively studied by aid of theoretical modeling [120] and actinometry [121]. Droplet size played a crucial role, with smaller particles reducing the scattering coefficient and thus resulting in improved light penetration [122]. Despite these limitations, photoinduced miniemulsion free radical polymerizations have been successfully performed and even employed for the encapsulation of pigments in UV-cured nanoparticles [10,123].

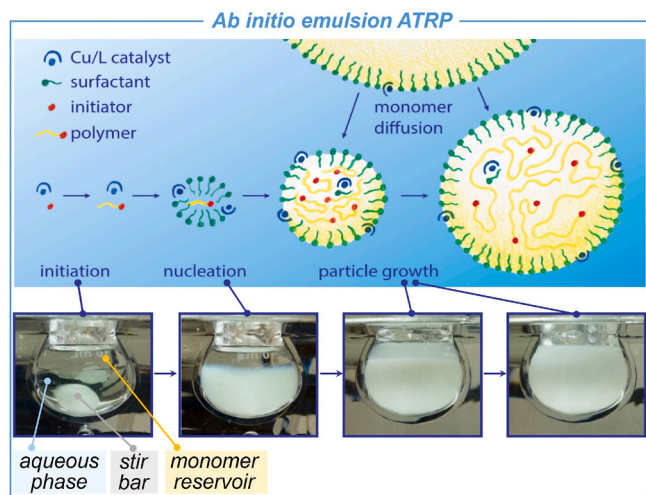
After the application of the Cu/TPMA-SDS catalytic system (see Section 3.1) in miniemulsion eATRP and ARGET ATRP, *photo*ATRP was investigated. Despite the turbidity of the heterogeneous media, photo-mediated miniemulsion ATRP was performed over a broad range of solid contents and particle sizes, achieved by tuning the surfactant amount [124]. In addition, excellent temporal control was achieved upon switching the UV light on and off multiple times. *Photo*ATRP was applied in *ab initio* emulsion polymerization of various methacrylate monomers, also by using an enzymatic degassing procedure [104].

Metal-free *photo*ATRP was also conducted in heterogeneous media. For example, by using Eosin Y as a photocatalyst and triethylamine as electron donor, well-controlled PMMA was prepared via photoinduced electron transfer (PET)-ATRP of MMA in Pickering emulsions, stabilized by cellulose nanocrystals [86].

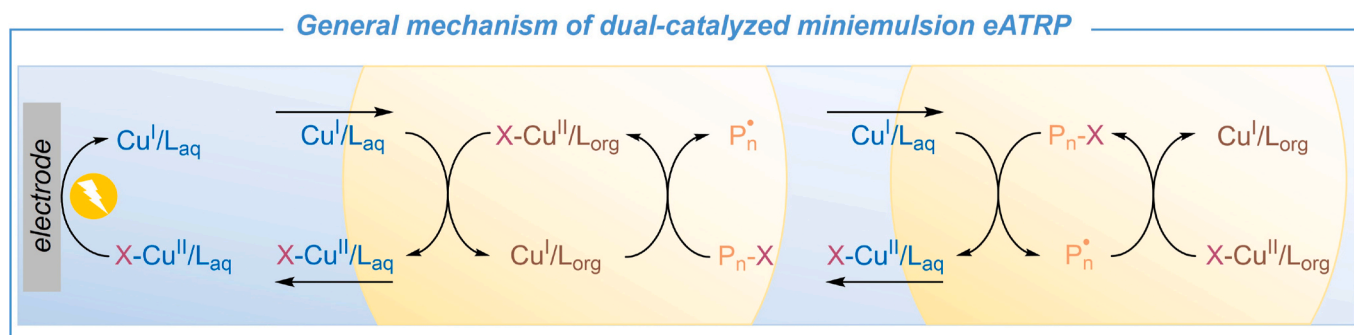
#### 3.3.3. Ultrasound/microwave-assisted ATRP

ATRP in dispersed media was performed by means of microwave irradiation and ultrasound. The use of microwave irradiation in ATRP generally results in significantly increased reaction rates and yields in comparison with other techniques [125]. The acceleration is attributed to the increased temperature and mass transport. In emulsion polymerization, microwave irradiation afforded nanoparticles with smaller average size and narrower size distribution compared to conventional heating, which typically yielded nanoparticles with size >100 nm. Conversely, combining microwave irradiation and emulsion ATRP, PEG-*b*-PSt nanoparticles with diameters in the 30–50 nm range were produced [126].

The use of ultrasound is a powerful strategy that enabled miniemulsion polymerization without chemical radical initiators or co-



**Scheme 8.** Schematics and photographs of an *ab initio* emulsion ATRP, which exploits a hydrophilic Cu/L catalyst strongly interacting with an anionic surfactant, and a hydrophilic alkyl halide initiator. Adapted with permission from Ref. [27].



**Scheme 9.** Proposed mechanism of miniemulsion polymerization by eATRP with a dual-catalyst system.

stabilizers, while maintaining fast polymerizations [127]. Acoustic cavitation provided radicals that sustained the polymerization, while the high shear forces limited the impact of Ostwald ripening. The interfacial and ion-pair catalyst system composed by Cu/TPMA-SDS was applied to miniemulsion *sono*ATRP [128]. Radicals generated in the aqueous phase by sonication effectively initiated and sustained the polymerization, which could be temporally controlled by switching ultrasound on and off.

### 3.4. Advanced techniques

#### 3.4.1. Oxygen tolerance

RDRP systems typically require a physical deoxygenation process, such as nitrogen bubbling or freeze-pump-thaw. The coupling of chemical deoxygenation reactions with RDRP simplified the reaction setup and allowed for conducting polymerizations in open-to-air conditions [129]. Glucose oxidase (GOx)-catalyzed oxygenation of glucose consumes oxygen efficiently, and thus it was applied to aqueous RAFT polymerization and ATRP [130–135]. The GOx-deoxygenation system was also implemented in miniemulsion and emulsion ATRP, leading to well-controlled synthesis of hydrophobic polymers [104,136]. Circular dichroism measurements demonstrated that the structure of GOx remained intact in the presence of anionic surfactant [136]. Lignin nanoparticles (LNPs) coated with chitosan and GOx enabled efficient stabilization of Pickering emulsions and simultaneous *in situ* enzymatic degassing of ATRP, without requiring hydrogen peroxide scavengers [137]. The enzymatic degassing eliminated the possibility of monomer evaporation during traditional degassing; moreover, the low cost of the stabilizer and deoxygenation reagents can favor the implementation in industrial settings, especially in the case of emulsion polymerizations.

#### 3.4.2. Cu removal

The biphasic nature of heterogeneous polymerizations can simplify catalyst removal thanks to the large surface area of the organic/water interface. In fact, in miniemulsion systems, the large interfacial surface facilitates the mass transport of the catalyst from polymer particles to the aqueous phase, provided that a sufficiently hydrophilic catalyst is used. At the end of a miniemulsion ARGET ATRP of BMA, the product was precipitated into methanol/water (1/1 by v/v) and analyzed by inductively coupled plasma-mass spectrometry (ICP-MS). Using the highly hydrophilic catalyst Cu/TPMA, the residual Cu in the polymer could be as low as 300 part per billion (ppb), which was 10 times less than the residual Cu obtained using the hydrophobic Cu/BPMDA\* (BPMDA\* = bis[2-(4-methoxy-3,5-dimethyl)pyridylmethyl]octadecylamine) catalyst [97].

Another strategy for Cu removal consists of destabilizing the ligand. After Cu/HMTA (HMTA = hexamethylenetetramine) catalyzed emulsion ATRP of MMA, HMTA was decomposed into  $\text{NH}_3$  and HCHO under acidic conditions (the optimal pH was 4–5) and  $\text{Cu}^{\text{II}}$  was released to the aqueous phase [138].

Moreover, Cu can be conveniently removed by electrolysis. This

method is especially efficient in polymer latexes due to the large organic/water interface area. Electrolysis was used to remove Cu from emulsion ATRP systems that employed a surfactant-ligand (SL, see Section 3.1). After polymerization, >98% of Cu was collected by electrolysis of the system that employed the SL, while only 50% Cu was recovered from a similar system employing a conventional hydrophobic catalyst. The improved efficiency was attributed to the anchoring of Cu/SL on droplets' surface, which decreased the diffusion resistance. Importantly, the latex stability was retained during the electrolysis. Purified polymer showed higher strength and higher antiaging performance than the untreated counterpart, as demonstrated in tensile tests [50].

## 4. Architectures by ATRP in dispersed media

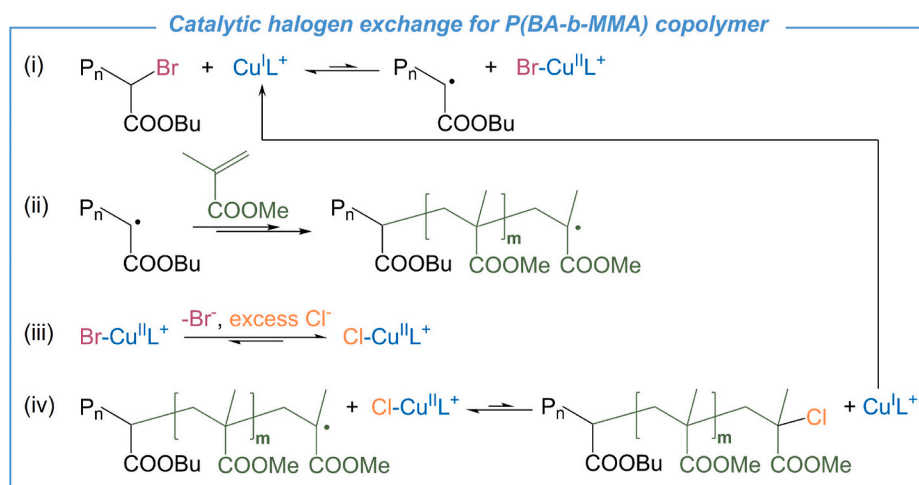
Polymers and copolymers with different compositions and topologies were prepared by ATRP, owing to the retention of chain-end functionality and the possibility of introducing multifunctional moieties (i.e., crosslinkers, mono/multi-functional (macro)initiators, inimers, macromonomers). In dispersed media, the polymerization confinement in droplets of limited size contributes to decreased chain-termination events and can be exploited to tune the polymer architecture.

### 4.1. Linear copolymers

Linear polymer chains represent the most common polymer architecture in ATRP. By tailoring the composition of monomer feed(s) and reaction conditions, statistical, block, and gradient copolymers could be synthesized in ATRP in dispersed media. Here we provide examples of block and gradient copolymers.

#### 4.1.1. Block copolymers

In ATRP, block copolymers are typically prepared by first polymerizing the monomer that gives a more active chain end (e.g., polymethacrylates or polystyrene macroinitiators), followed by polymerization of less active monomers (e.g., acrylates), in order to assure a good initiation efficiency for the second block. However, this sequence cannot be followed when preparing certain A-B-A triblock copolymers. Therefore, halogen exchange is typically used as an efficient way to chain-extend from a less active macroinitiator (MI) to a more active monomer. With halogen exchange, the limitation of mismatching monomer reactivity can be circumvented by switching from C–Br to less reactive C–Cl chain ends. This has been achieved by using  $\text{Cu}^{\text{I}}\text{Cl}/\text{L}$  in equimolar amount to  $\text{P}_n\text{-Br}$  MI in the chain-extension step [139–141]. However, this approach cannot be effectively applied in systems based on activator regeneration, since they operate with ppm amounts of catalysts. Thus, catalytic halogen exchange (cHE) was developed [142] and later implemented in miniemulsion ARGET ATRP to chain-extend a less active PBA-Br MI with a more active MMA monomer, using a catalytic amount of Cu (Scheme 10) [143]. Addition of 0.1 M NaCl or tetraethylammonium chloride to ATRP of MMA



**Scheme 10.** Mechanism of cHE for the chain extension of PBA-Br with MMA in the presence of excess  $Cl^-$ . Reprinted with permission from Ref. [143].

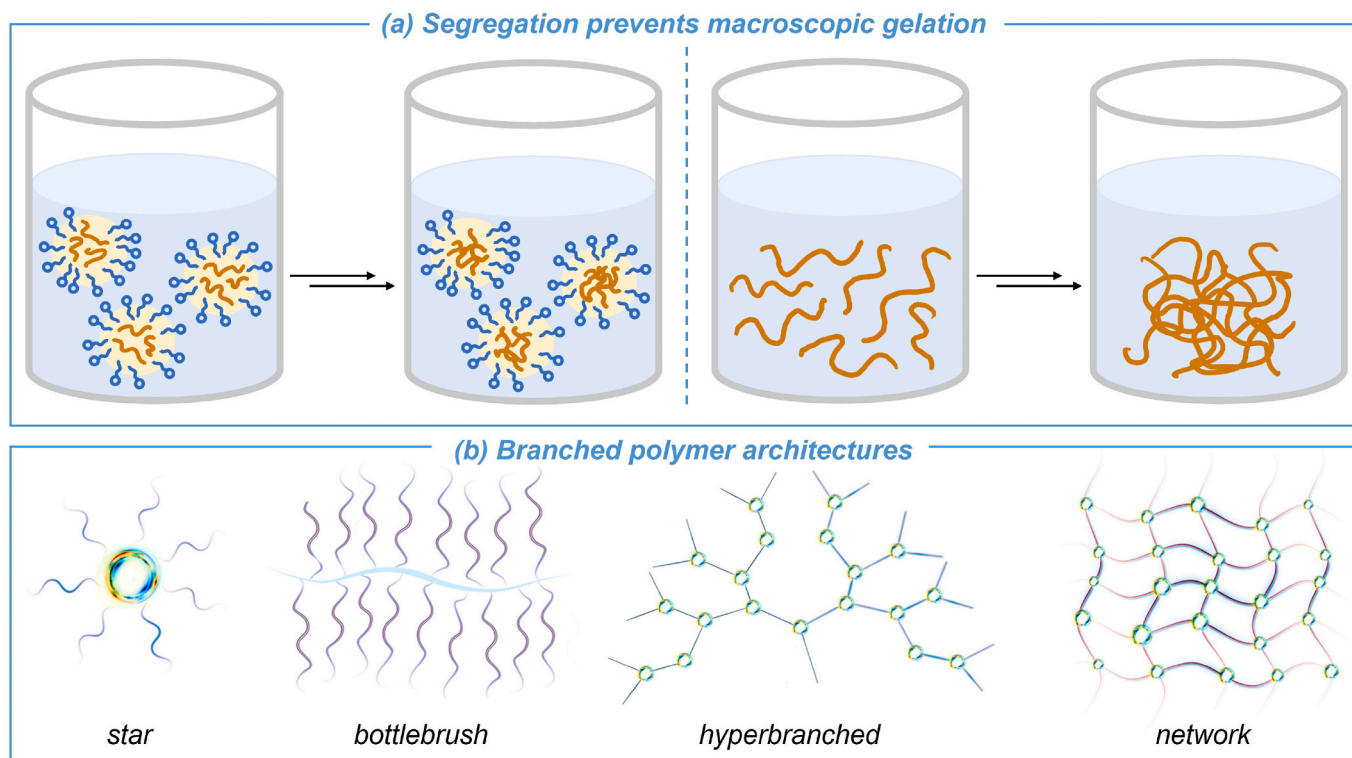
initiated by methyl 2-bromopropionate led to high initiation efficiency and polymers with low dispersity. Similar conditions were then employed in chain extension of PBA-Br MI with MMA to prepare P(BA-*b*-MMA) and P(MMA-*b*-BA-*b*-MMA). This technique allows for building various block copolymers with different structures and functionalities.

Moreover, block copolymers could be synthesized via either *in situ* or stepwise chain extension. After miniemulsion eATRP of BA reached 78% conversion, *in situ* chain extension was achieved by dispersion of *tert*-butyl acrylate (*t*BA) into the miniemulsion under ultrasonication followed by  $N_2$  sparging and electrolysis, resulting in PBA-*b*-P(BA-*co*-*t*BA) [96]. In stepwise chain extension, a solution of PBA-Br MI was isolated by precipitation from the miniemulsion system, then *t*BA was used in the organic phase of a second miniemulsion. The subsequent ATRP resulted

in P(BA-*b*-*t*BA) [96].

#### 4.1.2. Gradient copolymers

Copolymerizations of monomer mixtures by ATRP can result in statistical or gradient copolymers, depending on monomer reactivity [144, 145], but also feeding rate, and hydrophilicity. For monomers with different reactivity, such as acrylates and methacrylates, spontaneous gradient copolymers could be prepared by miniemulsion ATRP [146]. Conversely, for monomers with similar reactivity it was necessary to feed one monomer into miniemulsion polymerization media to produce “forced” gradient copolymers [146,147]. On the other hand, in emulsion ATRP one can exploit the different water solubility of monomers with similar reactivity to obtain spontaneous gradient copolymers. The monomer with higher water solubility will diffuse more rapidly through



**Scheme 11.** Schematics showing (a) the effect of polymer segregation in dispersed media preventing macroscopic gelation, and (b) various architectures for branched polymers.

the aqueous phase, therefore being incorporated first into the copolymer in comparison with the less water-soluble monomer. Thus, P(MMA-*grad*-BMA) and P(BMA-*grad*-LMA) (LMA = lauryl methacrylate) could be prepared by emulsion ATRP of the corresponding monomer mixtures, with no need for adopting a feeding strategy [104,148].

## 4.2. Branched structures

Compared to linear polymers, the distinct architecture and multiple chain-terminal groups of branched polymers endow higher solubility, lower solution/melt viscosity, less deformability, and more chain-end functionality [149]. In bulk and solution polymerizations, especially at high monomer concentrations, the increased number of initiation sites favors the occurring of crosslinking reactions, which can lead to macroscopic gelation. By switching from homogeneous systems to dispersed media, cross-termination reactions can be greatly decreased owing to the segregation of growing polymer chains (Scheme 11a), thus high conversions and low polymer dispersity can be achieved more easily. This feature is especially beneficial for the synthesis of bottlebrush, star, and hyperbranched polymers (Scheme 11b), as it will be described in the next paragraphs.

### 4.2.1. Molecular brushes

Molecular brushes, also known as bottlebrushes, comprise densely grafted side chains, allowing for decreased intermolecular entanglement and for the presence of multiple functionalities in the side chains [150–153]. This unique structure makes molecular brushes suitable for application as lubricants and surfactants, among many others. There are three methods to synthesize bottlebrush polymers by ATRP: “grafting-through”, “grafting-from”, and “grafting-onto”.

“Grafting-through” refers to a process where an oligomer/polymer chain bearing a vinyl group at one end is polymerized by ATRP into a bottlebrush structure. For example, AGET ATRP of OEOMA<sub>475</sub> (OEOMA with average MW 475) was initially conducted in aqueous solution [105]. Continuous feeding of AsAc and increasing monomer concentration resulted in higher conversion, but final polymers showed bimodal distribution of MW caused by bimolecular termination. Significantly improved polymerization control was obtained upon switching to an inverse miniemulsion system, where chain segregation effectively reduced the chances of termination reactions. The resulting polymers had desired MW and low dispersity.

The “grafting-from” method employs a polymer backbone with multiple initiation sites (*i.e.*, a multifunctional macroinitiator). ATRP was initiated from these sites to form densely packed side chains. However, in normal and AGET ATRP in solution, gelation typically occurred at 20–30% monomer conversion. Conversely, in miniemulsion systems eventual crosslinking occurs within the latex particles, with limited effect on the fluidity of the miniemulsion system even when monomer conversion reaches >80% [97].

Finally, “grafting-onto” could be conducted by attaching clickable functional groups to the backbone, followed by performing a click reaction. This approach was not yet used in dispersed media.

### 4.2.2. Star polymers

Star polymers represent a class of branched architectures with linear “arms” connected to a central branching point, typically referred to as the “core” [154–156]. Similarly to the “grafting-from” approach for the synthesis of bottlebrushes, star polymers have been mainly prepared via the “core-first” approach. Compounds with multiple hydroxyl groups (*e.g.*, cyclodextrin, glucose, tannic acid) can be transformed into (multi) functional ATRP initiators by substituting hydroxyl groups with C-X functionalities, typically  $\alpha$ -bromoisobutyrate groups. Cyclodextrin-based ATRP initiators with 14 C-Br sites were used to prepare stars with PBA and PBMA arms in miniemulsion via ARGET ATRP, using the Cu/TPMA-SDS catalytic system [97].

### 4.2.3. Hyperbranched polymers

Highly branched polymers, including dendrimers and hyperbranched polymers, possess highly compact structure, high branching density in the backbone, and numerous periphery groups, leading to many interesting properties, such as high solubility, low viscosity, high functional group density, and potential for cargo loading and release [157]. Dendrimers are regularly branched polymers with a dendritic, tree-like structure [158,159]. Hyperbranched structures do not necessarily have regular branches, however, in contrast to dendrimers, they are prepared via inexpensive one-pot synthesis while retaining highly branched architectures, high solubility, low viscosity and high functional group density. Hyperbranched structures with controlled number of branching sites were prepared by ATRP, through the copolymerization of an inimer (a monomer with an initiating group) with one or more conventional monomers [160–162]. The preparation of hyperbranched polymers via microemulsion ATRP enabled faster kinetics and the generation of polymers with higher MWs, narrower MW distributions and through faster polymerization processes than in typical solution polymerizations, where high dilution and low monomer conversions were needed to avoid gelation [102].

Microemulsion ATRP was also exploited to prepare hyperstar polymers, *i.e.*, core-shell structured star polymers that contain a highly branched polymer as the core and densely grafted radiating arms. This required the polymerization of an inimer to form an hyperbranched core with abundant C-Br initiating sites for the subsequent growth of radiating arms through the addition of a second monomer, in a one-pot microemulsion ATRP process [163,164]. When hydrophobic BA was employed as second monomer, BA molecules diffused into the latexes and swelled the hyperbranched polymers to form a seeded emulsion, minimizing hyperstar-hyperstar coupling events (Scheme 12). On the other hand, the use of a zwitterionic monomer, cysteine methacrylate, as second monomer enabled to stabilize the growing hyperbranched stars, owing to the electrostatic repulsion between charged arms and stars, which also avoided coupling at high conversion.

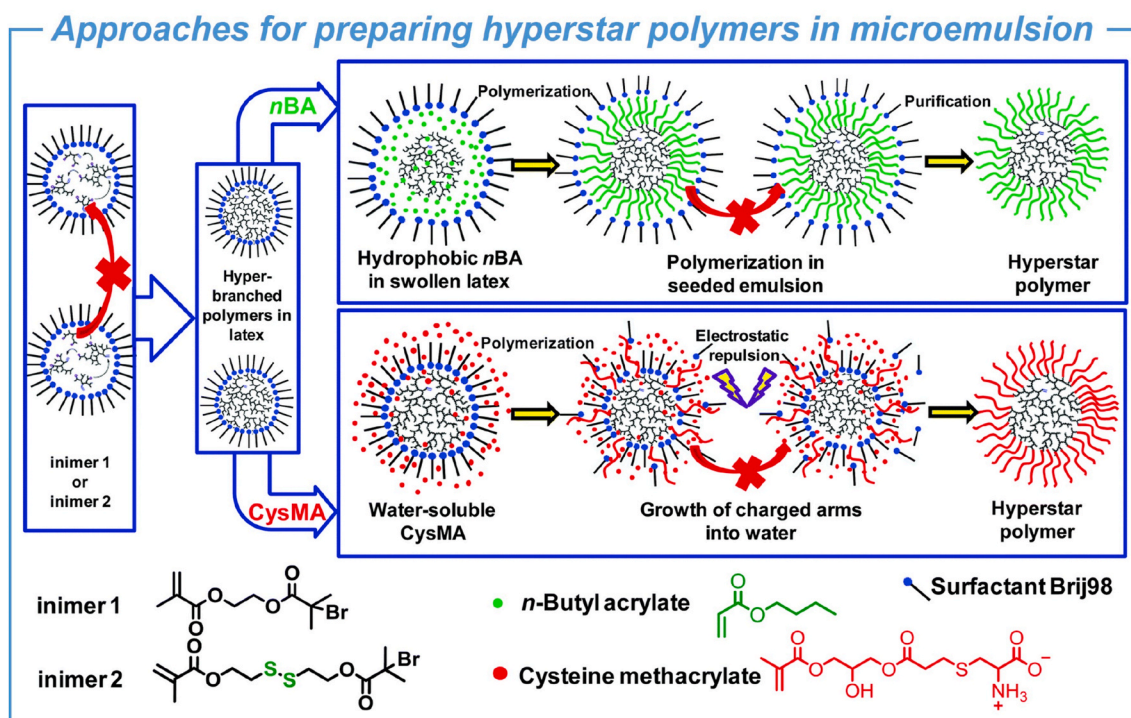
## 4.3. Nanostructures

The heterogenous nature of dispersed media has proven to be an excellent platform to produce nanostructured materials, generated either via (i) self-assembly of block copolymer surfactants, (ii) cross-linking polymers inside the dispersed phase, and (iii) exploiting the peculiar properties of the oil-water interphase.

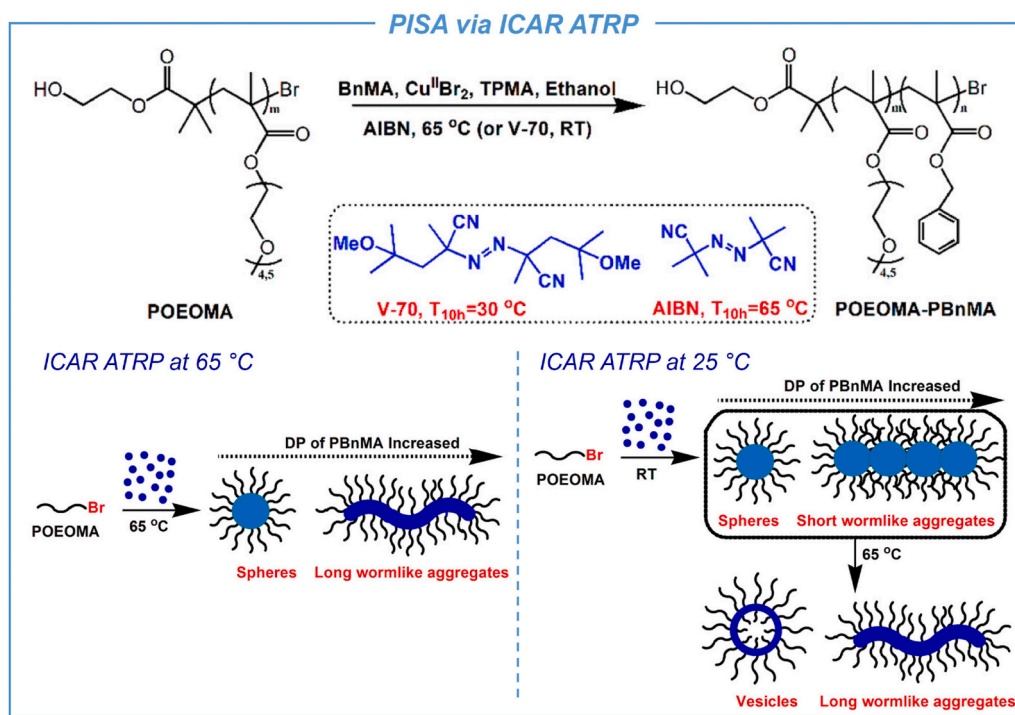
### 4.3.1. Nanostructures by self-assembly

Post-polymerization self-assembly of pre-formed amphiphilic block copolymers with incompatible blocks typically occurs in highly diluted copolymer solutions to form microphase separated structures. Instead, polymerization induced self-assembly (PISA) in aqueous dispersion with relatively high solid content (up to 50 wt%) is characterized by simultaneous polymerization and self-assembly by using a soluble macroinitiator that also acts as a stabilizer as the polymerization of a second soluble monomer proceeds. Upon reaching a critical chain length, the second block becomes insoluble, driving the reorganization of the block copolymer into a variety of nanoobjects via a dispersion polymerization approach [165]. RAFT polymerization has been frequently coupled to a PISA approach [166]. In contrast, the application of ATRP in PISA is limited by the partitioning of Cu complexes in the complex dispersed system.

ICAR ATRP with low Cu concentration was carried out using POEOMA-Br as the macroinitiator and stabilizer and poly(benzyl methacrylate) (PBnMA) as a core-forming block [167]. The system was homogenous in ethanol, but phase separated upon polymerization. Distinct architectures were obtained either at room temperature or at 65 °C, *i.e.*, below and above the  $T_g$  of PBnMA, respectively (Scheme 13). Another core-forming monomer, glycidyl methacrylate, underwent ring-opening reaction during PISA ATRP, allowing for the *in situ*



**Scheme 12.** Synthesis of hyperstar polymers in microemulsion systems. Reprinted with permission from Ref. [163].



**Scheme 13.** Schematic mechanism of PISA via ICAR ATRP of BnMA initiated by POEOMA-Br and different morphologies obtained by performing the polymerization at different temperatures. Reprinted with permission from Ref. [167].

formation of crosslinked nanoparticles [168]. Protein-polymer conjugates could be synthesized during ATRP induced self-assembly. The aqueous dispersion polymerization of 2-hydroxypropyl methacrylate (HPMA) from a hydrophilic protein (human serum albumin, HSA) modified with ATRP initiating groups yielded HSA-HPMA nanospheres and vesicles. During the PISA process, a model green fluorescent protein (GFP) was encapsulated *in situ*, and the polymeric architecture enabled

enhanced intracellular GFP delivery [169].

Multi-layer polymer particles could also be prepared by means of hydrophobic multiblock copolymers with incompatible compositions prepared in dispersed media. Sequential miniemulsion ATRP and *in situ* seeded emulsion ATRP yielded poly(isobutyl methacrylate)-*b*-polystyrene P(*i*BMA-*b*-St) exhibiting a core-shell structure. Upon subsequent alternating addition of *i*BMA and St, an onion-like, alternating

multilayered morphology was observed [113,114]. Similar polymer-vesicle latex particles were prepared by starved feeding of MMA to Br-modified vesicles particles [170].

#### 4.3.2. Crosslinked nanostructures

Chemically crosslinked nanoparticles are more stable against external stimuli and mechanical processing compared to self-assembled structures. The most straightforward recipe to prepare chemically crosslinked nanonetworks via polymerization in dispersed media is to incorporate a crosslinker, e.g., EGDMA. 2-Hydroxyethyl methacrylate (HEMA), 4-vinyl pyridine (4-VP) and PEGDMA were copolymerized in an inverse emulsion, forming a pH-sensitive hydrogel that underwent multiple swelling-deswelling cycles [171]. Similar PHEMA-POEOMA nanogels with uniform and controllable sizes were prepared in inverse miniemulsion by AGET ATRP, where the hydroxy groups from the HEMA moiety allowed for introducing photoinitiation sites for subsequent photopolymerizations [172].

In comparison with crosslinked nanoparticles prepared by conventional free radical polymerization (FRP), those made by ATRP had narrower molecular weight distribution, sharper glass transition [173], and improved loading efficiency [174]. Degradable nano-networks were prepared by ATRP utilizing a disulfide-containing crosslinker [175–177]. Cross-linkable monomers such as allyl methacrylate were incorporated into a block copolymer, where the allyl group could crosslink under UV irradiation, forming network structures [178]. Alternatively, other techniques such as ring opening metathesis polymerization (ROMP) and click-chemistry were conducted simultaneously with heterogeneous ATRP, forming crosslinked networks in one pot [179–181].

Nanoparticles consisting of a solid core and some polymer chain “hair” attached to the core surface are termed “hairy nanoparticles”. Common core materials include metal/metal oxide, silica nanoparticles, and polymer networks. Polymer network nanoparticles, generally prepared by emulsion/miniemulsion polymerization and functionalized with ATRP initiating groups were re-dispersed in monomer solution to form hairy nanoparticles by SI-ATRP. For example, ATRP initiating groups were immobilized onto P(St-co-HEMA) microspheres, enabling the grafting of 2,2,6,6-tetramethyl-4-piperidyl methacrylate [182].

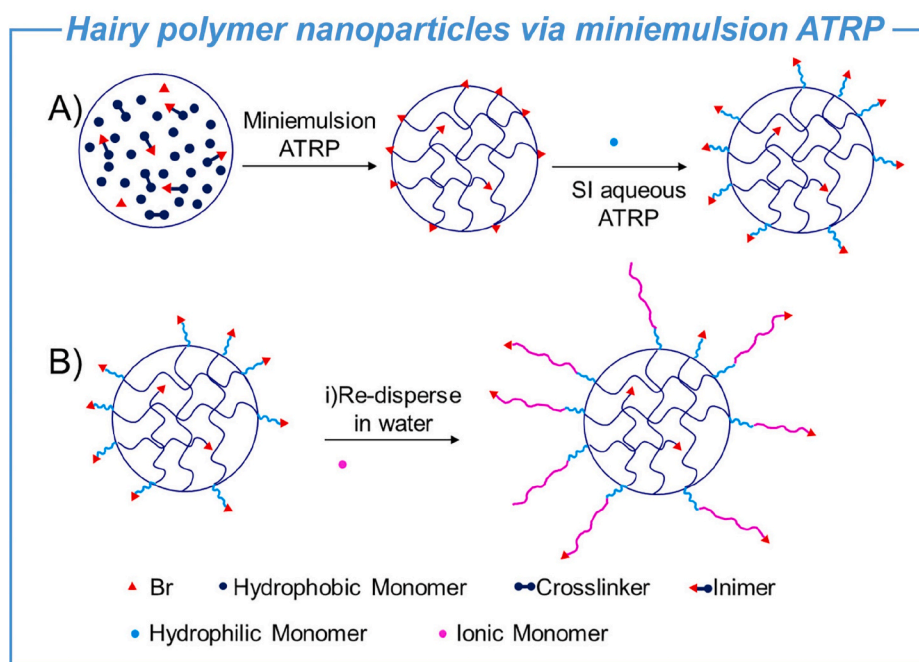
Hydrophilic polymer chains were grafted from hydrophobic cores, yielding amphiphilic hairy nanoparticles with poly(ethylene glycol) or polyzwitterionic-based corona (Scheme 14) [183].

Nanocapsules have attracted much interest due to the encapsulation and controlled release capability provided by their hollow structure [184,185]. Nanocapsules are typically prepared in miniemulsion polymerizations, by confining the polymerization within the water/oil interface [186]. PEO-PBMA-Cl, an inisurf bearing an ATRP initiating group in the hydrophobic fragment, was used to initiate miniemulsion ATRP of BMA at the water/monomer droplet interface, with polymer chains slowly growing inward in a controlled manner. In the presence of a crosslinker and an organic solvent, polymeric nanocapsules with high stability and good dispersibility in organic solvents were prepared [187]. The outer surface of the nanocapsules was further modified when using a difunctional reactive surfactant. Using  $N_3$ -PEO-PBMA-Cl yielded functional nanocapsules with  $N_3$  moieties on the surface, which allowed for attaching organic dye probes or additional polymers via click-chemistry [188].

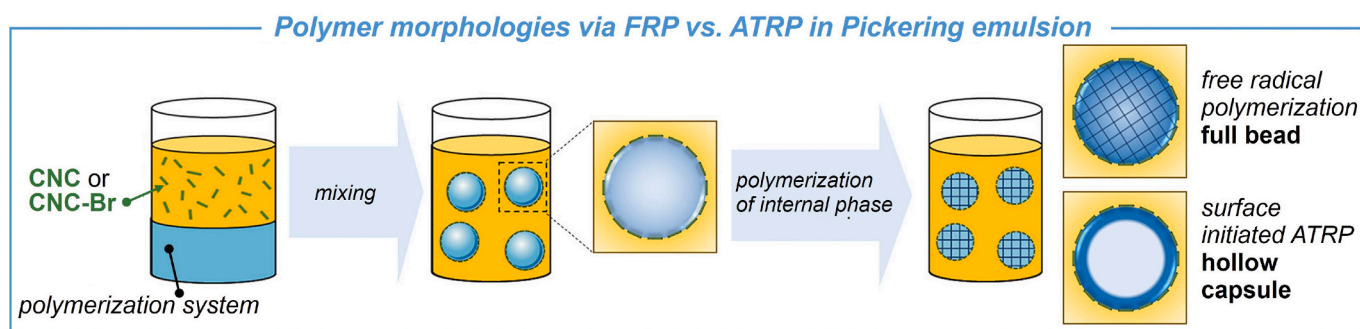
Similar nanocapsules were fabricated via Pickering emulsion ATRP, initiated at the oil-water interface. Materials with different morphologies were formed via either FRP or ATRP in Pickering inverse emulsion stabilized by CNCs and initiator-stabilized CNCs, respectively (Scheme 15) [189]. FRP formed beads, whereas ATRP resulted in hollow structures due to the initiation solely occurring from the oil/water interface. Similarly, when ATRP was performed on silica nanoparticles functionalized with initiator and immobilized at the interface of Pickering emulsions, a polymer network grew inwards, although it did not fill the whole available space of the polymerizing internal phase [190]. Therefore, the resulting polymer-inorganic hybrid has the shape of hollow capsules, which could be processed as semipermeable membranes that served as microdevices for drug or cell delivery.

#### 4.3.3. Polymer-inorganic hybrids and composites

Polymer-inorganic composites and hybrid materials combine the functionality and flexibility of polymers with the high strength of inorganic materials. Polymer-inorganic composites are systems where polymer and inorganic phases are mixed, and they are typically both present in aggregates of large dimensions. However, simple blending of



**Scheme 14.** Schematics of the preparation of amphiphilic hairy polymer nanoparticles by exploiting ATRP in miniemulsion. Reprinted with permission from Ref. [183].



Scheme 15. Different polymer morphologies achieved via FRP vs ATRP in Pickering emulsion. Adapted with permission from Ref. [189].

inorganic materials and hydrophobic polymers often leads to macroscopic phase separation, leading to difficulties in processing, inadequate structure heterogeneity, and poor mechanical properties [191].

Conversely, polymer-inorganic molecular hybrids are materials in which chemical bonds are established between the constituents, so that mixing is effectively occurring at the molecular level, and aggregation and surface defects are minimized [192]. Polymer-inorganic composites have unique properties, such as good mechanical and thermal stability, gas barrier performance, and flame retardancy [193–195].

Polymer-inorganic hybrids can be formed via miniemulsion ATRP from the surface of inorganic materials, which are well-dispersed in monomer droplets thanks to high-shear sonication; this allows for encapsulating inorganic materials in polymer latexes via covalent bonds [193,196–198]. SI-ATRP is a powerful tool to fabricate polymer-inorganic hybrids with improved properties, however polymerizations in solution are generally limited to low monomer conversion (~10%) and/or conducted in the presence of sacrificial initiators to avoid interparticle crosslinking and macroscopic gelation [11,199,200]. In contrast, the segregation of polymerization loci in miniemulsion SI-ATRP enables to reach high conversion without gelation. Polymers were grafted from CdS quantum dots [196], montmorillonite nanoclay [201], and silica nanoparticles [202] via miniemulsion SI-ATRP, yielding well-defined particle brushes. In emulsion ATRP, the electrostatic interaction between a negatively charged P(AA-co-BA)-Br macroinitiator and positively charged Gibbsite platelets facilitated the good dispersion and alignment of the platelets in the resulting polymer matrix, forming “muffin”-like encapsulated Gibbsite structures [203–205].

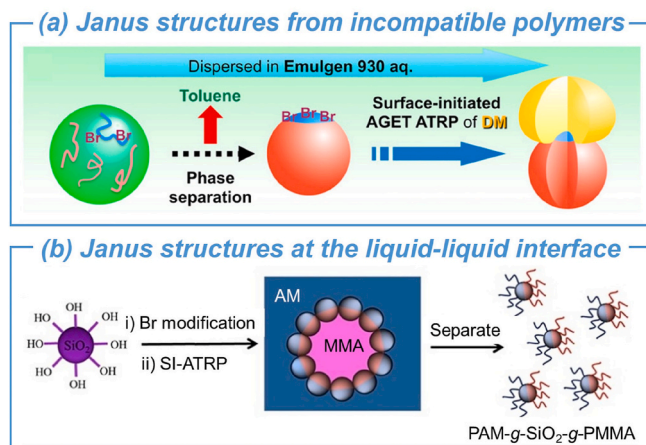
#### 4.4. Other polymeric architectures

##### 4.4.1. Janus structures

Janus structures are another example of complex polymer architecture, which consist of particles whose surfaces display two or more distinct physical properties [206]. Janus structures can be applied as particulate surfactants, imaging nanoprobe, and self-propelled colloidal materials capable of “smart” motion.

Self-assembly of incompatible (co)polymers in emulsion is one strategy to prepare Janus nanoparticles (Scheme 16a). For example, non-functional PMMA and functional P(St-BIEM) (BIEM = 2-(2-bromoisobutyryloxy)ethyl methacrylate, an ATRP inimer) were emulsified together and self-assembled into Janus composite particles during solvent evaporation. P(St-BIEM) accumulated on one side of the particle. Subsequently, poly(2-(dimethylamino)ethyl methacrylate) was grafted from the surface area occupied by localized C–Br initiation sites of P(St-BIEM), forming “mushroom” particles with controllable morphology [207].

In a Pickering emulsion, the Pickering agent itself can be transformed into a Janus particle via ATRP. Graphene oxide (GO) platelets, modified with an ATRP initiator, served as Pickering agents in a toluene/water emulsion. ATRP of toluene-soluble 2-(acryloyloxy)ethyl ferrocene-carboxylate (MAEFC) occurred only on the side of the platelet exposed to



Scheme 16. Different polymer morphologies achieved (a) by exploiting the self-assembly of incompatible polymers upon solvent evaporation to form Janus structures (DM: 2-(dimethylamino)ethyl methacrylate) (reprinted with permission from Ref. [207]); (b) by ATRP at liquid-liquid interface to form amphiphilic Janus particles (AM: acrylamide) (reprinted with permission from Ref. [208]).

the monomer solution. Subsequently, grafting of polydopamine led to Janus GO nanosheets [209]. In an emulsion stabilized by silica-Br nanoparticles and containing an hydrophilic and an hydrophobic monomer in the two phases (Scheme 16b), different polymer brushes were simultaneously grafted from the nanoparticles via SI-ATRP, forming amphiphilic Janus colloids with advanced emulsification properties [90,208]. The stable colloid structure prevented the particles from rotating during polymerization, giving rise to a clean Janus morphology.

##### 4.4.2. Highly porous polymer monoliths

Highly porous polymer monoliths have high surface area and thus can find application in separation, catalysis, and extraction [210]. pHIPE is a representative example of highly porous polymer monolith prepared through an emulsion templating approach. [57,58] The highly interconnected porosity and high surface area renders pHIPE materials suitable as liquid droplet elastomers and templates for molecular recognition materials [211,212]. Various technologies have been employed for pHIPE formation, including FRP, RDRP, step-growth polymerization, click reactions, etc. Among these approaches, RDRP (including ATRP and RAFT polymerization) provides more homogeneous network structures [58].

Typical HIPEs are water-in-oil emulsions, where the hydrophobic monomer(s) is dissolved in the continuous oil phase, while the internal phase represents over 74% of the total volume. The type and locus of ATRP initiation affects the macromolecular structure of pHIPEs [213]. When a conventional oil-soluble ATRP initiator was used by dissolving it

in the monomer phase, the final pHIPes presented rather spherical voids. When nanoparticles functionalized with ATRP initiators were employed, Pickering HIPEs were obtained, in which the type and locus of initiation affected the porous and macromolecular structure of the resulting pHIPes. If a highly organic-soluble nanoparticle ATRP initiator was used, then a pHIPE with rather spherical voids was produced and no preferential diffusion of monomer molecules to the interface was observed. Conversely, when a water-soluble conventional radical initiator was introduced in the system, then interfacial polymerization occurred, and polyhedral voids were formed. During interfacially initiated polymerization, the monomer diffused toward the oil/water interface and the polymerizing macromolecules “locked-in” the nanoparticles at the interface, affecting both the wall and pore structure.

Low density and degradable pHIPes are also of interest. Materials with very low density ( $0.06 \text{ g/cm}^3$ ) were prepared by using special star polymer surfactants by ATRP via an arm-first approach. The surfactants were active at a very low loading ( $<0.1 \text{ wt}\%$ ) [214]. Degradable pHIPes were prepared by incorporating disulfide crosslinkers in the network [215]. Bis(2-methacryloyloxyethyl)disulfide (DSDMA) crosslinker was copolymerized with 2-ethylhexyl methacrylate by AGET ATRP catalyzed by the hydrophobic catalyst  $\text{CuBr}_2/\text{BPMODA}$  (BPMODA = bis[2-pyridylmethyl]octadecylamine). The material had a uniform crosslinked structure which was degraded by tributylphosphine ( $\text{Bu}_3\text{P}$ ), and the resulting degraded product had  $M_n = 30,500$  and  $D = 1.6$ . The low molecular weight and relatively low dispersity indicated the good degradability of the pHIPE.

Similarly, ATRP was conducted in a medium internal phase emulsion (MIPE) system (where the internal phase is between 30% and 70%). The MIPE was stabilized by the synergy of Pluronic F127 and amphiphilic diblock glycopolymers [216]. The latter comprised a glycopolymer-block and a Br-terminated PSt block, thus serving as initiator for AGET ATRP of styrene. The resulting pMIPE exhibited a biocompatible, homogeneous structure with bimodal pore size distribution, showing potential for use in catalysis and biomedical applications.

## 5. Applications

The versatility of ATRP in dispersed media and the preparation of polymers with a broad range of architectures have opened the door to numerous applications. Polymers and copolymers made by ATRP in aqueous dispersed media have been tested for bio-related applications and for coatings. In the following paragraphs, several potential applications will be reviewed, including drug delivery, molecular recognition, bio-quantification, as well as the design of polymer coatings and films with electrocatalytic properties. These applications were supported by synthesizing smart (bio)materials with stimuli-responsive functionalities.

Several complex polymer structures, (e.g., vesicles, nanogels, and hydrogels) hold promise as drug carriers and other biomaterials. Limited biocompatibility and hydrophobicity could be overcome by PEGylation of the nanoobjects. For example, upon incorporation of PEOOMA chains by emulsion ATRP, the cytotoxicity of cationic nanogels was greatly decreased without compromising their antibacterial activity [217].

### 5.1. Drug loading and delivery

Polymer nanoparticles, including nanocapsules, nanospheres, and nanogels, are suitable materials for drug delivery [218]. Hydrophilic nanogels prepared by inverse miniemulsion/microemulsion ATRP have uniform network structure, and thus higher swelling ratios and better colloidal stability in comparison to analogous nanoobjects made by FRP. Moreover, they benefit from controlled degradability upon incorporation of functionalities with desired responsiveness. Nanogels made by ATRP in inverse mini/microemulsions could be loaded with

star-branched polymer nanoparticles (via *in situ* covalent incorporation), with carbohydrates and proteins (via *in situ* physical incorporation), with fluorescent dyes, anticancer drugs, and gold nanoparticles (via physical incorporation). The versatility of cargos and the biocompatibility of the nanogels imparted great potential for targeted drug delivery applications [219].

On the other hand, hydrophobic molecules could be loaded into polymer particles made in O/W systems. Dispersion polymerization of PEG, 2-(diethylamino)ethyl methacrylate (DEAEMA), and *tert*-butyl methacrylate (*t*BMA) led to nanoparticles, where each monomer had a different function: the short hydrophilic PEG chains provided biocompatibility to the outer surface of nanoparticles, the hydrophobic *t*BMA core facilitated the loading and release of hydrophobic fluorescein molecules, and the positively charged PDEAEMA could uptake negatively charged siRNA. Thus the cationic nanoparticles served as carriers for both nucleic acids and hydrophobic drugs [173].

The delivery of drugs could be achieved by incorporation of stimuli-responsive moieties, including thermo-responsive polymers, pH-responsive groups, degradable bonds, and magnetic  $\text{Fe}_3\text{O}_4$  [220]. Di(ethylene glycol) methyl ether methacrylate (M(EO)<sub>2</sub>MA) is a water-insoluble monomer, while its polymer has a lower critical solution temperature (LCST) of  $25^\circ\text{C}$ . The transition temperature of thermoresponsive P(M(EO)<sub>2</sub>MA-OEOMA-EGDMA) microgels could be tuned by changing the network composition [221]. The drug-releasing profile was controlled by either tuning temperature or by chemical reduction of disulfide bonds in DSDMA (Scheme 17), used in place of EGDMA. The magnetically loaded microgels were guided to particular body parts for the delivery of anesthetic drugs [222].

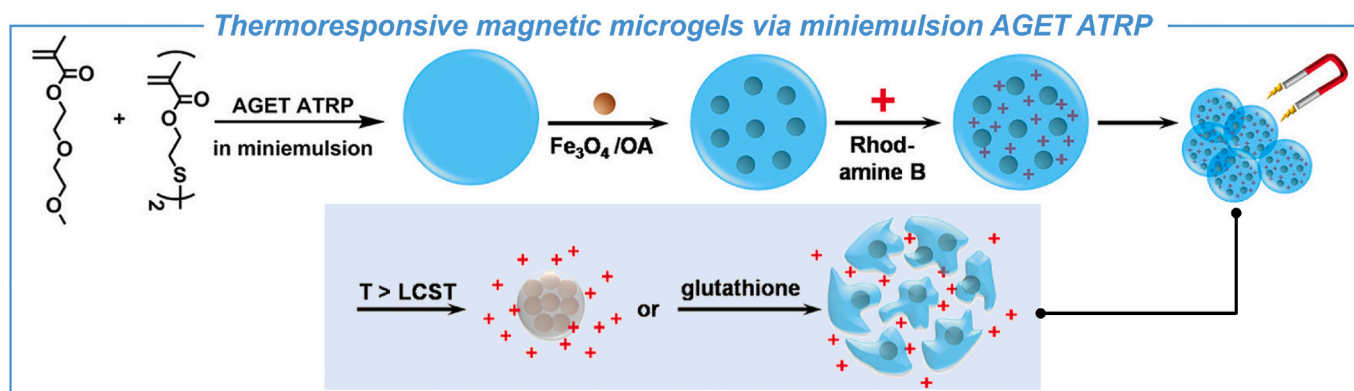
### 5.2. Molecular recognition

The recognition of molecules through devices with high reusability, high selectivity, and low ageing is essential for sensing and removal of toxic compound. Molecularly imprinted polymers (MIP)s were used for effective molecular recognition [223]. MIPs were prepared by copolymerization of functional monomers and crosslinkers in the presence of a template (i.e., the target molecule or a dummy molecule with a similar structure to the target molecule), followed by the removal of template molecules to generate tailor-made recognition sites, which resemble the shape, size and functionality of the template. The preparation of MIPs in dispersed media polymerization is advantageous over surface/film imprinting and surface graft imprinting because of the low toxicity, good dispersibility, and large adsorption capacity in dispersed media.

Indole MIP was synthesized by emulsion ATRP via copolymerization of 4-VP and vinyl modified  $\text{SiO}_2$  nanoparticles in the presence of EGDMA as crosslinker. Indole was incorporated by hydrogen bonding with 4-VP. The resulting indole MIP had high specific area with an equilibrium adsorption capacity of  $34.5 \text{ mg/g}$ , showing promise in removing indole from fuel oil [224]. Emulsion ATRP was used to synthesize superparamagnetic molecularly imprinted nanoparticles for selective recognition of tetracycline molecules from aqueous medium. Acrylate-modified  $\text{Fe}_3\text{O}_4$  was copolymerized into the MIP, allowing for the recognition of tetracycline with a capacity as high as  $12.1 \text{ mg/g}$ ; furthermore, the material could be reused multiple times [225]. MIPs prepared via emulsion ATRP from multifunctional initiation sites of yeast presented fast recognition of ciprofloxacin, high adsorption, and high reusability [226]. Precipitation eATRP of 4-vinylphenylboronic acid in the presence of sialic acid as template molecule yielded nano-MIPs with morphology and size tuned by varying the applied potential [118].

Glycopolymers bearing carbohydrates are highly effective in protein recognition due to the multifunctional carbohydrate side chains. Glycopolymer-modified colloidal particles prepared by emulsion ATRP methods allowed for the recognition of specific proteins. Chlorine-modified PSt nanoparticles were synthesized by emulsion polymerization, followed by SI-ATRP, to incorporate glycol-modified PSt chains on





**Scheme 17.** Thermoresponsive magnetic microgels for drug delivery prepared via ATRP in miniemulsion. Adapted with permission from Ref. [222].

the surface. The resulting particles coagulated in the presence of lectins, including Concanavalin A (Con A) or peanut agglutinin (PNA) through specific glycol recognition sites [92]. Glycopolymers-grafted nanoparticles were also casted into a film to recognize proteins on a surface. For example, a glycosylated amphiphilic block copolymer P (HEMAGI-*b*-BMA)-Cl was used as an inisurf (see Section 3.1) for BMA emulsion polymerization to prepare glycosylated core-shell particles. The resulting latexes were cast into polymer films with bioactive surface owing to the presence of PHEMAGI capable of specific binding of Con A [227].

ATRP in dispersed media was also applied to the preparation of highly selective filtration material. Hydrophilic  $\text{Fe}_3\text{O}_4$  particles used as Pickering agents were modified by ligand exchange with Br-containing carboxylic acid on one side, and subsequent ATRP of MMA led to amphiphilic, superparamagnetic Janus nanoparticles with excellent performance in oil purification [228].

### 5.3. Bio-quantification

Precipitation polymerization of *N*-isopropylacrylamide (NIPAAm) has been used to quantitatively detect hemoglobin, which acted as a catalyst for the ATRP of NIPAAm. The polymerization was conducted at 37 °C (i.e., above the LCST of PNIPAAm), and simple measurement of the turbidity could reflect the amount of hemoglobin in the system (Scheme 18a). The viability of the hemoglobin dose-turbidity formation rate assay both in solution and in physiological fluids proved the versatility of this method, which is also environmentally friendlier than established chemical assays for hemoglobin based on toxic reagents

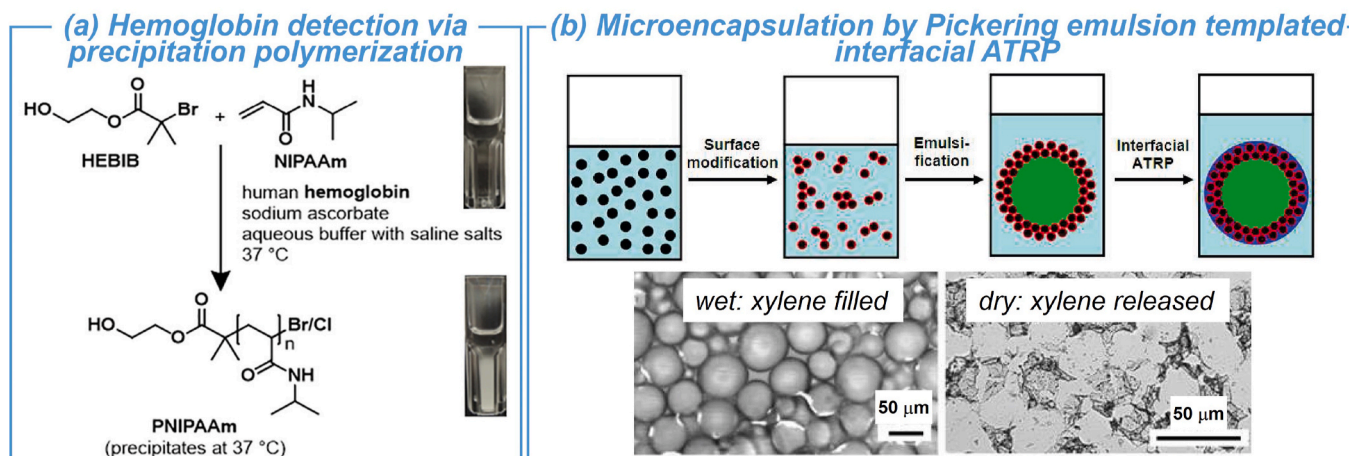
[229].

### 5.4. Coatings and electrocatalytic films

ATRP in dispersed media was translated from solution to surface polymerization for the preparation of polymer brushes [231]. A surface was functionalized with ATRP initiator and put in contact with an aqueous solution containing catalyst and hydrophobic monomer aggregates. Remarkably fast brush growth was observed, ascribed to the formation of monomer aggregates in the aqueous phase and to the beneficial role of hydrogen-bonding by interfacial water.

Self-healing coatings via microencapsulation exploit the release of flowable material from a microcapsule to restore cracks or damages. These approaches were based on mixing ATRP components in a micro-reactor (i.e., the microcapsule) that induced polymerization upon release of its constituents [232,233]. Preparation of solvent-based microcapsules via Pickering emulsion templated interfacial ATRP (PETI-ATRP) involved the electrostatic deposition of a polyanionic ATRP initiator onto cationic nanoparticle surfaces, which yielded modified nanoparticles (Scheme 18b) [230]. Subsequently, the microcapsules were synthesized by PETI-ATRP of *N,N'*-methylene bisacrylamide to form the shell wall. The method allowed encapsulation of core solvents (xylene, hexadecane, and perfluoroheptane) with different solubility properties, and the microcapsule wall-forming chemistry afforded the use of different vinyl monomers.

In another application, switchable latexes were prepared and employed in coating compositions that responded to changes in the environment. Using 1,1-(diethylamino)undecyl 2-bromo-2-



**Scheme 18.** (a) Precipitation ATRP of NIPAAm catalyzed by hemoglobin enabling hemoglobin quantification (adapted with permission from Ref. [229]); (b) Pickering emulsion templated interfacial ATRP for microencapsulation and release of various solvents (adapted with permission from Ref. [230]).

methylpropanoate as an amine-bearing inisurf (Scheme 19), the resulting PMMA polymer latexes could switch between aggregated and dispersed states using CO<sub>2</sub> and argon as triggers [234].

Crosslinked nanoparticles obtained in dispersed media were used to prepare catalytic films on electrodes. For example, surface-protected P(AN-*b*-BA) polymer nanoparticles were pyrolyzed into individual nanoporous carbon spheres with electrocatalytic properties [235]. These PAN-based nanoparticles were cast as an electroactive material with high surface area, for application as supercapacitors or for the oxygen reduction reaction. Surface-protected P(AN-*b*-BA) self-assembled polymer nanoparticles prepared by miniemulsion ATRP were pyrolyzed into individual nanoporous carbon spheres with better performance for CO<sub>2</sub> capture with a higher CO<sub>2</sub>/N<sub>2</sub> selectivity, and increased efficiency in catalytic oxygen reduction reactions, as well as improved electrochemical capacitive behavior, as compared to regular nanocarbon monoliths [235,236].

## 6. Conclusions and outlook

The last 15 years have witnessed important developments and increasing interest in performing ATRP in aqueous dispersed media for preparing well-defined polymers and nanoobjects. The availability of low-ppm ATRP techniques triggered the development of novel synthetic approaches for heterogeneous ATRP that used lower Cu loadings, facilitating the removal of Cu from the final latexes. Moreover, the design of reactive surfactants and catalytic systems capable of overcoming the limitations dictated by the partitioning of most Cu complexes among different phases enabled improved polymerization control. Noteworthy is the development of effective approaches for ATRP in emulsion, including the seeded-emulsion strategy, phase-transfer catalyst, surfactant-ligand complex, and a combination of ion-pair and interfacial catalysis via hydrophilic Cu complexes and anionic surfactants. Traditional *ab initio* emulsion is much easier to employ at large scale compared to miniemulsion or microemulsion methods, which require high shear forces and high surfactant loading, respectively. Moreover, oxygen scavenging strategies and catalytic halogen exchange simplified the reaction setup for a broader range of polymer compositions and architectures.

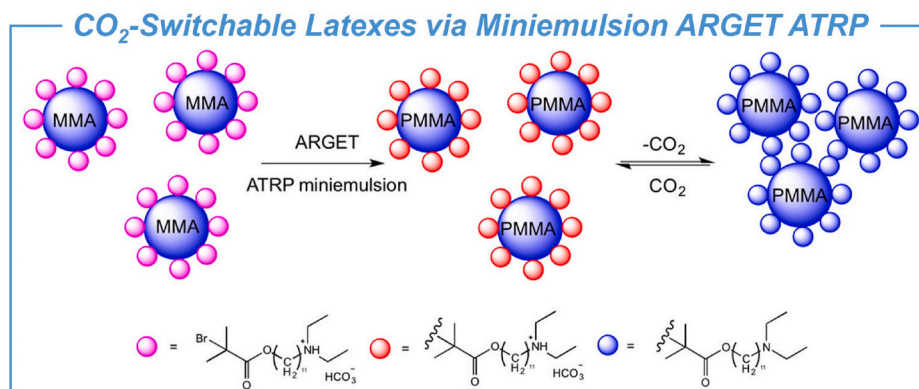
When performing ATRP in dispersed media, the segregation of polymerization loci into droplets of 50–500 nm diminished interparticle radical coupling reactions, thus high viscosity and macroscopic gelation were avoided, enabling to reach higher monomer conversion compared to homogeneous ATRP. This benefited the preparation of polymer bottlebrushes, hyperbranched structures, and inorganic-polymer hybrids with excellent control over polymer dispersity even at high monomer conversion. Various polymer architectures and topologies were achieved by exploiting self-assembly or crosslinking approaches, and by introducing inimers or multi-functional surfactants. The tunable

composition of polymers allowed for their use for molecular recognition and bio-quantification. The hydrophobic environment within polymer nanocapsules or nanogels and the incorporation of stimuli-responsive functionalities enabled the loading and delivery of hydrophobic drugs. Nanocapsules were designed for potential application in self-healing coatings.

Innovations in dispersed media ATRP are expected to come from improved mechanistic understanding, as recently illustrated by the design of the Cu/TPMA-SDS catalytic system, which outperformed most catalysts in terms of polymerization control and ease of product purification. This advancement eliminated the need for developing hydrophobic Cu complexes or dual-catalyst systems. In-depth studies of catalyst partitioning and interactions with other components can guide the rational design of reactive surfactants, ligands, or phase-transfer complexes.

Mechanistic analysis could be promoted by computational studies and simulations, although examples of computational studies of dispersed media polymerizations are still quite rare. PREDICI, a kinetic-based modeling tool, was successfully used for modeling ATRP under homogeneous conditions [237,238], even for bottlebrush preparation [239]. However, only one report used PREDICI for the simulation of (semi)batch emulsion ATRP of styrene [240]. A Design of Experiment (DoE) approach was used to assess the influence of five independent variables (catalyst, initiator, temperature, reducing agent and surfactant loadings) on monomer conversion, polymer average molecular weights, and dispersity in AGET emulsion ATRP. Analysis of 5 fractional factorial experiments showed that temperature was the most influential factor [241].

The translation of academic research on ATRP in dispersed media into industrial applications depends on the multidisciplinary collaboration among chemists and engineers for reaction scale-up, as well as with biologists and medical researchers for the preparation of biomaterials and efficient drug-delivery systems. Roughly half of commercial coatings are prepared by dispersed media polymerizations, and several polymer-based products, including paints, creams, and medical treatments are sold in a dispersed state. The industrial use of heterogeneous ATRP systems is promoted by simple and low-cost reactions setups, as in the case of *ab initio* emulsion ATRP, which could be readily integrated into existing reactors for emulsion FRP. Indeed, emulsion ATRP was already scaled up to the 2 L volume [242]. Upon optimizing the reaction conditions, including temperature and reagent ratios, PMMA with dispersity of 1.17 was produced, without appreciable coagulation [242,243]. Despite the complexity of heterogeneous emulsion ATRP systems, empirical models showed that temperature strongly affects the rate of polymerization,  $M_n$  and  $\mathcal{D}$ . Moreover, the surfactant amount and stirring speed affected the rate of emulsion ATRP, while the nature and amount of ligand mostly influences  $M_n$  and  $\mathcal{D}$  of the formed polymer [244]. Improved understanding of the influence of various parameters,



Scheme 19. General concept of CO<sub>2</sub>-switchable PMMA latexes prepared via ARGET ATRP in miniemulsion. Reproduced with permission from Ref. [234].

achieved through modeling and high-throughput experimentations, as well as continuous advancement in reaction design, is expected strongly promote the industrialization of ATRP in dispersed media in the coming years.

### Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: K Matyjaszewski reports financial support was provided by National Science Foundation.

### Data availability

Data will be made available on request.

### Acknowledgements

Fundings from the National Science Foundation (CHE 2000391 and DMR 2202747), the European Union – NextGenerationEU, and the University of Padua under the 2021 STARS Grants@Unipd programme “Photo-e-cat” are gratefully acknowledged.

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