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# Polymerizations by RAFT: Developments of the Technique and Its Application in the Synthesis of Tailored (Co)polymers

Mona Semsarilar\* and Volker Abetz\*

Reversible addition–fragmentation chain transfer (RAFT) polymerization is an increasingly popular method of controlled radical polymerization and remarkable advances is made in recent years. This polymerization technique offers great chances for more sustainable routes to obtain tailor-made polymers with high precision. This article may be of interest not only for readers familiar with the technique, but also to newcomers to the field or colleagues, who are looking for more sustainable or safer polymerization techniques to obtain an extensive number of possible polymer structures. After an introduction to RAFT polymerization, different novel paths to carry out RAFT polymerization are discussed in terms of their potential and also advancements in the polymerization technology such as polymerization induced self-assembly or carrying out the polymerization in continuous flow reactors are highlighted. At the end some upcoming application areas of polymers prepared by RAFT are presented.

## 1. Introduction

In synthetic polymer chemistry, controlled polymerizations are of particular interest when tailored (co)polymers with a narrow dispersity of chain lengths and compositions are the aim. Controlled polymerizations are chain growth reactions. Living anionic polymerization is probably the most well known type, as this polymerization (at least in some cases) can run without termination or side reactions.<sup>[1]</sup> Cationic polymerization, on the other hand, suffers from side reactions and termination reactions in most cases and therefore could not be considered a living polymerization.<sup>[2]</sup> Condensation reactions could also be living polymerizations. Examples are enzymatic polymerizations<sup>[3]</sup> or polycondensation of monomers with tailored reactivities.<sup>[4]</sup>


Radical polymerizations are of particular interest, as compared to ionic polymerizations as radicals could polymerize larger variety of double bond containing monomers. Besides homopolymers and block copolymers, controlled radical polymerizations also allow the synthesis of random and gradient copolymers in an easier fashion as compared to other polymerization techniques.

While radical polymerization is known since a long time and it is of great commercial relevance, only during the last decades great efforts have been undertaken to introduce control mechanisms in radical polymerization. In comparison to living polymerizations, where no termination reactions occur, controlled radical polymerizations are never truly living, since termination reactions could not be eliminated. However, the probability of their occurrence is largely reduced because of a significantly decreased concentration of active polymerizing radicals, which are in equilibrium with a nonradical or a less active radical species that cannot initiate or terminate a polymerization by themselves. This may happen in different ways, which are characteristic for the different types of controlled radical polymerization. The active growing chain radical can transform into a nonradical species by a reversible redox reaction (atom transfer radical polymerization, ATRP), or it can combine with a less-active radical (nitroxide mediated polymerization, NMP). Also formation of a less active radical is possible by reacting with a suitable transfer agent (RAFT polymerization). RAFT polymerization has gained a lot of interest during the last years due to its compatibility to a large family of functional monomers often not suitable for other

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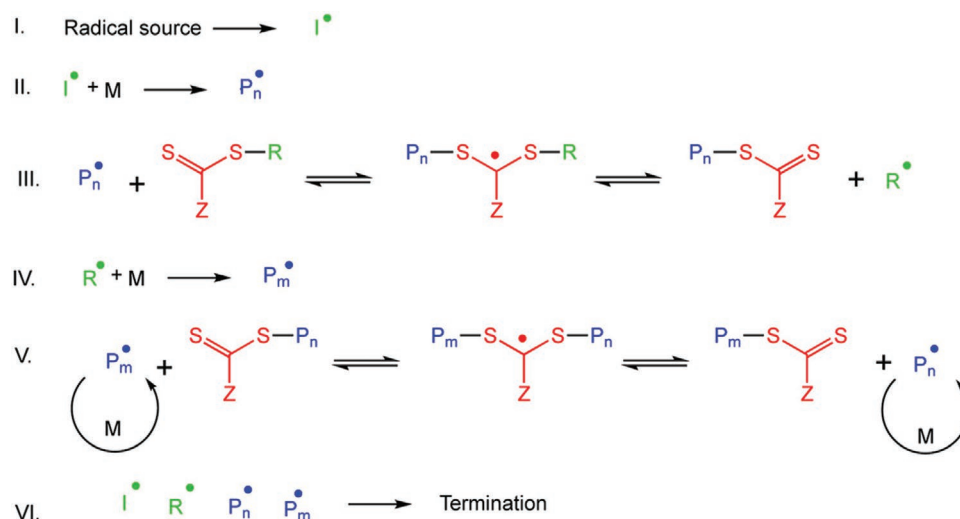
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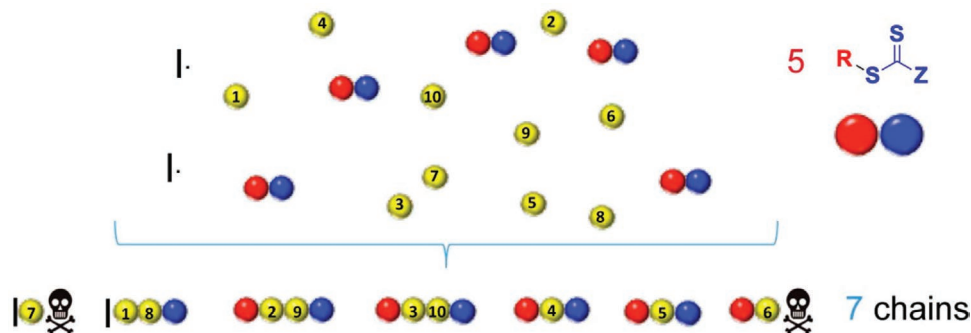


**Figure 1.** Proposed mechanism of reversible addition–fragmentation chain transfer polymerization. Reproduced with permission.<sup>[10]</sup> Copyright 2017, American Chemical Society.

controlled radical polymerization techniques. RAFT process was first reported by Moad and co-workers in 1998.<sup>[5–7]</sup> RAFT is a controlled radical polymerization recently labeled as reversible deactivation radical polymerization (RDRP) by IUPAC.<sup>[8]</sup> This simple polymerization technique mimics the characteristics of living polymerization as well as flexibility of a radical process, making it a versatile and powerful tool to synthesize complex architectures with predictable molecular weight, low molar mass dispersity ( $\mathcal{D}$ ), high end-group fidelity, and capacity for continued chain growth. The mechanism of RAFT relies on the equilibrium between the active and dormant chains, which is reached by a degenerative transfer.<sup>[9]</sup> In such a system the overall number of radicals stays constant during the activation–deactivation process, hence a source of radicals is necessary (i.e., initiator). At the activation step, radicals add to the chain transfer agent (CTA also known as RAFT agent), leading to the equilibrium between the active and dormant species (**Figure 1**). The chain transfers steps that form the foundation of the RAFT mechanism are degenerate as it includes the reversible transfer of the functional chain end-group between the dormant chains and the propagating radicals. At any point of polymerization, since the rate of addition–fragmentation equilibrium is higher than that of the propagation, all chains should

have a similar degree of polymerization (DP). As mentioned a radical source is required to adjust the polymerization rate as well as the number of living chains (chains capped with the RAFT agent) under certain conditions. In RAFT polymerization, the number of dead chain could be predicted and controlled ahead of polymerization since the sum of added radicals directly dictates the number of “dead” chains (chains undergone bimolecular termination). RAFT mechanism results in formation of four groups of chains: 1) chains initiated by RAFT agent R- group and capped with the thiocarbonylthio end-group (living chains); 2) chains initiated by the initiator and capped with the thiocarbonylthio end-group (living chains); 3) chains initiated by RAFT agent R- group with no end-group (dead chains); 4) chains initiated by the initiator with no end-group (dead chains) (**Figure 2**).

Kinetics of RAFT polymerization is similar to that of conventional radical polymerization. The factors influencing the rate of RAFT polymerization according to Equation (1) are therefore 1) propagation rate ( $k_p$ ), 2) monomer concentration ( $M$ ), 3) initiator efficiency ( $f$ ), 4) decomposition rate coefficient of the initiator ( $k_d$ ), 5) initiator concentration ( $I_0$ ), and 6) termination rate coefficient ( $k_t$ ). By adjusting the factors mentioned above it is possible to enhance the “livingness” of the system.



**Figure 2.** Schematic representation of the RAFT process. Two radicals (I) are introduced in a system containing ten monomers (yellow) and five RAFT agents (red R-group and blue  $Z-C(=S)-S$ -group). Polymerization leads to seven chains comprising two dead chains and five living chains. The livingness of the system L (%) is therefore  $5/(5+2) \times 100 = 71\%$ . Reproduced with permission.<sup>[10]</sup> Copyright 2017, American Chemical Society.



Livingness is expressed in Equation (2) where  $[CTA]_0$  and  $[I]_0$  are the initial concentrations of chain transfer agent and initiator, respectively. Term “2” refers to the number of primary radicals with certain efficiency ( $f$ ). The term  $1 - f_c/2$  represents the number of chains produced in a radical–radical termination event with  $f_c$  being the coupling factor ( $f_c = 1$  refers to 100% bimolecular termination by combination;  $f_c = 0$  means 100% bimolecular termination by disproportionation)

$$R_p(t) = K_p [M] \sqrt{\frac{fk_d [I]_0 e^{-k_d t}}{k_t}} \quad (1)$$

$$L = \frac{[CTA]_0}{[CTA]_0 + 2f [I]_0 \left(1 - \frac{f_c}{2}\right) (1 - e^{-k_d t})} \quad (2)$$

RAFT system is able to generate living chains that could be further extended by addition of monomer. Since the number of dead chains is only dictated by the number of radicals present, independent from monomer conversion, block copolymers can be prepared with 100% monomer conversion. Although addition of initiator for each chain extension will result in formation of homopolymer (dead) chains that can be predicted and minimized via tuning the amount of initiator added.<sup>[10–14]</sup> In principle also radical-forming impurities such as peroxide containing solvents (for example, tetrahydrofuran or dioxane) may be sufficient to perform RAFT polymerizations with reasonably good control.<sup>[15]</sup>

## 2. Novel Developments in RAFT Mechanism/Chemistry

### 2.1. Photo-RAFT

As described previously, in the process of RAFT, the chain transfer agent reacts rapidly with the free radicals generated from a suitable radical source. Traditionally, the polymerization is initiated via addition of radicals. Free radical initiators could be generated via different stimuli such as heat, light (UV), redox catalyst, ultrasound, electrochemical or enzymes in order to control the activation and deactivation steps. Photoregulation is a good method to provide high degrees of spatial and temporal control over RAFT polymerization as well as the low-cost and abundance of light sources. Regulating the RAFT polymerization by using photosensitive species the polymerization could be switched “on” and “off.” Photoregulation could be accomplished via the use of 1) photosensitive RAFT agents, 2) external photoinitiators, 3) photocatalysts, and 4) nonreactive photoadditives.

#### 2.1.1. Photosensitive RAFT Agents

The color of the RAFT agents suggests that they absorb light in the visible region. Irradiation under suitable wavelength, the weak C–S bond in the CTA undergoes homolytic decomposition to produce carbon-centered and stable sulfur-centered radicals. The carbon-centered radicals would then initiate the

polymerization, while the sulfur-centered radicals act as the controlling agent. Unlike the thermoinitiated RAFT polymerization, such initiation does not depend on any external source of radicals resulting in polymers with no “impurities.”

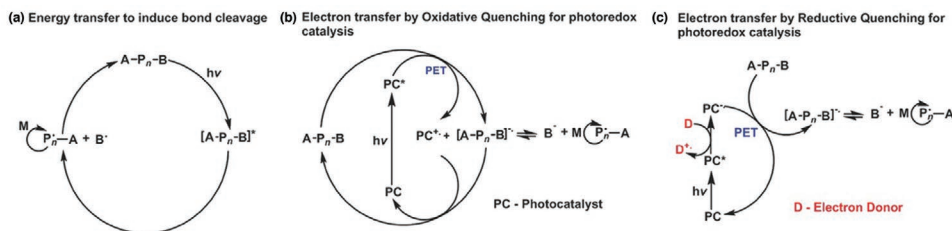
The use of cleavable RAFT agents have led to synthesis of well-controlled block and graft (co)polymers under UV irradiation at room temperature. It should be noted that using UV irradiation over a long period would lead to the irreversible degradation of the RAFT chain end and gradual loss of control over the polymerization. One possible way to avoid such degradation is the use of long-wave UV or visible light irradiation.<sup>[16–18]</sup>

#### 2.1.2. Use of External Photoinitiators

This is very similar to thermal initiation pathway with the difference that the initiator is activated by light. Photoinitiators are molecules or combination of molecules that can undergo photodecomposition (under UV or visible light irradiation) to release free radicals. Unlike photoiniferter or photoactivated RAFT polymerization discussed above, the roles of the radical initiator and CTA are separated in photoinitiated RAFT polymerization. In photoinitiated RAFT polymerization, as in classical RAFT, the appropriate CTA for the particular monomer class, the suitable photoinitiator and the efficient light source need to be carefully chosen. It has been reported that in general trithiocarbonates are less light-sensitive as compared to dithioesters that decompose significantly when exposed to light.<sup>[19,20]</sup> Also majority of the efficient photoinitiators such as (2,4,6-trimethylbenzoyl)diphenylphosphine oxide are phosphines which are known for cleaving the RAFT chain-end.<sup>[21]</sup> The significant advantage of this strategy is the high polymerization rates (fast polymerization even at room temperature) compared to other photo-regulated RAFT polymerizations, which makes the strategy suitable for polymerization of temperature-sensitive compounds. In a recent review Li et al. summarize the most efficient photoinitiators and the suitable monomer/solvent combinations.<sup>[17]</sup> Despite the advancement and the numerous studies published on the subject, this pathway still suffers from the following restraints: 1) limited choice of available photoinitiators, 2) most photoinitiators only active in the UV region, 3) photolysis of RAFT moieties under UV radiation leading to degradation, and 4) photocontrol over initiation step and not the subsequent propagation and chain transfer steps. The challenge would be to develop more efficient photoinitiating systems working under visible light.<sup>[17]</sup>

#### 2.1.3. Use of Photocatalysts

In recent years many photocatalysts active in the range of visible-light or near-infrared regions have been synthesized and used in organic synthesis.<sup>[22–24]</sup> This advancement inspired Hawker and Fors to develop the concept of photocatalyzed ATRP.<sup>[25]</sup> This worked paved the way to combine the photoredox catalysis and photoiniferter properties of the RAFT agents bringing along the concept of photoinduced electron transfer RAFT (PET-RAFT) first reported by Boyer and co-workers, where an iridium and ruthenium transition metal



**Figure 3.** Photomediated controlled/radical polymerization (photo-CRP). a) Energy transfer to induce bond cleavage, b) electron transfer through oxidative cycle to induce photoredox catalysis, and c) electron transfer through reductive cycle to induce photoredox catalysis. Reproduced with permission.<sup>[28]</sup> Copyright 2017, Wiley-VCH GmbH.

complexes were used as the photoredox catalyst. The mechanism involves the excitation of the photocatalyst under visible light irradiation, triggering electron transfer to the thiocarbonylthio moiety, reducing it to form radicals, which subsequently initiates the RAFT process and also form thiocarbonylthio anionspecies (chemically stable by themselves or via complexing with electron-deficient transition metals). Later, the radical might eventually interact with the oxidized photocatalyst to “reset” the system and complete the catalytic cycle.<sup>[26]</sup> In the energy transfer mechanism, the excited photocatalyst transfers the energy to the thiocarbonylthio compound generating propagating radicals for polymerizing monomers as well as forming thiocarbonylthio radicals that rapidly recombine to produce dormant RAFT polymer chains.<sup>[26,27]</sup> The control over the polymerization is achieved through a combination of degenerative chain transfer and reversible termination.<sup>[27]</sup> The nature of the PET-RAFT mechanism allows the control of the polymerization via controlling the state of the light source. Consecutive cycles of switching the light “off” (no polymerization) and “on” (polymerization) allow an excellent control over the RAFT polymerization. The comparison between the electron- and energy-transfer mechanisms is summarized in **Figure 3**.<sup>[28]</sup> Different types of photocatalysts have so far been used in the PET-RAFT process. These are mainly, metal complexes, metal oxides, metal-free inorganic materials, and organic fluorophores.<sup>[29]</sup> The main advantages of the photocatalytic RAFT polymerization are 1) elevated polymerization rates, 2) suitable for a range of solvents with varying polarities, 3) tolerance toward the presence of oxygen in the polymerization media, and 4) absence of initiator. Since the first report on PET-RAFT by Boyer team, a tremendous amount of work has been carried out in developing and advancing the concept. There are several extensive review articles gathering this rich literature that would be a good source for readers interested in the field.<sup>[16,17,22–24,27]</sup>

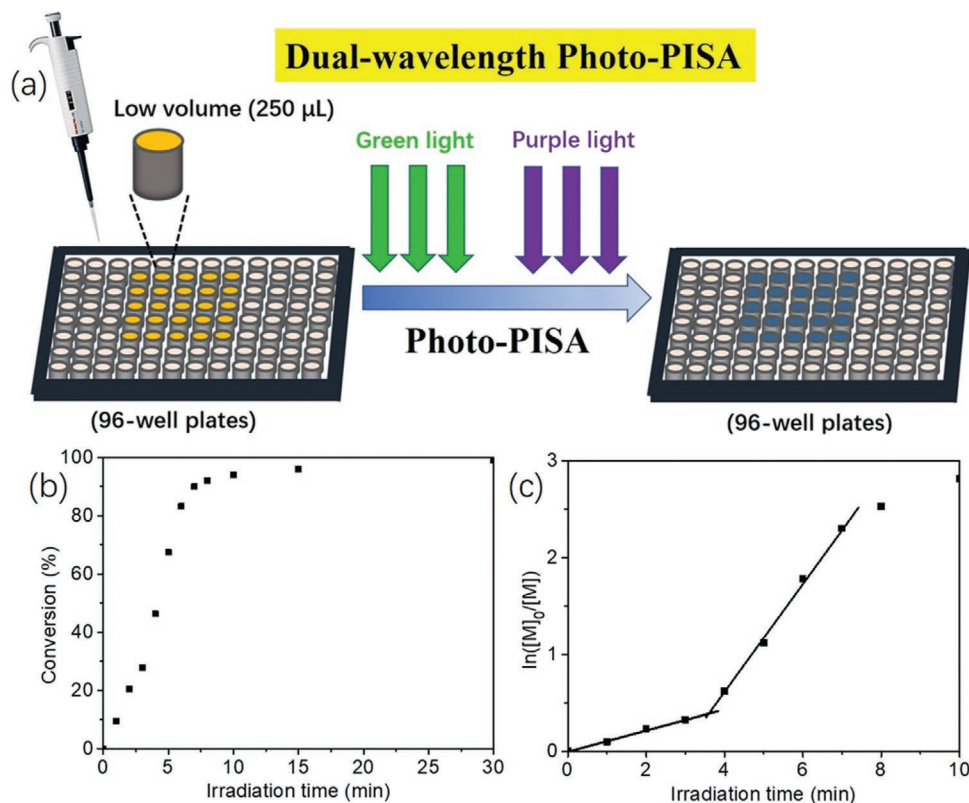
## 2.2. RAFT in Presence of Oxygen (O<sub>2</sub> Tolerated RAFT)

Oxygen is a radical scavenger. It inhibits radical polymerization by reacting with the propagating radicals to form peroxy species leading to termination of the radical chains.<sup>[30]</sup> The classical way to remove the molecular oxygen from reaction mixture is degassing and replacing the air containing oxygen with an inert gas such as nitrogen or argon prior to polymerization. The air removal could also be performed with repetitive freeze–pump–thaw cycles which are a slightly more tedious method as

compared to replacing the air with a second gas. Each of these methods has its own disadvantages, especially concerning the environment and sustainability. Inert gases are scarce and expensive. Performing cycles of freeze–pump–thaw are time consuming and energy demanding. Also these methods increase the possibility of losing volatile reagents and they are difficult to be performed on large volume reaction mixtures. A third and perhaps easier and more efficient solution could be the addition of sacrificial agents that would react with oxygen. However, the concern with this method would be the inertness of the reagent in the polymerization media and their removal from the final product. Among the different RAFT polymerization techniques, it has been shown that the PET-RAFT polymerization could be carried out successfully in presence of oxygen. Oxygen tolerance in PET-RAFT is attributed to 1) conversion of the molecular oxygen into singlet oxygen by intermolecular triplet–triplet annihilation of energy transfer from the excited photoredox catalyst to molecular oxygen, and 2) reaction of singlet oxygen with the solvent or other added reducing agents such as tertiary amines, ascorbic acid, anthracene, limonene, thioethers, etc. There is often an induction period of several hours during irradiation where oxygen is consumed such as when Ir(ppy)<sub>3</sub> and Ru(bpy)<sub>3</sub>Cl<sub>2</sub> are used as photoredox catalysts. However, when the system is mediated by zinc tetraphenylporphyrin (ZnTPP) no induction periods are reported. Also no variation has been observed in polymerization rates between reactions performed in presence and absence of oxygen. This suggests that ZnTPP is an excellent singlet oxygen generator, which could convert the molecular oxygen into singlet oxygen relatively fast. Also the use of reductant agents such as triethylamine and ascorbic acid that could quench the singlet oxygen would make it possible to perform the polymerization without the deoxygenation procedure.<sup>[26,31–35]</sup>

In a recent study, Tan and co-workers report an efficient photoinitiated polymerization-induced self-assembly (photo-PISA) with excellent oxygen tolerance through dual-wavelength type I photoinitiation and photoinduced deoxygenation. Dual-wavelength photo-PISA of 2-hydroxypropyl methacrylate (HPMA) in water was induced by green light and purple light using SPTP and eosin Y in the presence of ascorbic acid (AscA). Dual wavelength photo-PISA of isobornyl acrylate or benzyl methacrylate (BzMA) in alcohol/water was induced by red light and blue light using bis(acyl) phosphane oxide and ZnTPP in the presence of AscA. The kinetic studies performed, suggested that high monomer conversions could only be achieved when dual-wavelength light irradiation was used. The versatility of this system demonstrated by reactions performed in flow reactor





**Figure 4.** a) Schematic illustration of dual-wavelength photo-PISA performed in a 96-well microliter plate. b) Polymerization kinetics of dual wavelength aqueous photo-PISA of HPMA performed in a 96-well microliter plate ( $[\text{HPMA}]:[\text{PPEGMA14-CDPA}]:[\text{Eosin Y}]:[\text{AscA}] = 200:1:0.05:1$ ). c) Plots of  $\ln([M]_0/[M])$  versus irradiation time for dual-wavelength aqueous photo-PISA of HPMA performed in a 96-well microliter plate. Reproduced with permission.<sup>[31]</sup> Copyright 2020, American Chemical Society.

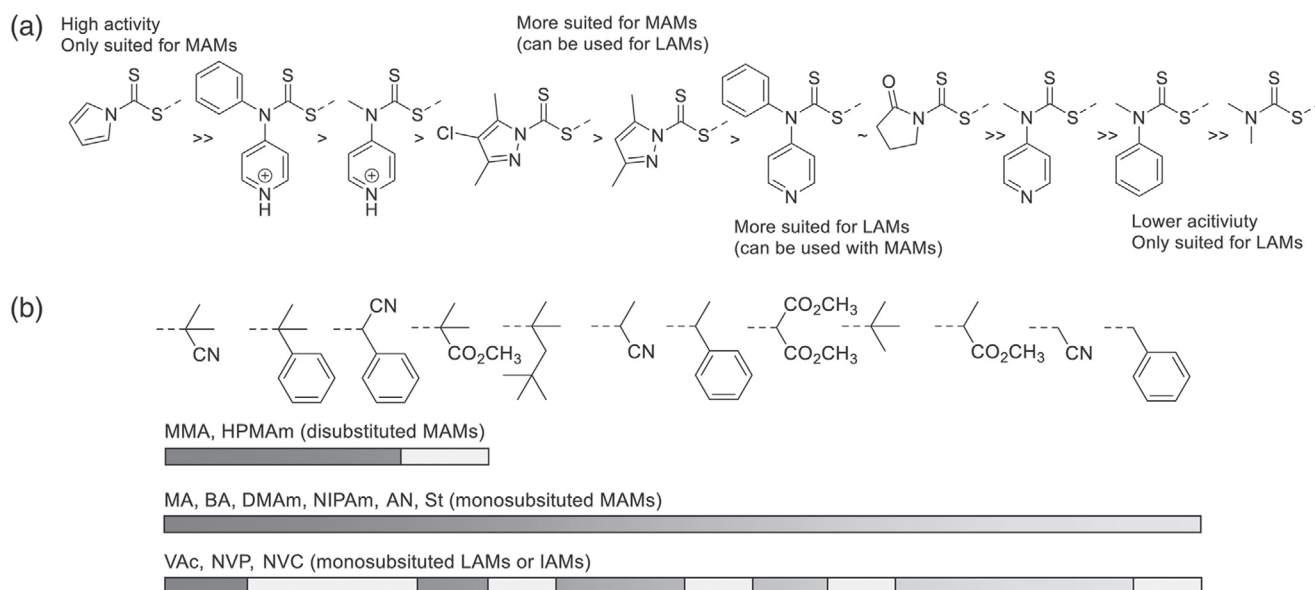
and 96-well microliter plate with excellent oxygen tolerance, show the capacity of RAFT system for the preparation of copolymers at both low volumes and large scales within a short time without inert atmosphere (Figure 4).<sup>[31]</sup>

Apart from PET-RAFT, Fenton-mediated RAFT polymerization also shows oxygen tolerance. Qiao and co-workers from university of Melbourne have reported a well-controlled RAFT process initiated by the hydrogen peroxide radicals generated through Fenton reaction (see Section 2.6). This technique provides high and continuous flux of radicals resulting in almost 100% monomer conversions in very short period of time (less than 30 min). These characteristics make the system tolerable toward the dissolved oxygen in the reaction media. Almost identical polymers in terms of molecular weights, dispersities, and chain-end functionality are achieved when polymerizations are conducted in presence or absence of oxygen.<sup>[36,37]</sup>

### 2.3. Universal RAFT Agents

The crucial factor for a successful RAFT process is the appropriate choice of the CTA also referred to as the RAFT agent. The choice of the RAFT agent depends on the monomer class (more activated (MAM) and less activated (LAM) monomers) and conditions used. This is fairly simple since detailed guidelines on monomer class and suitable RAFT agents for them do

exist.<sup>[11,12,14]</sup> Despite the existence of comprehensive guidelines and an extensive choice of suitable CTAs for each monomer class, some have taken a keen interest in developing a more “universal” chain transfer agent that could control the polymerization of both monomer classes as well as allowing the preparation of low  $\bar{D}$  poly(MAM)-*block*-poly(LAM)s by sequential monomer addition. Zard and co-workers reported the use of dithiocarbamates (e.g., *N,N*-dialkyldithiocarbamates) as universal RAFT agent.<sup>[38]</sup> Although it has been demonstrated that this group of RAFT agent are able to control the main three monomer classes (styrene, (meth)acrylic, and vinyl ester)<sup>[39]</sup> (Figure 5), however most are still not efficient enough to simultaneously control MAMs and LAMs.<sup>[40]</sup> In 2009 the CSIRO group reported a new class of stimuli-responsive RAFT agents that could offer good control over polymerization of both MAMs and LAMs with narrow molecular weight distributions.<sup>[41]</sup> The approach is based on developing a switching mechanism to modify the electronic properties of the dithiocarbamate nitrogen in a simple manner, which could be performed; 1) in situ during polymerization, 2) rapid, and 3) reversible. The main criteria for such switching is based on protonation of (or interaction with a Lewis acid by) a conjugated nitrogen. Since then it has been demonstrated by different groups that switchable RAFT agents such as *N*-(4-pyridinyl)-*N*-methyldithiocarbamates, could be used to prepare block copolymers under different polymerization regimes (bulk, solution, emulsion,



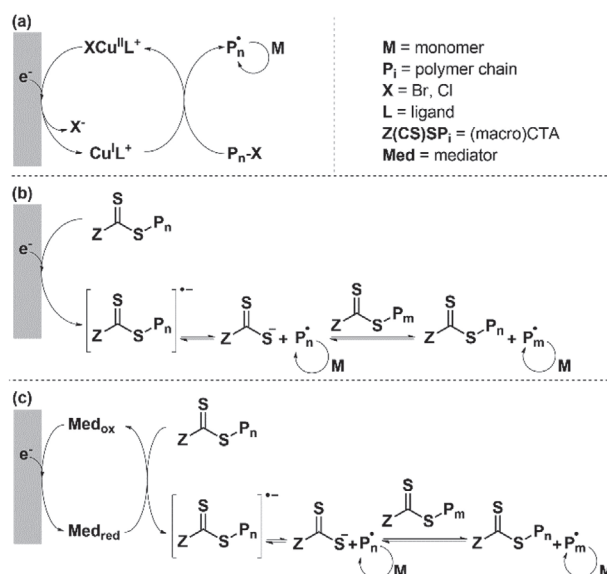
**Figure 5.** a) Effect of “ZC(=S)S-” group on activity of dithiocarbamates in RAFT polymerization. Activity increases from right to left. b) Effect of R groups on activity of dithiocarbamates in RAFT polymerization. MAM, more activated monomer; LAM, less activated monomer; IAM, intermediate activated monomer; AN, acrylonitrile; BA, butyl acrylate; DMAm, *N,N*-dimethylacrylamide; HPMAm, *N*-(2-hydroxypropyl)methacrylamide; MA, methyl acrylate; MMA, methyl methacrylate; NIPAm, *N*-isopropylacrylamide; NVC, *N*-vinylcarbazole; NVP, *N*-vinylpyrrolidone; St, styrene; VAc, vinyl acetate. Reproduced with permission.<sup>[40]</sup> Copyright 2019, The Royal Society of Chemistry.

PISA, etc.).<sup>[42–46]</sup> Later in 2016, Moad and co-workers developed a class of dithiocarbamate CTAs with a balanced activity toward both monomer classes without the need of switching making the synthesis of poly(MAM)-*block*-poly(LAM)s possible.<sup>[47]</sup>

## 2.4. Electrochemically Mediated RAFT (eRAFT)

A green alternative to generate radicals for the RAFT process is the use of electrical current. Besides being environmentally friendly, the electrochemical regulation offers unique opportunities, such as readily tuneable parameters and suitable tools for simultaneously triggering and monitoring the process as well as being applicable in industrial processes as demonstrated in the case of electrochemically mediated ATRP.<sup>[48]</sup> After their success in eATRP, Matyjaszewski and co-workers looked into the possibility of controlling the RAFT polymerization a similar pathway. Their initial work on eRAFT proved to be much more complicated than eATRP since in the case of ATRP, the Cu/L complexes have well-defined and reversible redox behavior, whereas the electrochemical reactivity of RAFT agents are unexplored and often result in irreversible redox processes that could not produce radicals. Direct application of electrochemical stimuli to traditional RAFT system failed to control the polymerization because the electrochemical reduction of the CTA-generated fragments that were further reduced to anions. To circumvent this issue, a radical source such as benzoyl peroxide or 4-bromobenzenediazonium tetrafluoroborate could be added to generate the radicals needed via electrochemical reduction.<sup>[49]</sup> In a later work the same authors look into the use of different types of mediators for the eRAFT process. Their thorough study shows that the use of tetraphenylporphyrin (TPP) could be a decent solution. The TPP-mediated eRAFT of

acrylates at room temperature gave polymers with low dispersity and molecular weights matching theoretical values, even at low mediator ratios. However, the process (**Figure 6**) was slow, and some decomposition of the CTA was observed.<sup>[50]</sup> In the light of the work reported by Matyjaszewski, further work on eRAFT should focus on either developing a suitable RAFT agent that could tolerate direct electroreduction or trying to find more effective mediators to optimize the electrochemical setup.



**Figure 6.** a) Mechanism of electrochemically mediated ATRP and b) envisioned mechanisms of electrochemically mediated RAFT via b) direct and c) mediated electrolysis of a CTA. Reproduced with permission.<sup>[50]</sup> Copyright 2019, American Chemical Society.



## 2.5. Sulfur Free RAFT (SF-RAFT)

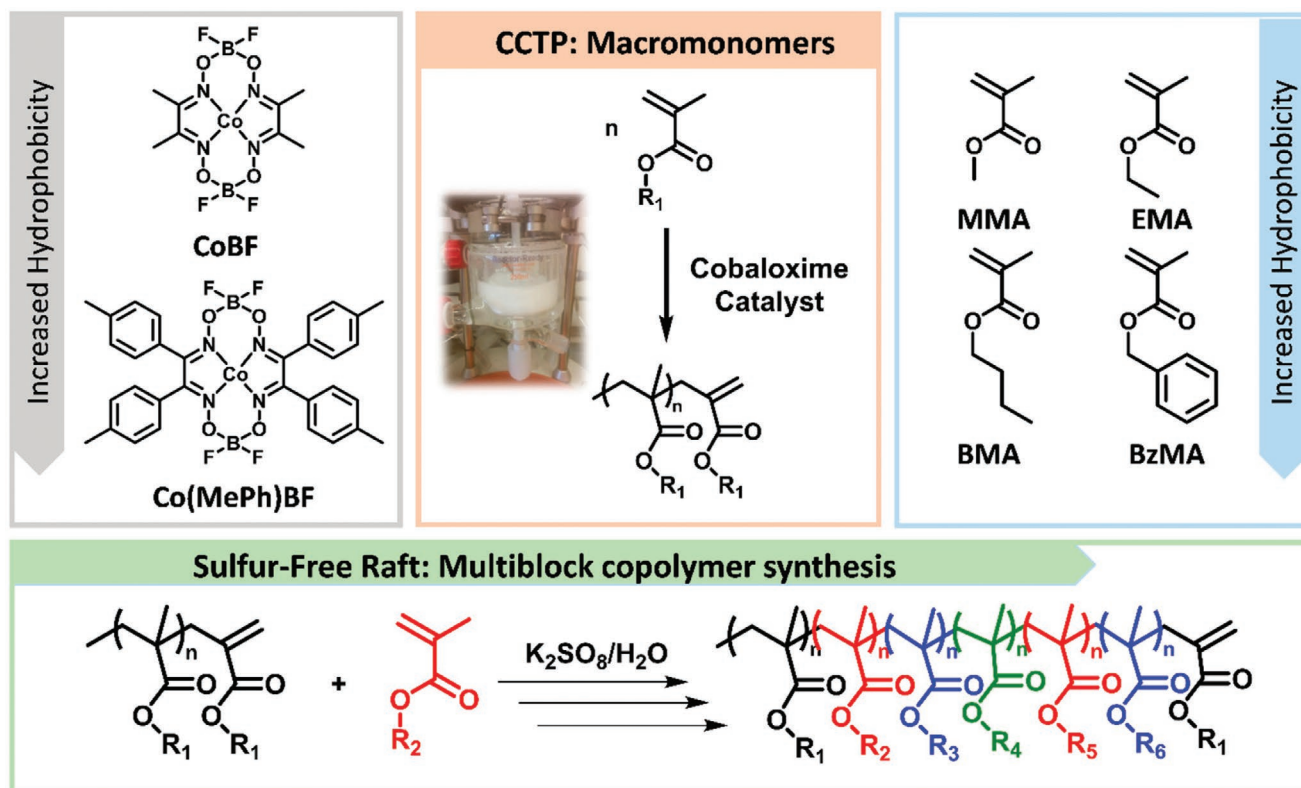
The concept of sulfur free-transition metal polymerization combined with free radical emulsion polymerization was developed by the team of Haddleton at University of Warwick.<sup>[51]</sup> This method uses vinyl terminated macromonomers obtained via catalytic chain transfer polymerization (CCTP) of methacrylates as a CTA.<sup>[51]</sup> The main advantages of this method as compared to classical RAFT polymerization is the elimination of the toxic di/trithioesters making the approach environmentally and bio friendly and also fully translatable to industry as it is performed in emulsion. CCTP, which is mediated by a family of low spin cobalt(II)/cobalt(III) compounds, is the most efficient CTA for the polymerization of methacrylates.<sup>[52]</sup> The low spin cobalt(II) macrocycle can abstract a hydrogen atom from a propagating polymethacrylic radical to form a Co(III)-H intermediate and an oligomer with terminal vinyl group. The resulting compound with the unsaturated terminal group could act as a macromonomer to control the polymerization of methacrylates. This (sulfur free RAFT) polymerization for controlling the synthesis of methacrylic copolymers was first reported by Krstina et al.<sup>[53]</sup> The mechanism here proceeds via a chain transfer to macromonomer followed by fragmentation to produce a macroradical (derived from the macromonomer), that can initiate a second monomer to form block copolymers. The propagating polymer would then grow and add the second monomer. The polymerization proceeds via a competing chain transfer to residual macromonomer in an addition-fragmentation process similar to RAFT as mediated by sulfur containing CTAs. This method is mainly suitable for the methacrylate monomer family as the chain transfer activity is much less pronounced for monomers which do not contain  $\alpha$ -methyl groups such as acrylates and styrenes. With acrylates and styrenes the resulting polymer would contain an internal double bond which is less favored in terms of both steric hindrance and electronic configuration.<sup>[51,54,55]</sup> Using SF-RAFT, the Haddleton group has demonstrated that well-defined, high precision multiblocks (hepta-, undeca-, and heneicosa-block copolymers) could be prepared using methyl methacrylate (MMA), butylmethacrylate (BMA), BzMA, and 2-ethyl hexylmethacrylate monomers. To show the robustness of the method and its applicability in industry, higher-molecular-weight multiblock copolymers were synthesized in a quantitative manner ( $\approx 80$  g scale).<sup>[51]</sup> They also reported the synthesis of AB block and comb-shaped copolymers through SF-RAFT sequence controlled emulsion polymerization. They were able to show that macromonomers with dispersities as low as 1.2 could be synthesized via identifying the limits and optimizing the system.<sup>[54]</sup> To expand the scope of this method they also used four different macrochain transfer agents (mCTA) to mediate the synthesis of diblocks and sequence-controlled methacrylic multiblock copolymers. Poly(methyl methacrylate) (PMMA), poly(*n*-butyl methacrylate), poly(ethyl methacrylate), and poly-*b*-benzyl methacrylate (PBzMA) with similar  $M_n$  ( $\approx 4300$  g mol<sup>-1</sup>) were prepared through CCTP in emulsion. The resulting mCTAs were used as macroinitiators in “in situ” synthesis of diblock copolymers. It was shown that deca- and hexablock multiblock copolymers with varying degrees of polymerization (DP = 10–50 per block,  $M_n = 7000$ – $55\,000$  g mol<sup>-1</sup>) could be prepared, with controlled

molecular weights, quantitative conversions (>99%), and low dispersities ( $D \approx 1.2$ ) in the absence of classical polymerization reagents (Figure 7).<sup>[55]</sup> Using a similar approach the same group synthesized vinyl-terminated oligomers that served as hydrophilic emulsifier/surfactants in polymerization of diblock copolymers with butyl and methyl methacrylate via SF-RAFT. These polymers were solubilized with various concentrations of ammonium hydroxide to be used in surfactant-free emulsion polymerization of butyl methacrylate using persulfate acting as both initiator and stabilizer. The resulting latex was stable with no signs of coagulation even at solid contents as high as 40%.<sup>[56]</sup> Sulfur free RAFT polymerization has also been employed in PISA process for synthesis of colloidal stable particles. Bon and co-workers have shown the successful application of methacrylate-based macromonomers as RAFT agents in PISA. Seeded emulsion polymerization conditions, where the seed is composed of self-assembled amphiphilic macromonomers, demonstrate both control over chain-growth and dynamic transformations of the block copolymer colloidal structures. They show that PISA was not successful starting from a macromonomer solution due to particle nucleation and the associated monomer partitioning obstructing the PISA process. This study is a good example that waterborne polymer dispersions of intricate particle morphology could be synthesized without the use of conventional organosulfur-based RAFT agents.<sup>[57]</sup>

## 2.6. Fenton RAFT

In the quest for finding a more efficient, robust, green, economically and industrially viable method to initiate RAFT polymerization, Reyhani et al. looked into using the well-known Fenton chemistry.<sup>[37]</sup> Described in 1894 for the first time by Fenton, the oxidation reaction of malic acid by hydrogen peroxide in the presence of ferrous ions was described where hydroxyl radicals had the role of oxidants. In 1946, Baxendale and co-workers used the radicals produced through the Fenton reaction for free radical polymerization of vinyl monomers. Their major observation was the enhanced polymerization rates as compared to polymerizations conducted using peroxides as initiators. Inspired by the work done on the coupling of Fenton reaction and FRP of vinyl monomers Qiao and co-workers reported the first Fenton-RAFT polymerization where they use ammonium ferrous sulphate and peroxide to generate radicals for the ultrafast (1–15 min.) polymerization of dimethyl acrylamide, *N*-acryloylmorpholine, and hydroxyethyl acrylate in water at ambient temperature.<sup>[58]</sup> Full monomer conversions, polymers with low dispersities and molecular weights matching the theoretical values were achieved via optimizing the Fenton reagent ratios ( $[H_2O_2]_0/[Fe^{2+}]_0$ , and  $[Fe^{3+}]_0/[Fe^{2+}]_0$ ). They also demonstrated that Fenton-RAFT process was relatively tolerant toward air or dissolved oxygen; however, the resulting polymers had broader SEC chromatograms compared with the polymers synthesized in the absence of oxygen. Given the properties of the described polymerization (rapid reaction times in aqueous media), the technique is particularly interesting for polymerization in biologically friendly environments. To do this, the glucose oxidase  $GO_x$  was used.  $GO_x$  is usually used in RDRP as an oxygen removal reagent where its by product is peroxide. The polymerization was activated by the





**Figure 7.** Schematic diagram showing the concept of the synthesis of sequence-controlled multiblock copolymers by the use of macromonomers as macro chain transfer agents (CTA). Catalyst type and concentration are optimized as to provide macromonomers of the desired  $M_n$  which subsequently serve as CTA in the free radical polymerization of methacrylic monomers. Reproduced with permission.<sup>[55]</sup> Copyright 2018, American Chemical Society.

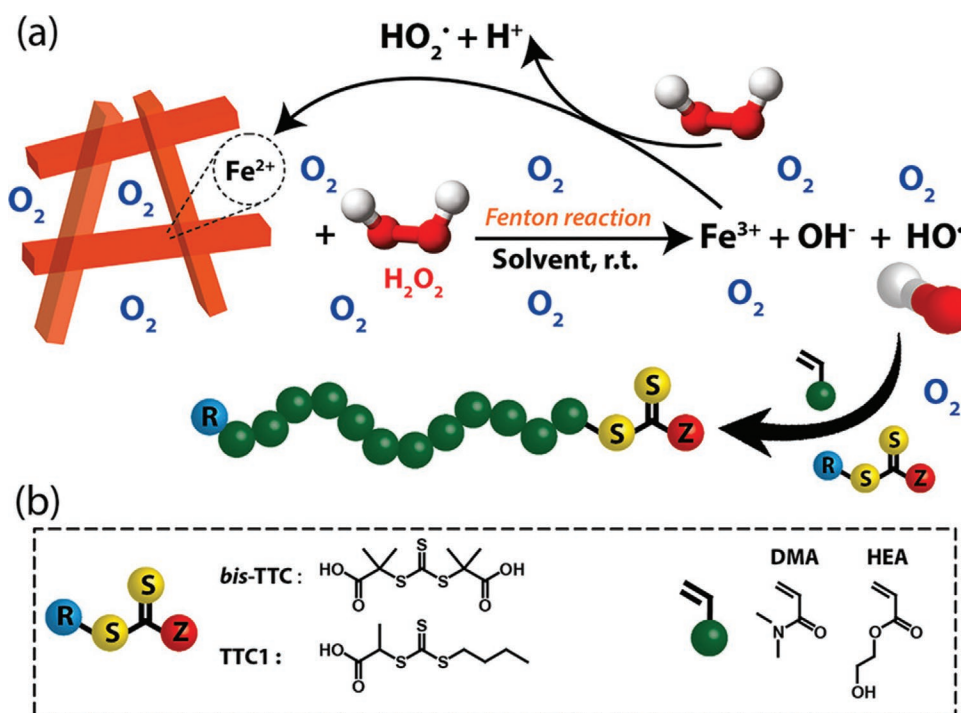
GO<sub>x</sub>-generated H<sub>2</sub>O<sub>2</sub>, and the iron containing hemoglobin (Hb). Such polymerization under aqueous conditions resulted in polymers with narrow dispersities and molecular weights matching the theoretical values.<sup>[59]</sup> The Fenton-RAFT system was also carried out under semibatch conditions where continuous flow of peroxide radicals is provided during the polymerization via using a syringe pump. By restricting the immediate flux of initiating radicals and ensuring sustained radical generation decreases the unwanted radical reactions resulting in full monomer conversions and polymers with high chain-end fidelity.<sup>[60]</sup> In a later work the same team, showed that ultrahigh molecular weight polymers (up to  $20 \times 10^6$  Da) within relatively short time ( $\approx 6$ ) could be synthesized by slow production of radicals through a semibio-Fenton-RAFT process. The semibio refers to the fact that Hb was replaced with ammonium ferrous sulphate to make the reaction faster.<sup>[61]</sup> Removal of the residual catalyst (ammonium ferrous sulphate and Hb) from the final polymer product is a major problem in Fenton mediated RAFT polymerization. To solve the problem, Qiao and co-workers, elegantly used iron (II)-based metal organic frameworks (Fe(II)-MOF).<sup>[62]</sup> They showed that the MOF structure was stable under the operational conditions and fully recyclable at the end of the polymerization by a simple centrifugation step. They further developed the use of MOF structures in the Fenton-RAFT process by using core-shell magnetic MOFs. The Fe<sub>3</sub>O<sub>4</sub>@Fe(II)-MOF nanoparticles exhibited high surface areas and catalytic activity (Figure 8). When coupled with hydrogen peroxide, the magnetic catalyst provided an efficient temporal control over the RAFT polymerization

initiated by the Fenton reaction. Also the recyclability of these nanoparticles would be much easier than the powder MOF due to their size and magnetic properties.<sup>[63]</sup>

### 3. Novel Developments in RAFT Process

#### 3.1. PISA

Amphiphilic block copolymers in general are able to form nano-objects of various different morphologies via self-assembly. Development of controlled/"living" polymerization has greatly influenced the production of well-defined amphiphilic block copolymers nano-objects. Classically the self-assembly of the amphiphilic block copolymers are performed in dilute solutions ( $\approx 1\%$  wt) using multisteps postpolymerization procedures.<sup>[64]</sup> PISA is a simple and attractive method for preparation of block copolymer nanoparticles at high concentrations. In a typical PISA (Figure 9), a soluble homopolymer (A) is chain extended with a second monomer in a suitable solvent such that the growing second block (B) gradually becomes insoluble (at a critical DP) driving the in situ self-assembly, forming AB block copolymer nanoparticles. In general, spherical micelles are observed first and as the length of the second block increases the nanoparticle morphology evolves to higher orders often passing through spherical micelles, worms/fibers, vesicles and bilayers. Other less usual morphologies such as lamellae,<sup>[65]</sup> framboidal vesicles,<sup>[66]</sup> spaced concentric vesicles,<sup>[67]</sup> yolk/shell



**Figure 8.** a) Schematic illustration of the non-deoxygenated MOF-Fenton-RAFT polymerization initiated by the generated hydroxyl radicals via heterogeneous catalysis of Fe(II)-MOF particles. b) Chemical structures of the employed trithiocarbonates (TTCs): S,S'-Bis( $\alpha,\alpha'$ -dimethyl- $\alpha'$ -acetic acid) trithiocarbonate (bis-TTC) and 2-(((butylthio)carbonothioyl)thio)propanoic acid (TTC1) and monomers: DMA and HEA. Reproduced with permission.<sup>[62]</sup> Copyright 2018, American Chemical Society.

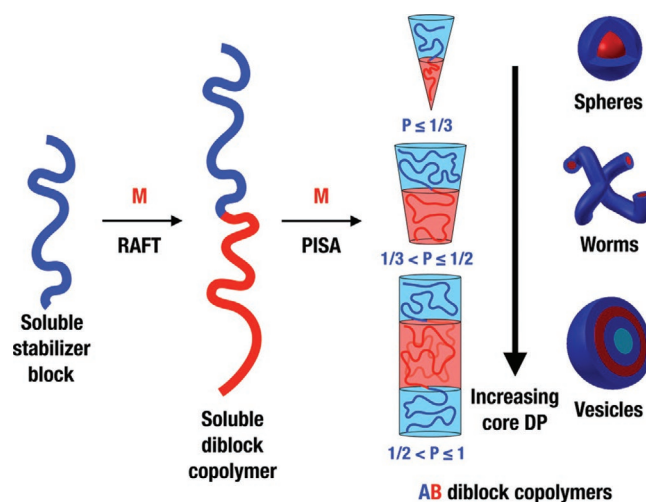
particles,<sup>[68]</sup> large compound vesicles,<sup>[69,70]</sup> and doughnuts<sup>[71]</sup> have also been prepared via PISA. This wide range of morphologies demonstrates the versatility of the PISA method.

Nano-objects prepared through PISA are mainly kinetically entrapped due to limited chain mobility of the core-forming/solvophobic block.<sup>[73–75]</sup> To produce higher order morphologies, the polymerization of the solvophobic block should be conducted above the glass transition temperature ( $T_g$ ) of the core-forming growing chains as well as presence of a cosolvent (often the monomer) to swell, plasticize, and facilitate the evolution of the generated assemblies toward higher orders. In comparison to conventional self-assembly methods, PISA can be conducted at high concentrations (up to 50% w/w solids content) in 1 (one-pot) or 2 steps (synthesis of macro-CTA followed by chain-extension) eliminating the tedious classical postmodification steps. In theory, PISA could be performed using any RDRP technique, however, up to date majority of the reported examples have used RAFT as the polymerization technique. This demonstrates the versatility and tolerance of RAFT to a broad range of reaction conditions, monomer families and solvents (water, organic, ionic liquids, mineral oils,  $scCO_2$ , etc.).

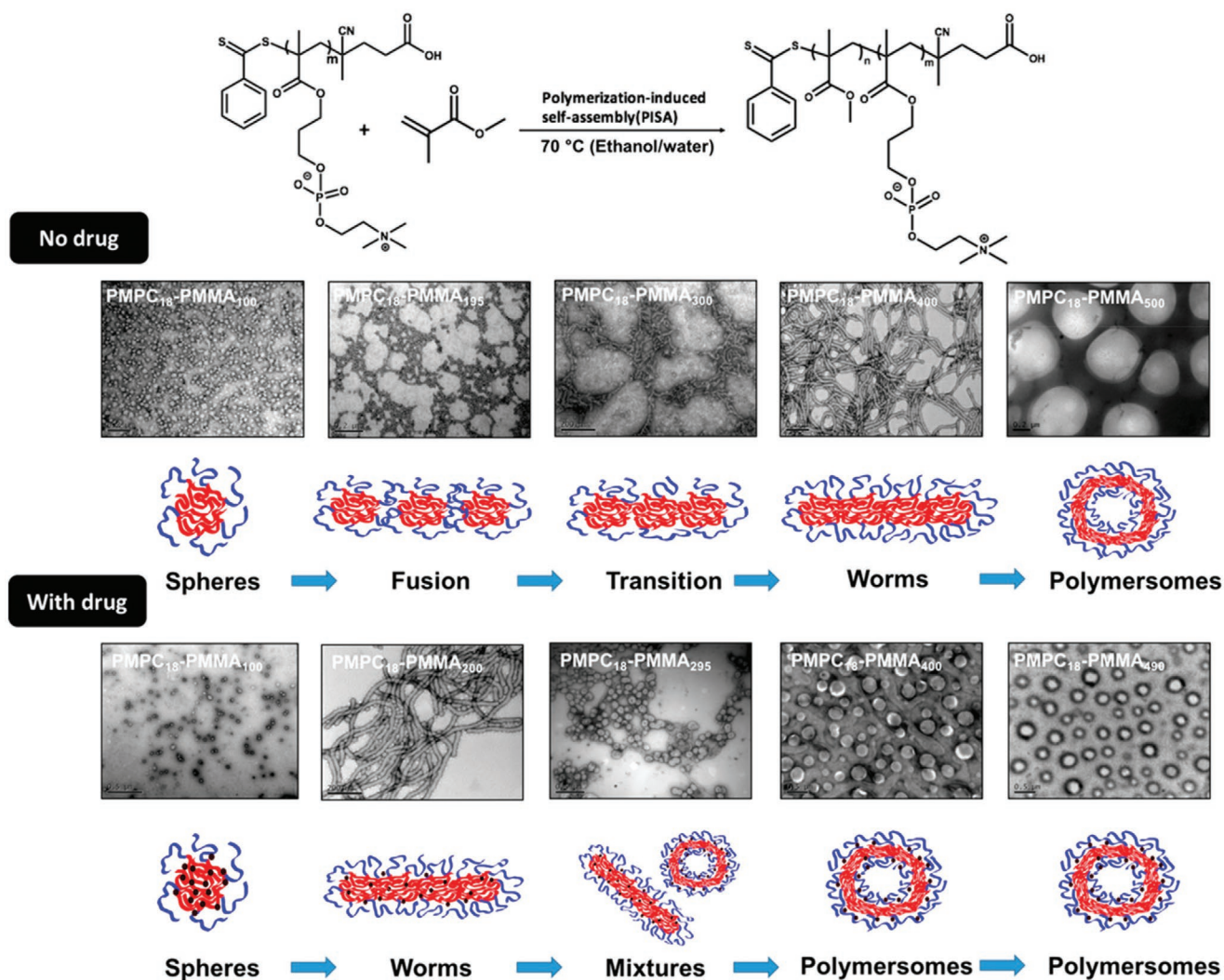
Almost a decade has passed since the first report on the in situ self-assembly during polymerization. In these years researchers have been mainly focused on understanding the system and the pathways of the in situ self-assembly and how it is different from the classical pathways. Many different monomer, solvent, and block combinations have been investigated. An enormous amount of efforts have been put into characterization of the PISA systems both in terms of the control over the polymerization and kinetics as well as the self-assembly and the

resulting nanoparticles. It is only in the last few years that PISA has been used to prepare functional materials for different applications such as drug delivery, coatings, viscosity modifiers, and membranes to mention a few.

PISA is a very prolific subfield of RAFT polymerization. Up to the moment of preparing this article there have been more than 20 review articles published on RAFT-mediated PISA, looking into different aspects of the technique.<sup>[72,76–85]</sup> Only in 2020 (by September) there have been more than 100 papers



**Figure 9.** Schematic of the synthesis of diblock copolymer nano-objects via polymerization-induced self-assembly (PISA). Reproduced with permission.<sup>[72]</sup> Copyright 2016, American Chemical Society.



**Figure 10.** Schematic of the PISA synthesis of PMPC<sub>18</sub>-PMMA<sub>n</sub> (top). The evolution of morphology with extension of the hydrophobic block is shown with cartoons and TEM images without curcumin (middle) and with curcumin (bottom; scale bars = 200 and 500 nm). Reproduced with permission.<sup>[86]</sup> Copyright 2020, American Chemical Society.

published on the topic. Here we focus mainly on the latest and the most outstanding reports on RAFT-PISA prepared nano-objects.

Self-assembled nanoparticles have long been used for bio-applications, notably drug delivery. PISA self-assembled nano-structures have also been used for different biological applications. Stenzel and co-workers have done thorough studies on how concentration of model drugs change the self-assembly of the block copolymers and shifts the phase diagram in the PISA process (Figure 10).<sup>[86]</sup> They have also shown that unlike the common belief, hydrophobic drugs could interact with the hydrophilic shell rather than the hydrophobic core-forming block. They also established the correlation between the morphology, density of the stabilizing block and the amount of loaded drug with the cellular uptake in cancer cells.<sup>[86]</sup> In a similar study, spherical cationic nanoparticles with PMMA cores were prepared via emulsion polymerization in water. In this study the authors show that in order to get the hydrophobic drug (doxorubicin) in the core of the particles the drug needs

to be blended with the MMA monomer prior to polymerization in water. The results suggest that this is a viable method for high concentration loading and the effect of the loaded particles on the cancer cells were much more prominent compared to non-encapsulated doxorubicin.<sup>[87]</sup> Hydrophobic drugs could also be loaded in the core of the particles in the form of monomer. Hong and co-workers showed that polymerization of a camptothecin containing monomer as the core-forming block using two macro-CTAs (cationic and neutral) leads to formation of spherical particles. At physiological pH the particles stay stable and uncharged while at acidic conditions (similar to the environment of a tumor) positive charges are introduced on the surface of the particles. This charge reversal helps both the internalization of the particles in tumor cells as well as the gradual release of the camptothecin from the particle core via reduction of the disulphide bond.<sup>[88]</sup> Diverse types of particles with potential bioapplications could be prepared using PISA. For example, hybrid polymer-inorganic nanoparticles could be prepared through the interaction between  $\beta$ -cyclodextrin



decorated nanoparticles prepared via PISA and gold nanoparticles decorated with adamantane.<sup>[89]</sup> Other recent examples of PISA prepared particles with potential bioapplication are peptide-,<sup>[90–92]</sup> deoxyribonucleic acid-,<sup>[93]</sup> nitrilotriacetic acid-,<sup>[94]</sup> and dextran-decorated particles.<sup>[95]</sup>

The many phase diagrams constructed for PISA formulations show that the pure worm/fiber phase is very narrow and often easy to miss. A strategy to expand this phase and to be able to control the fibers dimensions is to use crystalline core forming monomers. The Chen team from Beihang University, demonstrated that by using monomers containing stilbene and biphenyl would lead to formation of nanowires with highly ordered internal structure.<sup>[96–98]</sup> It is also possible to synthesize rigid nanowires by using a host–guest strategy. Shen and co-workers reported preparation of 1D nanowires through a cyclodextrin-mediated aqueous PISA. Dispersion polymerization of the host–guest complex between cyclodextrin and ferrocenyl-methyl acrylate using a poly(ethylene oxide) (PEO) containing mCTA proved to be a simple method for preparation of nanowires with controlled length.<sup>[99]</sup>

Other than linear block copolymers, stars and branched architectures have also been prepared via PISA. The article by Zeng et al. demonstrated how 4-armed RAFT agents (both Z and R approach) could be used to prepare branched block copolymer nanoparticles. Their results suggest that better control over molecular weights and distributions could be achieved by using the Z-RAFT approach. Better control over the morphology of the nanoparticles could be achieved by using a binary mixture of the two RAFT agents.<sup>[100]</sup> Branching has also been used as a strategy to form star shaped nanoparticles. Initially linear poly(*N*-isopropyl acrylamide)-*b*-polystyrene (PNIPAM-*b*-PS) block copolymer was synthesized under dispersion PISA conditions forming spherical nanoparticles. At the second stage divinylbenzene (DVB) cross-linker was added as the 2nd core-forming block cross-linking the particles without altering the spherical morphology of the particles. Solvent challenge with block selective solvents confirmed the successful core-cross-linking of the particles. These particles also exhibited thermoresponsive behavior due to the presence of the PNIPAM chains on the surface.<sup>[101]</sup> In a similar manner Seo group prepared star shaped nanoparticles by controlled cross-linking copolymerization of styrene and DVB or 1,2-bismaleimidoethane (BMI) in the presence of a polylactide macrochain transfer agent in acetonitrile. The in situ cross-linking with BMI yielded spherical particles while using DVB transformed the spherical micelles to elongated and branched shapes. Both formulations resulted in dense cross-linking and stabilizing the morphologies obtained.<sup>[102]</sup>

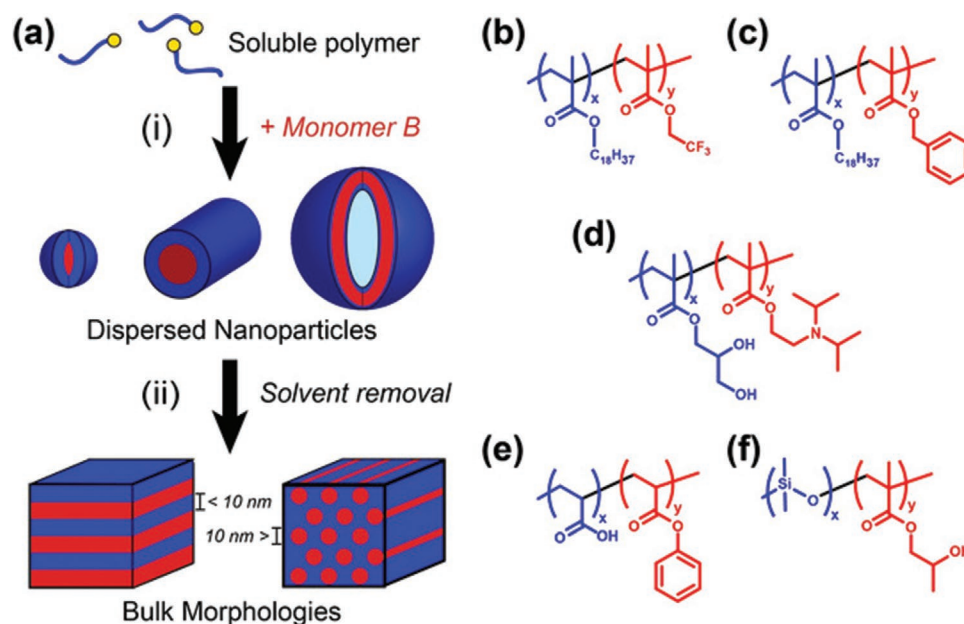
Eco-friendly monomers and solvents have also been used in PISA process. For example, menthyl acrylate (MnA) has been used as a biobased core-forming monomer in a mixture of ethanol/water using a polyacrylic acid macro-CTA. The fast polymerizations of MnA gave high final conversions and well-controlled amphiphilic diblock copolymer spherical particles.<sup>[103]</sup> Photo and flow polymerization have also been used as a mean to produce nanoparticles in an environmentally friendly manner. Low temperature photo-RAFT-PISA polymerization of poly(*N*-acryloylpyrrolidin)-*b*-polystyrene (PAPy-*b*-PS), yields monodisperse nanospheres with tunable size exhibiting

thermosensitive character (hydrodynamic diameter linearly increasing with the temperature between 10 and 70 °C).<sup>[104]</sup> Other PISA prepared thermoresponsive nanoparticles have been synthesized via and BAB triblock copolymer of poly(*N,N*-dimethylacrylamide)-*b*-poly(diacetone acrylamide),<sup>[105]</sup> or nanogels based on poly(oligo(ethylene glycol) methyl ether acrylate)-*b*-poly(*N*-acryloyl glycinamide) in aqueous media.<sup>[106]</sup> Binary mixtures of PEO and poly(glycerol monomethacrylate) (PGMA) macro-CTAs were used to prepare diblock copolymers by polymerizing thermoresponsive poly(hydroxypropyl methacrylate) (HPMA). By varying the ratio of the binary macro-CTAs and the length of the core-forming block both morphology and thermoresponsive behavior of the block copolymers could be controlled.<sup>[107]</sup>

Recently Boyer and co-workers reported a single-step, one-pot process for the synthesis of self-assembled nanoparticles using PISA. This gradient polymerization where the monomer reactivities have been chosen so that the hydrophilic monomer (oligo(ethylene glycol) methyl ether methacrylate) polymerized first, and the hydrophobic monomer (diacetone acrylamide) polymerized later. The gradient copolymers self-assembled in situ to form spheres and worms stabilized with poly(ethylene glycol) methyl ether methacrylate chains. This single-step gradient copolymerization approach to PISA is more efficient than conventional two-step syntheses.<sup>[108]</sup>

Aqueous photo-PISA has also been used to prepare multi-compartment polyion complexes (PIC). A cationic monomer (histamine acrylamide) was polymerized in the presence of anionic diblock copolymer micelles (poly(2-acrylamido-2-methylpropanesulfonic acid)-*b*-poly(diacetone acrylamide)) at 25 °C. The polymerization yielded a cationic diblock copolymer that coassembled with the anionic micelles. The incompatibility of nonionic block and growing PICs ensured the nanoscale phase separation to form mutually incompatible domains. This hierarchical electrostatic self-assembly implements structural hierarchy via programmable self-assembly to form multicompartement PIC micelles and their monolayer colloidal nanosheets and nanocages.<sup>[109,110]</sup>

Armes and co-workers in their latest publication report the use of RAFT-mediated PISA to prepare high  $\chi$ -low *N* diblock copolymers that form well-ordered nanostructured materials in the solid state (**Figure 11**). They used five different diblock copolymers (poly(stearyl methacrylate-*b*-2,2,2-trifluoroethyl methacrylate) (PSMA-PTFEMA), poly(stearyl methacrylate-*b*-benzyl methacrylate) (PSMA-PBzMA), poly(glycerol monomethacrylate-*b*-2(diisopropylamino)ethyl methacrylate) (PGMA-PDPA), poly(acrylic acid-*b*-phenylacrylate) (PAA-PPhA), poly(dimethylsiloxane-*b*-2hydroxypropyl methacrylate) (PDMS-PHPMA), and found that a range of copolymer morphologies could be accessed by adjusting the mean degree of polymerization of the core-forming block, and the minimum DP required to ensure well-defined solid-state morphologies correlated well with that required for the onset of micellization in solution. Pre-organization of the diblock copolymer chains in nanoparticles significantly expedited the onset of ordering during thin film and bulk material preparation compared to the corresponding molecularly dissolved copolymer chains under the same processing conditions. In principle, this facilitates lower annealing temperatures and/or shorter annealing times. The use of eco-friendly solvents next to the facile and efficient nanoparticle



**Figure 11.** a) Schematic representation of (i) the preparation of a concentrated dispersion of AB diblock copolymer nano-objects via polymerization-induced self-assembly (PISA) and (ii) their transformation into bulk nanostructures following solvent removal. Five diblock copolymers examined in the present study include: b) PSMA-PTFEMA, c) PSMA-PBzMA, d) PGMA-PDPA, e) PAA-PPhA, and f) PDMS-PHPMA. Reproduced with permission.<sup>[111]</sup> Copyright 2020, Wiley-VCH GmbH.

synthesis by PISA offer decisive advantages over the complex multistep synthesis and processing steps that are all too often required to produce conventional high  $\chi$ -low  $N$  diblock copolymers.<sup>[111]</sup>

Lately, there has been a huge progress in using RAFT to control the polymerization of certain monomers previously judged not suitable for RAFT. Ethylene is the simplest and the cheapest vinyl monomer and is industrially obtained by coordination-insertion catalytic polymerization or by free radical polymerization of ethylene. Polyethylene (PE) is apolar, which is a problem with some applications such as adhesion and printability. The solution to this problem is to introduce polar moieties into the PE chains to form copolymers. The first example of such a copolymer was made via RAFT mediated PISA in dimethylcarbonate (DMC). Well-defined PEO-*b*-PE block copolymers were synthesized using a PEO modified *N,N*-diphenyl dithiocarbamate macro-CTA. The block copolymers self-assembled into nano-objects in situ as expected for a PISA process. The crystalline nature of the PE segment induced a variety of morphologies including worms.<sup>[44]</sup> Another example of a previously unreported block copolymer is the synthesis of an all-poly(ionic liquid) block copolymer nanoparticles with various morphologies by aqueous RAFT-PISA relying on the use of isomeric ionic liquid monomers (where one isomer is hydrophilic and the other hydrophobic) giving rise to macromolecular building blocks with antagonistic solution behavior in water.<sup>[112]</sup> Among the latest work reported are the (co) polymerizations of styrene via PISA. Abetz and team report the preparation of poly(3-vinylpyridine)-*b*-poly(styrene) diblock copolymer particles using a P3VP mCTA aqueous under emulsion polymerization. PISA approach allowed synthesis of diblock copolymers with high monomer conversion and high molecular weights. Thin films were prepared via spin-coating from the obtained

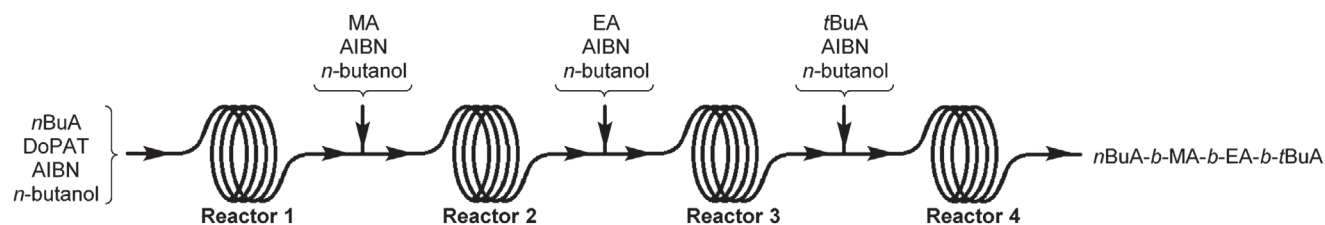
diblock copolymer latex. After annealing at different temperatures, the thin films displayed interesting microphase-separated structures according to their composition and annealing temperature.<sup>[113]</sup>

An efficient and scalable PISA approach was also described for synthesis of poly(*N,N*-dimethylacrylamide)-poly(styrene-pentafluorostyrene), PDMA-*b*-P(*St-alt*-FS), block copolymers. The alternating nature of the core-forming block allowed faster and full polymerization of styrene under concentrated dispersion conditions. The in situ morphologies observed extended transition sequence from initial spheres to final inverse mesophases (passing through worms, vesicles, large compound vesicles (LCVs), sponge-like particles and cubosomes) as the function of increasing DP of the core-forming block, solid content, and nature of the (co)solvent used (to increase chain mobility). Given the high concentration and the continuous chain growth and reorganization as the unique driving force, PISA could be a practical and general approach for the preparation of inverse mesophases.<sup>[114]</sup>

### 3.2. Flow Polymerization

Chemical synthesis could be carried out in different ways, with batch or flow processes being the most prominent ones. In many syntheses the management of heat exchange is important, as in strongly exothermic reactions the developed heat must be removed from the reaction in order to avoid side reactions or uncontrolled autoacceleration of the reaction, leading to unpleasant events such as explosions. In polymerizations the heat management may become challenging if the viscosity of the reaction system increases due to the increasing molecular weight of polymers and this makes stirring more difficult and





**Figure 12.** Schematics of a cascade reactor to synthesize multiblock copolymer in a continuous mode. Reproduced with permission.<sup>[122]</sup> Copyright 2017, The Royal Society of Chemistry.

less efficient. In this context the surface to volume ratio of the reactor is very important for the heat transfer. In big batch reactors the surface to volume ratio is lower than the ratio for smaller reactors with the same shape. This results in larger temperature gradients in the reactor. As a consequence there would be less uniformity in the reaction unless a very efficient stirring/mixing prevents the build-up of such temperature gradient in the reactor. Side reactions and bad reproducibility of the products may result from insufficient control over the temperature gradient within the reactor and insufficient temperature control.<sup>[115,116]</sup> Therefore scaling up of polymerization is limited for exothermic polymerization reactions as the heat flow may become insufficient in bulk or solution polymerizations, unless heat exchange devices are incorporated into the reactor. In suspension or emulsion polymerizations this is not so much of an issue, as the “reactors” are in fact small droplets or micelles of typically hydrophobic monomers in a water matrix, where viscosity of the whole system is not largely affected by the molecular weight of the formed polymers. Another strategy is to carry out the polymerization in flow. Here the reactions are carried out in tubes or capillaries and the surface to volume ratio is getting larger for thinner capillaries, where the management of heat exchange is easier and more controlled. This allows processes to run faster (for example, exothermic reactions at higher temperatures) without loss of control and it results in higher conversion rates under safe operation conditions.<sup>[115,116]</sup> Parameters such as the geometry of the flow reactor, the flow rate and viscosity of the reaction medium are some of the parameters to be considered, as in very good controlled polymerization reactions the distribution of residence time within the reactor should be kept narrow.<sup>[117]</sup>

The advantages of free radical and controlled radical polymerizations carried out in flow reactors versus polymerizations carried out in batch were demonstrated by Junkers.<sup>[118]</sup> This article also describes many technical details about flow chip design and online analytical tools.

Different types of polymerizations in continuous flow have already been developed before introduction of this technology to RAFT polymerization. As flow reactions are highly controllable, they are attractive for tailor-made complex structures, for example by connecting several flow reactors in sequence. The synthesis of block copolymers could be performed in sequence flow reactors as it had been used in the case of living anionic polymerization for synthesis of homopolymers and block copolymers.<sup>[119–121]</sup> Using RAFT polymerization, multiblock copolymers could also be synthesized in a continuous mode using cascade reactors as was demonstrated for the synthesis of poly(*n*-butyl acrylate)-*b*-poly(methyl acrylate)-*b*-poly(ethyl acrylate)-*b*-poly(*t*-butyl acrylate) (PnBuA-*b*-PMA-*b*-PEA-*b*-PtBuA)

tetrablock copolymer, which could be obtained in a quantity of 150 g within a day (Figure 12).<sup>[122]</sup>

Initiation of the radical polymerization by light rather than thermally induced radical polymerization is an interesting approach as it allows a certain decoupling between polymerization rate (increasing with temperature) and radical formation (depending on the light intensity). While the penetration depth of light is short, in a batch reactor the overall reaction rate remains small, while in a thin capillary of a flow reactor the light reaches the whole reaction volume. An overview of different photo-RAFT polymerizations in flow reactors was given in a recent perspective paper.<sup>[123]</sup> Here we therefore highlight only some examples. Using a trithiocarbonate photoiniferter and different methacrylates, homopolymers and block copolymers (the latter ones in a cascade of microreactors) with good control of dispersity could be polymerized within 1 h.<sup>[124]</sup> One of the challenges in RAFT polymerization is slow reacting monomers such as styrene and isoprene. Especially isoprene is a very slow reacting monomer and difficult to polymerize in a satisfactory manner using conventional batch polymerization. It is demonstrated that the continuous flow operation in a microreactor allows the use of high temperatures in a photo-RAFT process, allowing the polymerization of homo-, di-, and triblock copolymers of styrene and isoprene, including polystyrene-*b*-polyisoprene-*b*-polystyrene (PS-*b*-PI-*b*-PS) triblock copolymer, a well-known thermoplastic elastomer.<sup>[125]</sup> Also PISA under flow using photo-RAFT was demonstrated successfully using macro-RAFT agents based on poly(oligo(ethylene glycol) methacrylate) (POEGMA) or poly(oligo(ethylene glycol) acrylate) (POEGA) in alcohol, polymerizing acrylates or methacrylates.<sup>[126]</sup> Using electron/energy transfer-RAFT (PET-RAFT) polymerization under aqueous conditions was used to synthesize poly(dimethyl acrylamide)-*b*-(poly(diacetone-*stat*-dimethyl acrylamide)) with various block lengths and ratios to study their self-assembled structures (worms, jellyfish, vesicles).<sup>[127]</sup>

Also photoinduced PET-RAFT polymerization was investigated in flow and led to very good results as demonstrated for the polymerization of several acrylamides and acrylates leading to polymers with still active end groups having molecular weights up to 100 kDa within a couple of minutes.<sup>[32]</sup> PET-RAFT polymerization was also investigated under different operation conditions and it could be shown that pressure variations (slug-flow) could lead to superior results compared to a continuous flow under constant pressure, which is attributed to a better mixing within the reactor tubes and the narrower residence time distribution.<sup>[128]</sup> Another way to get a better mixing within a tube is the application of a semicontinuous plug-flow, where small reaction volumes within the tube are separated by inert

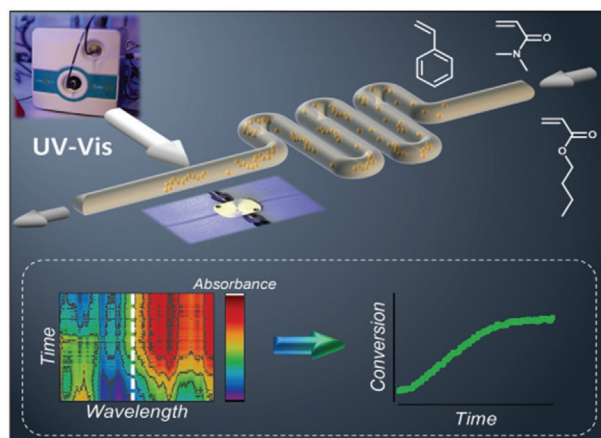
gas bubbles by injecting the gas in a pulsed manner into the tube filled with the polymerization mixture before it passes through the reactor.<sup>[129]</sup> Using PET-RAFT, this method delivered well controlled polymers in individual reacting compartments. Depending on the residence time in the reactor and by adjusting the flow rate, varying molecular weights could be reached. In the same passage a second monomer could be introduced before reaching the second reactor. Thus different homopolymers and block copolymers could be synthesized in this way and collected separately and enable to generate different tailored molecular weights and compositions.<sup>[129]</sup>

An important task in flow polymerizations is the control of the reaction mixture product quality in a continuous way. A variety of analytical tools have been developed. Among them size exclusion chromatography (SEC) as an online method was demonstrated as a useful online monitoring method in batch polymerization<sup>[130]</sup> before online SEC was combined with a continuous flow system and programmed to control the polymerization parameters of the flow reactor in order to produce a polymer with tailored molecular weights.<sup>[131]</sup> Also electrospray ionization mass spectrometry could be coupled with a microreactor for online detection of RAFT polymerization process and allowed to follow the growth of the polymer with high precision.<sup>[132]</sup> Online monitoring with nuclear magnetic resonance spectroscopy (NMR) has also become available and was applied to flow RAFT polymerizations successfully.<sup>[133,134]</sup> Compared to NMR there are less studies using (near) infrared spectroscopy to monitor RAFT polymerizations. While inline infrared spectroscopy in flow reactions was applied before,<sup>[135]</sup> and FTIR spectroscopy was used to monitor polymerizations such group transfer polymerization<sup>[136]</sup> and RAFT polymerization in  $\text{scCO}_2$ ,<sup>[137]</sup> so far this method was not applied in flow polymerizations. As compared to the already discussed methods, a very fast and cheap monitoring technique is UV-vis spectroscopy, readily used to study conversion in RAFT polymerizations.<sup>[138]</sup> While in the study specific absorptions were used for the analysis, in a recent work it was shown that also the optical density determined from the baseline in the spectra could be used to determine the conversion, as the optical density increased during the polymerization (Figure 13). To calibrate the relationship between conversion and change in optical density, NMR was used for calculating the conversions in a flow reactor working under RAFT polymerization conditions.<sup>[139]</sup>

## 4. Novel (Co)polymers by RAFT and Their Properties

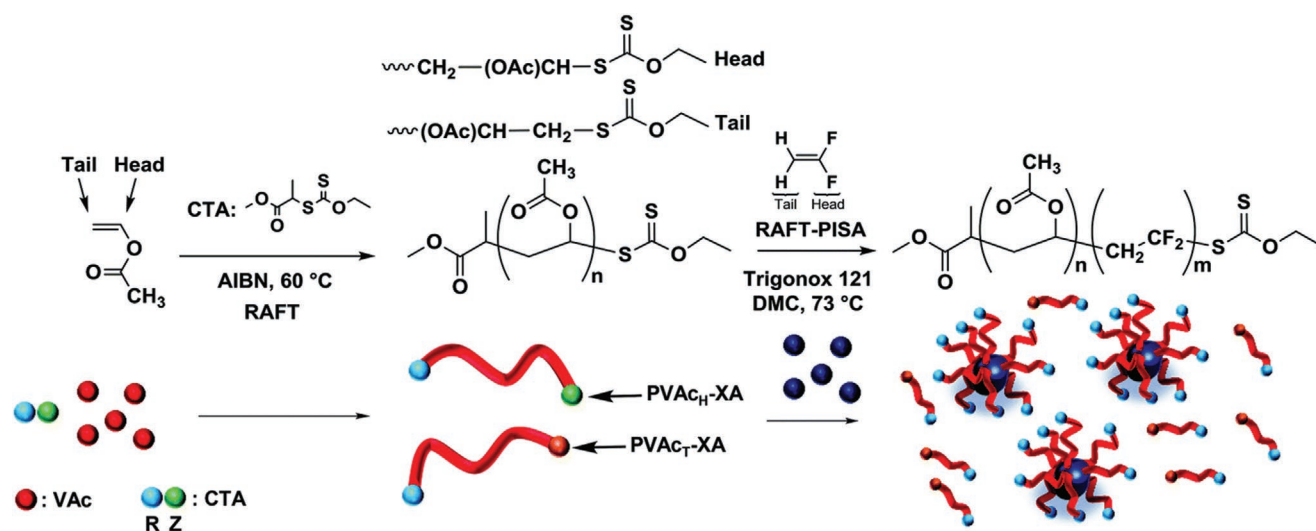
### 4.1. Fluorine-Containing Polymers

Fluoroolefins are vinyl organic compounds composed of hydrogen, fluorine and carbon, with fluorine atoms or trifluoromethyl groups borne by the vinyl carbons. Polymers made from these fluorinated monomers form an interesting class of material with special properties that find use in high-tech applications. Among polyfluoroolefins poly(vinylidene fluoride) (PVDF) is the most studied as it has remarkable properties such as thermal stability, chemical inertness to solvents, oils, and acids (but not to bases), and piezo-, pyro-, and ferroelec-



**Figure 13.** Schematics of a photo-RAFT homopolymerizations of fast and slow monomers in a microreactor, which can be monitored by an inline UV-vis spectrometer using a wavelength beside specific absorptions. Reproduced with permission.<sup>[139]</sup> Copyright 2020, Wiley-VCH GmbH.

tricity.<sup>[140,141]</sup> PVDF, like most polyfluoroolefins, is synthesized by conventional radical polymerization. RDRP polymerization of VDF is very difficult. Iodine transfer polymerization (ITP) of VDF was first reported in 1979.<sup>[142]</sup> However, in ITP the transfer constant is not high enough to ensure perfectly good control over the dispersity of the produced chains. In addition, loss of the iodine atom at the chain ends results in polymers with higher molar mass and dispersity than expected. In the last decade, Ladmiraal and co-workers have looked into controlling the polymerization of VDF using MADIX/RAFT polymerization. Their first report on the MADIX controlled solution polymerization of VDF in DMC provided a thorough and detailed report on the efficient polymerization conditions of VDF to prepare PVDF polymers with high end-group functionality and low dispersity. Also they inventoried for the first time, all the reactions occurring during the course of the MADIX solution polymerization of VDF (transfer to solvent, reverse additions, irreversible transfer, and nondegenerative exchange reactions).<sup>[143]</sup> Their following work shed more light on these side reactions taking place during the controlled radical polymerization of VDF, and they underlined the limits of the method.<sup>[144,145]</sup> Their findings (combining experimental and DFT calculations) suggest that well-defined PVDF chains with high end-group functionality could be synthesized over a relatively large range of molar masses if the conversions are kept lower than  $\approx 30\%$ . This is due to the gradual accumulation of less reactive  $\text{PVDF}_T\text{-XA}$  chains formed by head-to-head VDF additions causing a dramatic slowing down of the degenerative transfer mechanism, and resulting in a significant loss of control over the polymerization. Having defined the most adequate conditions to synthesize PVDF via RAFT polymerization, the team in Montpellier explored the possibility of preparing different architectures containing PVDF blocks. Different diblock copolymers were prepared. The first example described the chain extension of PVDF macro-CTA with poly(vinyl acetate) (PVAc) via sequential monomer addition to afford well-defined PVDF-*b*-PVAc block copolymers. TGA and DSC analysis confirmed the thermal stability of the polymer as well as the miscibility of the PVAc and PVDF blocks.<sup>[146]</sup> The PVAc block



**Figure 14.** Synthesis and self-assembly of PVAc-*b*-PVDF block copolymers by RAFT dispersion polymerization of VDF in DMC using PVAc macro-CTAs. Reproduced with permission.<sup>[148]</sup> Copyright 2017, The Royal Society of Chemistry.

was then converted to poly(vinyl alcohol) (PVA) through saponification of the ester group to give a PVDF-*b*-PVA amphiphilic block copolymers that could readily self-assemble into spherical nanoparticles with PVDF cores and PVA shells in water.<sup>[147]</sup> In another study, the synthesis of PVAc-*b*-PVDF block copolymer nanoparticles via PISA was investigated (**Figure 14**). Here a well-defined xanthate functionalized PVAc was block extended with VDF in DMC under dispersion RAFT polymerization conditions. The growing amphiphilic block copolymer self-assembled in situ to form unusual flake-like crystalline structures that were able to further assemble into desert rose-like branched micrometer-sized objects. The assembly of these objects was described as most probably governed by the crystallization of the PVDF block.<sup>[148]</sup>

Other linear amphiphilic diblock copolymers were also synthesized by utilizing copper-mediated click chemistry, where the PVDF block was synthesized using a xanthate CTA bearing an azide functionalized Z group. The hydrophilic block (poly(2-dimethylamino ethyl methacrylate); PDMAEMA) was synthesized via ATRP using an alkyne-functionalized initiator. Upon synthesis and full characterization the two well-controlled blocks were covalently linked via CuAAC click reaction to afford the PVDF-*b*-PDMAEMA block copolymer. The self-assembly of these diblocks in water with varying pH (pH = 2–10) resulted in the formation of crumpled spherical aggregates of different sizes depending on the length of the PDMAEMA block. Rigid rod-like structures with a diameter of ≈8 nm and lengths ranging from 30 nm to 1 μm were also formed. The rigidity and the electron density of these structures as observed under electron microscopy suggested the presence of crystalline PVDF cores formed most likely through crystallization driven self-assembly.<sup>[149]</sup> The same group also reported the preparation of symmetrical ABA triblock copolymers containing PVDF via thia-Michael addition. Thiol-ended PVDF prepared via aminolysis of the xanthate terminated PVDF chains were coupled with a telechelic poly(ethylene glycol) diacrylate in one-pot. The resulting ABA triblock copolymer was then self-assembled using different solvent mixtures (N-methyl-

2-pyrrolidone (NMP) or tetrahydrofuran (THF)/H<sub>2</sub>O or ethanol) and assembly methods (micellization and nanoprecipitation) to produce a range of crystalline morphologies from spheres to bundled rods.<sup>[150]</sup> Well-defined xanthate capped short PVDF chains were also converted to macromonomer using aminolysis/thia-Michael addition via a one pot reaction. The resulting methacrylate macromonomer (PVDF-MA) was used to prepare well controlled copolymers with methyl methacrylate.<sup>[151]</sup> Stars and dendrimers containing PVDF segments were also synthesized. The use of a 4-arm xanthate CTA allowed the synthesis of PVDF stars. The arms extremities of this star PVDF were then functionalized with methacrylate moieties via aminolysis/thia Michael addition and the resulting product was copolymerized with a telechelic perfluoropolyether dimethacrylate (PFPE-MA) via thia-Michael addition to be used in preparation of cross-linkable coatings<sup>[152]</sup> with enhanced adhesion on metal surface. A similar strategy was utilized to prepare polymer conetworks from benzaldehyde-functionalized 4-arm-star PVDF and benzaacylhydrazide-functionalized 4-arm star poly(ethylene glycol) (PEG). These semirigid conetworks exhibited good electrochemical stability and satisfactory ion conductivity.<sup>[153]</sup> More elaborated structures containing PVDF segments such as dendrimers were reported by Ouali and co-workers. A novel fluorinated dendrimer decorated with alkyne end-groups and ω-azido PVDF branches were synthesized using CuAAC. These dendrimers displayed crystalline disc-like zones of ≈5 nm. In addition, thin films prepared from these dendrimers had enhanced hydrophobic character with water contact angles of 108°. <sup>[154]</sup> Similar dendritic structures bearing pyrene functionalities were also synthesized and used to coat magnetic cobalt nanoparticles through noncovalent bonding.<sup>[155]</sup> These PVDF coated magnetic particles displayed thermoresponsive behavior whereby the noncovalent interactions were partially reversible upon heating. Such material combined several different properties that could find application in high-tech applications. The Ladmira team also demonstrated that photoinitiated RAFT polymerization could also be used to prepare well-defined PVDF. This polymerization was performed under light irradiation at room



temperature, using household white LED lamps as the light source, O-ethyl-S-(1-methoxycarbonyl)ethyl dithiocarbonate as CTA and Tris(2-phenylpyridine) iridium(III) ( $\text{Ir}(\text{ppy})_3$ ) as photoredox catalyst. The  $\text{Ir}(\text{ppy})_3$  was used to accelerate the polymerization. Such conditions allowed the synthesis of PVDFs with narrow molar mass distributions and high chain-end fidelity at low conversions. However, as reported in the case of thermal RAFT polymerization, the gradual accumulation of less reactive  $\text{PVDF}_{\text{T-Xa}}$  and dead  $\text{PVDF}_{\text{H}}$  chains resulted in the loss of control over the polymerization.<sup>[156]</sup> In collaboration with Kamigaito's group the same team also investigated the possibility of synthesizing block copolymers via combination of cationic and radical RAFT polymerizations. Their first work reported the synthesis of poly(ethyl vinyl ether)-*b*-poly(vinylidene fluoride) (PEVE-*b*-PVDF) block copolymers via sequential combination of cationic RAFT polymerization of vinyl ethers and radical RAFT polymerization of VDF using a dithiocarbamate chain transfer agent.<sup>[157]</sup> In a second article they use the same approach to prepare block copolymers containing another fluoroolefin, chlorotrifluoroethylene (CTFE), namely, poly(ethyl vinyl ether)-*b*-poly(chlorotrifluoroethylene-*alt*-ethyl vinyl ether) (PEVE-*b*-P(CTFE-*alt*-EVE)). Two pathways were investigated: 1) synthesis of a PEVE block by cationic RAFT polymerization from a P(CTFE-*alt*-EVE) macro-CTA prepared using radical RAFT copolymerization, and 2) synthesis of a P(CTFE-*alt*-EVE) block by radical RAFT copolymerization from a PEVE macro-CTA prepared by cationic RAFT polymerization. The 2nd pathway led to poorly defined block copolymers due to mediocre chain end-fidelity of the P(CTFE-*alt*-EVE) macroCTA. By contrast, the cationic RAFT polymerization of EVE afforded PEVE macro-CTAs with high chain-end fidelity and chain extension reactions resulted in well-defined PEVE-*b*-P(CTFE-*alt*-EVE) block copolymers with low dispersities ( $\bar{D} < 1.35$ ).<sup>[158]</sup>

RAFT was revealed as a powerful polymerization technique to prepare well-defined fluoroolefins-based architectures once the peculiar reactivities of these monomers and the impact of this reactivity on the RAFT mechanism had been understood.

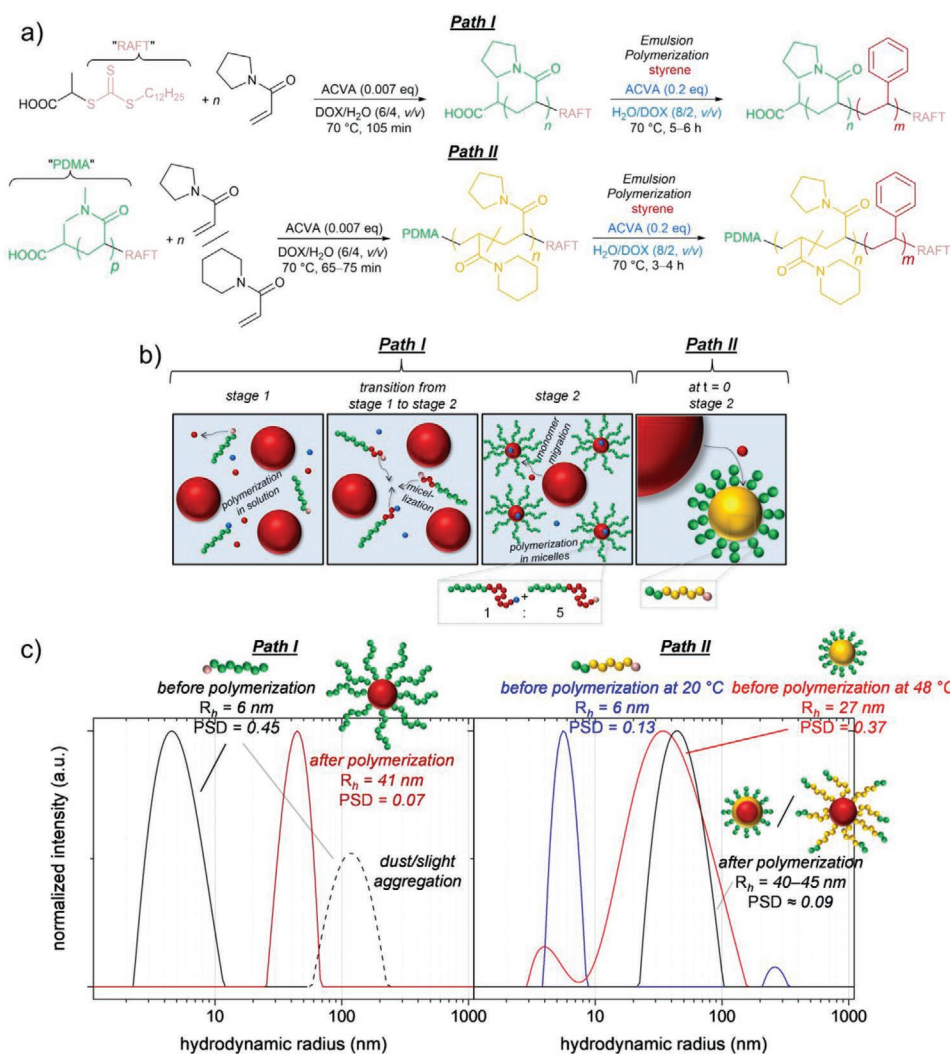
#### 4.2. Stimuli-Responsive Polymers

Responsive polymers are polymers that can adapt their structure to their environment. They could respond to a variety of external stimuli such as light, electrical current, thermal, mechanical, redox, pH, chemical, environmental, and biological signals.<sup>[159]</sup> Functional groups leading to the responsiveness could be included in a polymer structure via different approaches: 1) polymerization of functional monomers, 2) postpolymerization modification, and 3) using functional RAFT agents or functional initiators for other types of chain polymerizations. The major class of stimuli-responsive polymers are: 1) thermoresponsive (displaying lower or upper critical solution temperatures (LCST or UCST)), 2) pH-responsive, 3) redox-responsive (metallopolymers and polymers containing disulphide bonds), 4) light or photoreponsive (polymers containing functional moieties such as coumarine, truxylic acid, azobenzene, and spiropyran<sup>[160]</sup>), and 5) chemical-responsive.

Here we summarize the very recent reports on stimuli-responsive (co)polymers by RAFT.

In a series of articles, Abetz and co-workers have prepared well-defined copolymers featuring stimuli-responsive character. They report for the first time the controlled synthesis of poly(*N*-acryloylpiperidine-*ran*-*N*-acryloylpyrrolidine) (PAPi-*ran*-PAPy) with LCST between 3 and 47 °C.<sup>[161]</sup> They synthesized PAPy-*b*-P(APi-*ran*-APy) block/random copolymers with tunable temperature-induced self-assembly in aqueous solution. The onset of micellization depended on the phase transition, which had linear dependency to the APi/APy molar ratio. These copolymers behaved more like gradient than block copolymers at 60–70% block similarity. The observed transition was completely reversible suggesting partial hydration of the micelle core and a dynamic structure.<sup>[162]</sup> They later synthesized amphiphilic triblock copolymers via surfactant free emulsion polymerization where this random copolymer formed the central block (PDMA-*b*-P(APi-*ran*-APy)-*b*-PS). In presence of dioxane as cosolvent well-defined block copolymers and stable latexes were formed (Figure 15).<sup>[163]</sup> In a separate study they use RAFT polymerization to synthesize a biocompatible thermoresponsive polymer based on (2-(*N*-morpholino)ethyl methacrylate) monomer that can undergo three-step aggregation upon heating in water. These three steps were studied very carefully and a hypothetical mechanism was proposed.<sup>[164]</sup> Understanding the solution behavior of this polymer, they also synthesized amphiphilic block copolymers with styrene (polystyrene-*b*-poly(2-(*N*-morpholino)ethyl methacrylate).

To reach molecular weights above 100 kDa, polystyrene was first polymerized using anionic polymerization. The PS was then converted to a macro-CTA via chain-end modification followed by the RAFT polymerization of the 2-(*N*-morpholino)ethyl methacrylate in a mixture of dioxane and toluene (3:1 v/v). In aqueous solution, the block copolymer self-assembled into monodispersed micelles responsive toward temperature, pH, kosmotropic and chaotropic salts.<sup>[165]</sup> As mentioned previously, polymers with UCST are not as explored as their counterparts showing LCST. Abetz and co-workers have recently reported a green route to synthesize polymethacrylamide (PMAAm) via a cost-efficient photoiniferter RAFT polymerization. The synthesized PMAAm showed thermoreversible UCST phase transitions in water/ethanol mixtures (17–35 wt% ethanol). Parameters affecting the phase transition between 10 and 80 °C depended on ethanol content, polymer concentration, and chain length.<sup>[166]</sup> Polymers with dual thermo- and pH-responsive behavior are extremely attractive as they find application in the growing field of drug delivery. Some of the latest reports are based on linear di- and triblocks where one block is the well-studied poly(*N*-isopropylacrylamide) to confer the thermoresponsivity and other blocks often contain a weak acid or base such as (meth)acrylic acid and 2,2 dimethyl ethyl (meth)acrylate (DMAEMA). Some examples are: PDMAEMA-*b*-PNIPAm-*b*-POEGA,<sup>[167]</sup> PDMAEMA-*b*-PNIPAm where the 2 blocks are connected via a host–guest interaction based on pillar[5]arene and viologen (Figure 16),<sup>[168]</sup> PAA-*b*-PNIPAm,<sup>[169]</sup> PMAA-*b*-PNIPAm,<sup>[170]</sup> and PNIPAm-*b*-PDOPA where the PNIPAm chain ends are modified with a 3,4-dihydroxy-L-phenylalanine moieties forming spherical nanoparticles with temperature/pH dual-stimuli-responsive character.<sup>[171]</sup> Other examples



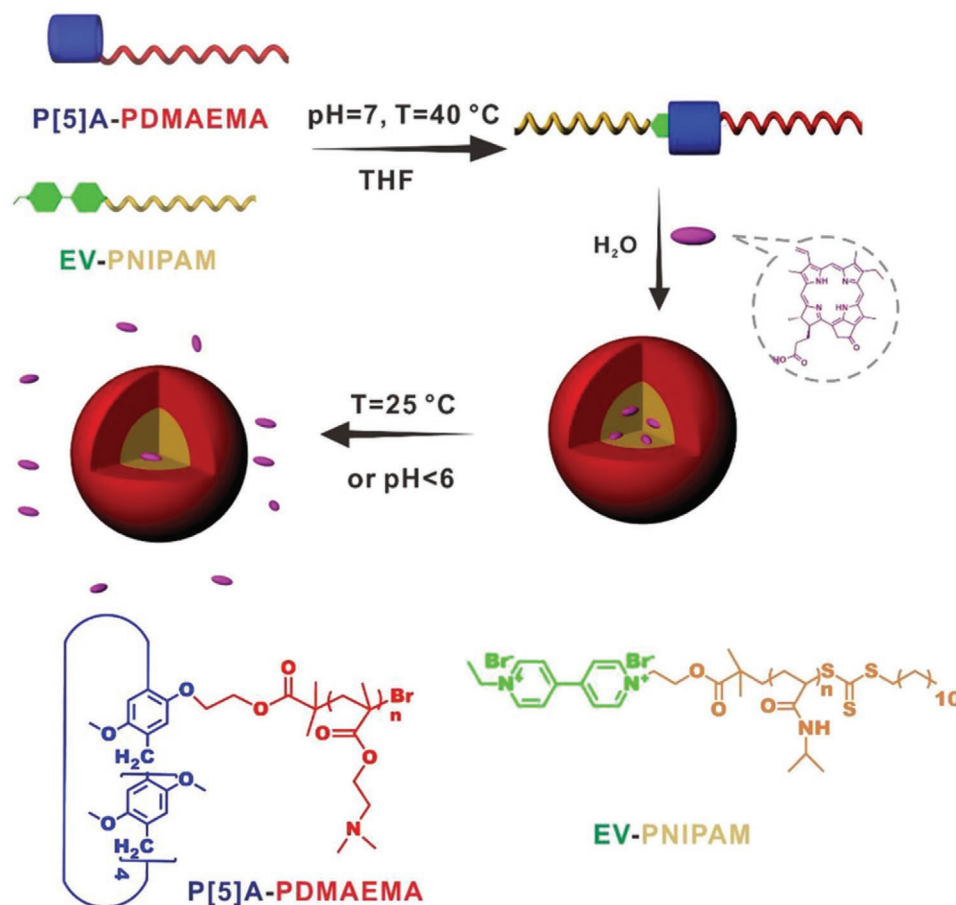
**Figure 15.** Synthetic pathways to the targeted thermo-responsive styrenic block copolymers. a) Path I: Synthesis of PAPI-*b*-PS via emulsion polymerization. Path II: Synthesis of PDMA-*b*-P(API-*co*-APy)-*b*-PS via emulsion polymerization using a nanoreactor approach. b) Mechanism for emulsion polymerizations. c) Particle size distributions, hydrodynamic radii ( $R_h$ ) and particle size dispersities (PSDs) of the initial polymer/solvent systems and of the final latexes. Reproduced with permission.<sup>[163]</sup> Copyright 2017, MDPI.

including PNIPAM-*b*-P(DPA-*co*-TPE) and P(NIPAM-*co*-TPE)-*b*-PDPA where tetraphenylethylene (TPE) is used as a single-color “turn on” fluorescence probe used to differentiate temperature or pH stimulus in solutions or in the cells.<sup>[172]</sup> Apart from temperature and pH polymers responsive to other types of stimuli have also been prepared. Triblock terpolymer (poly(acrylic acid)-*b*-poly(4-hydroxystyrene)-*b*-poly(1-(4-(1-methyl-1,2-dicarba-clo-dodecaborane-2-yl methyl)-phenyl)ethylene)) (PAA-*b*-PHS-*b*-PSC) sensitive to pH and the addition of CsF where the PHS and PSC blocks become more hydrophilic upon addition of CsF salt allowing to have control over polymer–water interactions.<sup>[173]</sup>

Polymers responsive to light, Ph, and reduction reactions were prepared by synthesizing a random copolymer containing azobenzene, DMAEMA, and polyhedral oligomeric silsesquioxane. The hydrophobic pendent azo groups could undergo trans-*cis* isomerization under UV light irradiation, while under reductive environment they were reduced to more hydrophilic aniline functionalities.<sup>[174]</sup> Additional examples of redox-responsive

copolymers are composed of PEGA and NIPAm, with organic arsenical acrylamide monomer (AsAm) incorporated in either the core-forming PNIPAm block (PEGA-*b*-P(NIPAm-*co*-AsAm)) or the corona-forming PEGA block (P(PEGA-*co*-AsAm)-*b*-PNIPAm). The polymers underwent simultaneous self-assembly and cross-linking, via the organic arsenical pendant groups, under reductive conditions (to reduce As(V) to As(III)) in the presence of polythiol reagents as cross-linkers.<sup>[175]</sup> A different novel multiresponsive block copolymer containing disulphide bonds was prepared via combination of ATRP and RAFT polymerization. The copolymer was composed of hydrophilic poly(oligo(ethylene oxide) monomethyl ether methacrylate) (POEOMA) and hydrophobic polymethacrylate block having multiple disulfide pendants (PHMssEt). This degradable amphiphilic block copolymer displayed pH/redox response due to the presence of dual acidic pH-labile acetal linkage and reductively cleavable disulfide bonds.<sup>[176]</sup> Unlike the common approaches taken by most Mecerreyes and co-workers synthesized dual-responsive macromonomers via RAFT using a





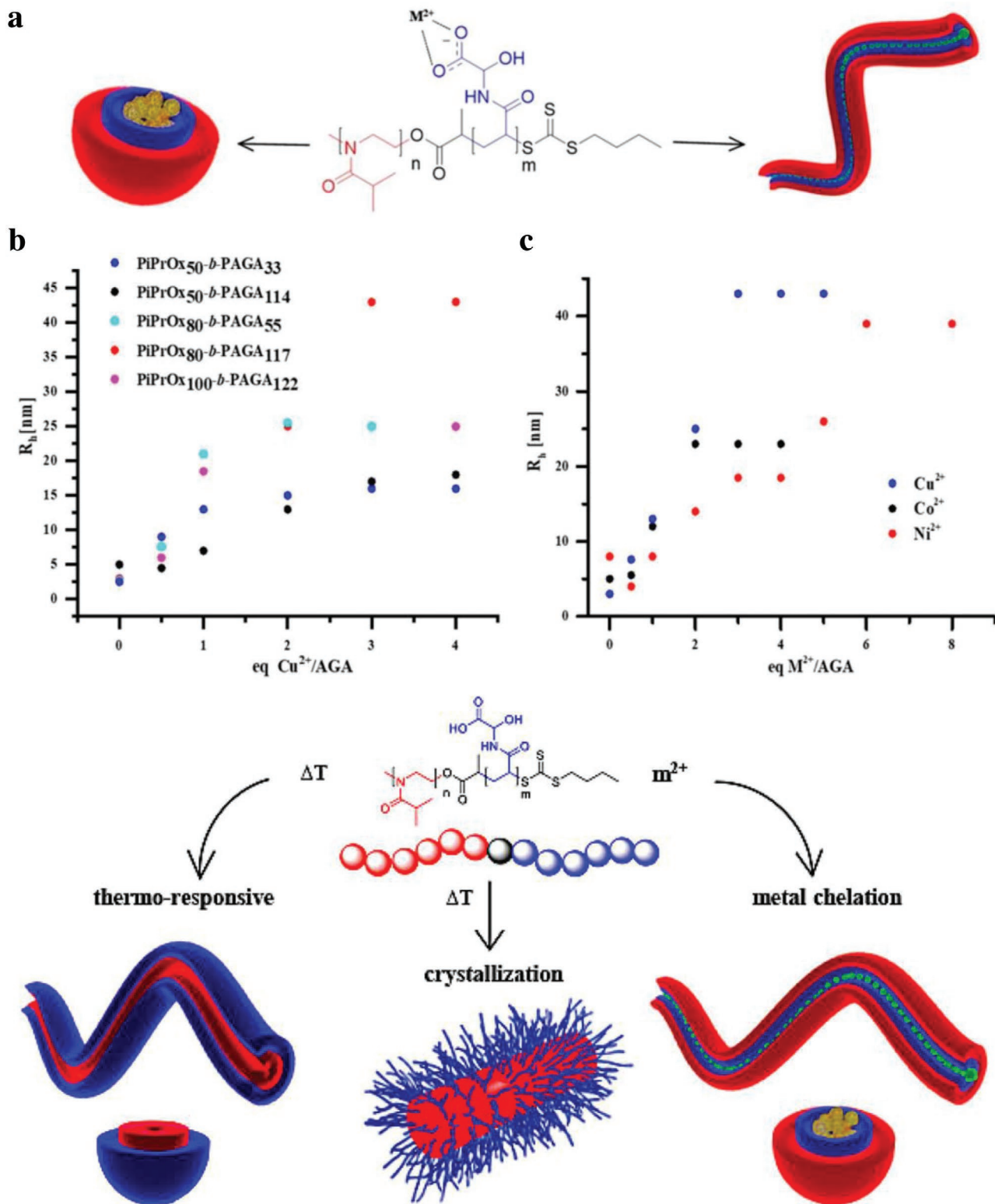
**Figure 16.** Orthogonal construction, self-assembly, and the process of pH-/thermocontrolled release of photosensitizers based on supramolecular diblock copolymers via host-guest interactions between P[5]A-PDMAEMA and EV-PNIPAM. Reproduced with permission.<sup>[168]</sup> Copyright 2019, Wiley-VCH GmbH.

novel propylenedioxythiophene (ProDOT) based chain transfer agent. At the first step three different ProDOT end capped macromonomers were synthesized:  $\alpha$ -ProDOT-poly(methyl methacrylate) (ProDOT-PMMA),  $\alpha$ -ProDOT-poly(ethylene glycol methyl ether methacrylate) (ProDOT-POEGMA), and  $\alpha$ -ProDOT-poly(*N*-isopropylacrylamide) (ProDOT-PNIPAM) leading to formation of semiconjugated polymers in form of aqueous dispersions. The PEDOT-PNIPAM showed thermos-responsive character with volume phase transition between 26 and 34 °C depending on the composition and the polymer length.<sup>[177]</sup> At the second step these three macro-CTAs were used to homopolymerize 3,4-ethylenedioxythiophene (EDOT) monomer by chemical oxidative polymerization. Schacher and co-workers take yet a different approach, using crystallization and metal chelation as a tool to prepare dual responsive block copolymers (Figure 17). They synthesize poly(2-*iso*-propyl-2-oxazoline)-*b*-poly(2-acrylamido glycolic acid) (PiPrOx-*b*-PAGA) double hydrophilic block copolymers by combination of ring-opening and RAFT polymerization. The block copolymers were responsive toward several external triggers: 1) PiPrOx segment underwent coil-to-globule transition upon heating above the cloud point temperature, 2) PAGA block chelated M<sup>2+</sup> metal ions, forming nanostructured hybrid structures, and 3) prolonged heating above the T<sub>cp</sub> of PiPrOx block resulted in formation of anisotropic micelles via crystallization-

driven solution self-assembly. They also demonstrated that the cloud point temperature of PiPrOx-*b*-PAGA micelles could be tuned between 30 and 68 °C by either varying the PiPrOx-PAGA ratio or by the amount of metal ions added. These interesting inorganic-organic hybrid materials could find application in diverse fields such as (photo)catalysis, sensors, or drug delivery systems.<sup>[178]</sup>

### 4.3. Multiblock Copolymers

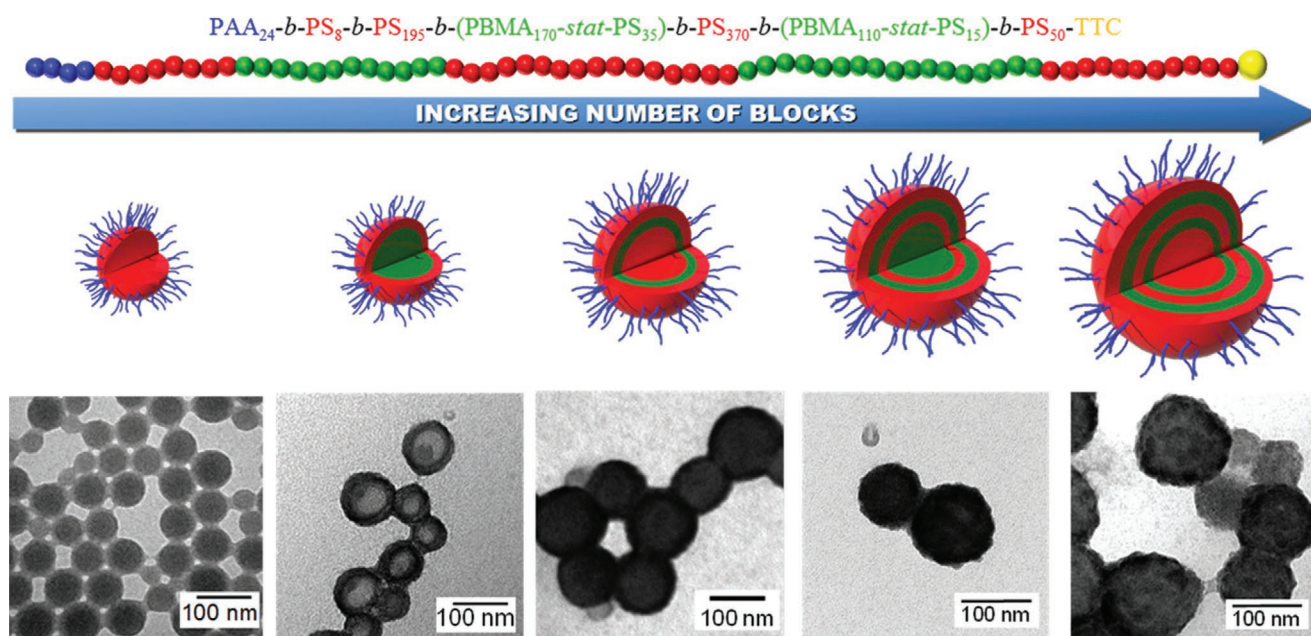
Nature is able to produce highly defined polymers, such as proteins and nucleic acids. These biopolymers have perfectly controlled structures that arise from the perfect control over their sequential repeat units. This precision is vital to life since their highly specialized functions depend on the controlled over the sequence regulation of the repeat units bearing functionalities along the polymer backbone. To be able to mimic such structures via synthetic chemistry, the challenge is to develop a method to sequence-regulate synthetic macromolecules. Multiblock copolymers are original structures that to a large extent could mimic biopolymers exhibiting well-controlled primary structure. Despite their promises, these structures have mainly been limited to only a few blocks, with relatively broad



**Figure 17.** a) Schematic depiction of the aggregation of PiPrOx-*b*-PAGA by the addition of metal ions, b) hydrodynamic radii for different PiPrOx-*b*-PAGA (1.0 mg mL<sup>-1</sup>) block copolymers after the addition of varying amounts of Cu<sup>2+</sup>, and c) Rh for the aggregates formed by PiPrOx<sub>80</sub>-*b*-PAGA<sub>117</sub> (1.0 mg mL<sup>-1</sup>) and various metal ions at different ratios. Reproduced with permission.<sup>[178]</sup> Copyright 2020, American Chemical Society.

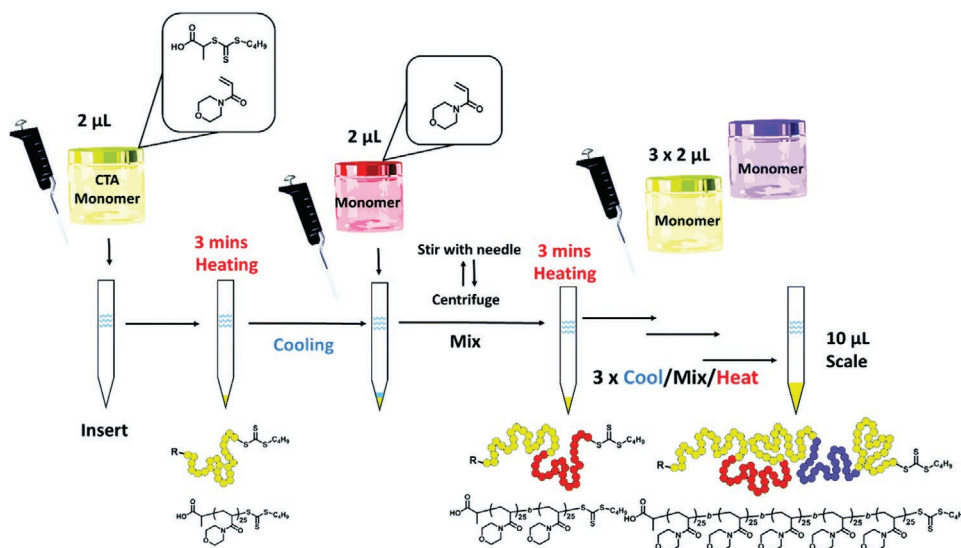
molecular weight distribution and their synthesis typically requires a demanding process (low conversion, purification between each block formation, etc.). Classical RAFT controlled polymerizations have been employed extensively for synthesizing such multiblock copolymers.<sup>[179–189]</sup> In 2013, Perrier and co-workers reported for the first time a RAFT controlled synthetic route that could provide multiblock copolymers combining precisely defined, high-order structures of well-defined molecular weight distributions with a wide range of functional groups.<sup>[190]</sup> This simple and scalable synthesis was based on a one-pot, sequential polymerization at very high yields (over 99%). In this first report the synthesis of a dodecablock (repetitions of four different sequences of ten units each), a hexablock (repetitions of five different sequences of 5–25 units each) and an icosablock (20 blocks containing repetitions of three different sequences of on average three units each) with exceptionally narrow molecular weight distributions, was reported. The main key to the success of such polymerization relies on the fine tuning of the reaction conditions such that polymerization proceeds to full conversion, in a reasonably short period of time with minimized number of generated dead/unreactive chains (chains produced via bimolecular termination or irreversible transfer reactions involving propagating radicals). As discussed previously in Section 2, the number of chains originating from termination reactions in a degenerative transfer polymerization can be readily predicted from the number of radical initiators consumed, which is based on the initial stoichiometry. Therefore by reducing the amount of initiator used the number of “dead” chains would be suppressed. However, this would lead to lower polymerization rates. At the same time polymerization rates also depend on monomer concentration, temperature and solvent. By fine tuning the conditions such that the polymerization proceeds to full conversion in a reasonable time, using a very low ratio of initiator-to-RAFT agent, near perfect well-

controlled multiblock copolymers could be synthesized in grams scale. Perrier and team perfect their initially described system for polymerization of multiblock copolymers in a series of articles by examining and independently tuning different polymerization factors such as monomer functionality, reaction solvent, temperature, and time<sup>[191–193]</sup> as well as establishing the limits of their system via statistical analysis, simulation, and modeling.<sup>[194,195]</sup> Upon complete understanding of the system more complex architectures were also synthesized using the described method. For example, multisegmented bottle-brush structures from acrylamides,<sup>[196]</sup> functional core cross-linked star shaped structures<sup>[197]</sup> as well as graft multiblock copolymers from styrene and maleic anhydride to be used as viscosity modifiers in mineral oils.<sup>[198,199]</sup> The described sequence controlled approach has also been used to synthesize a single chain multiblock copolymer bearing foldable segments via supramolecular forces (hydrogen bonding). This folding results in formation of secondary structures mimick protein structures.<sup>[200]</sup> Until recently, all the reported sequential multiblock copolymers had been prepared via solution polymerization. Zetterlund and co-workers have demonstrated that such polymerization could also be carried out under emulsion conditions combining precision and control. Short amphiphilic diblock copolymers were synthesized using solution polymerization and then transferred to water forming seed particles that acted as nanoreactors in the sequential RAFT emulsion polymerizations of high molar mass (>100 000 g mol<sup>-1</sup>) multiblock copolymers. Two examples of multiblocks (deca and hepta) containing different 100 unit blocks with precise control over polymer composition with narrow dispersities were given. This batch process without any intermediate purification steps performed in environmentally friendly solvent (water), would be very attractive to the industry.<sup>[201]</sup> Later the same authors also showed that this strategy could be used to prepare nanoparticle from commodity



**Figure 18.** Schematic illustration of the synthesis of nanoengineered multilayered particles. Each step of the growing particle is represented, showing the expected morphology after each cycle of polymerization. Reproduced with permission.<sup>[202]</sup> Copyright 2019, American Chemical Society.





**Figure 19.** “Master Mix” where monomer, CTA, initiator and solvent were added into the microvolume inserts using a regular air displacement micropipette. Sequential chain extension was performed via repeating cycle to yield a pentablock copolymer. All the polymerizations were carried out in the presence of open air. Reproduced with permission.<sup>[204]</sup> Copyright 2019, The Royal Society of Chemistry.

monomers (methacrylates, acrylates, and styrene) (**Figure 18**). High molecular weight (up to  $140\,000\text{ g mol}^{-1}$ ) multiblock copolymers were prepared in short time periods (up to 3 h) by exploiting the segregation effect (compartmentalization) within the polymeric nanoparticles. The presence of chemically incompatible blocks multi-layered nanoparticles were formed as a result of microphase separation and the formation of a well-defined structure within the nanoparticles. The advantages of this approach is no intermediate purification step, relatively high solid content, good colloidal stability with no flocculation/coagulation, and near full monomer conversion.<sup>[202]</sup>

Sequential multiblock copolymers have also been performed at both high and low scales. In 2014, CSIRO team reported the first fully unattended preparation of quasiblock copolymer libraries in an automated synthesizer. This high-throughput, one pot approach enabled the synthesis of a wide range of copolymer compositions with optimized reaction conditions (up to 71 different quasi-block copolymers, including BAB, CBABC, ABC, and ABCD compositions).<sup>[203]</sup> By contrast, down-scaling has also been reported for the synthesis of such block copolymers. Basically the Perrier team has demonstrated that their original multiblock sequence prepared using acrylamides could also be prepared in microvolume insert vials ( $10\ \mu\text{L}$  with a set lower limit of  $2\ \mu\text{L}$ ) with good control (**Figure 19**). Pentablock copolymers with a final volume of  $10\ \mu\text{L}$  could be synthesized demonstrating the ultrafast RAFT and a high-throughput method for preparation of multiblock copolymers.<sup>[204]</sup>

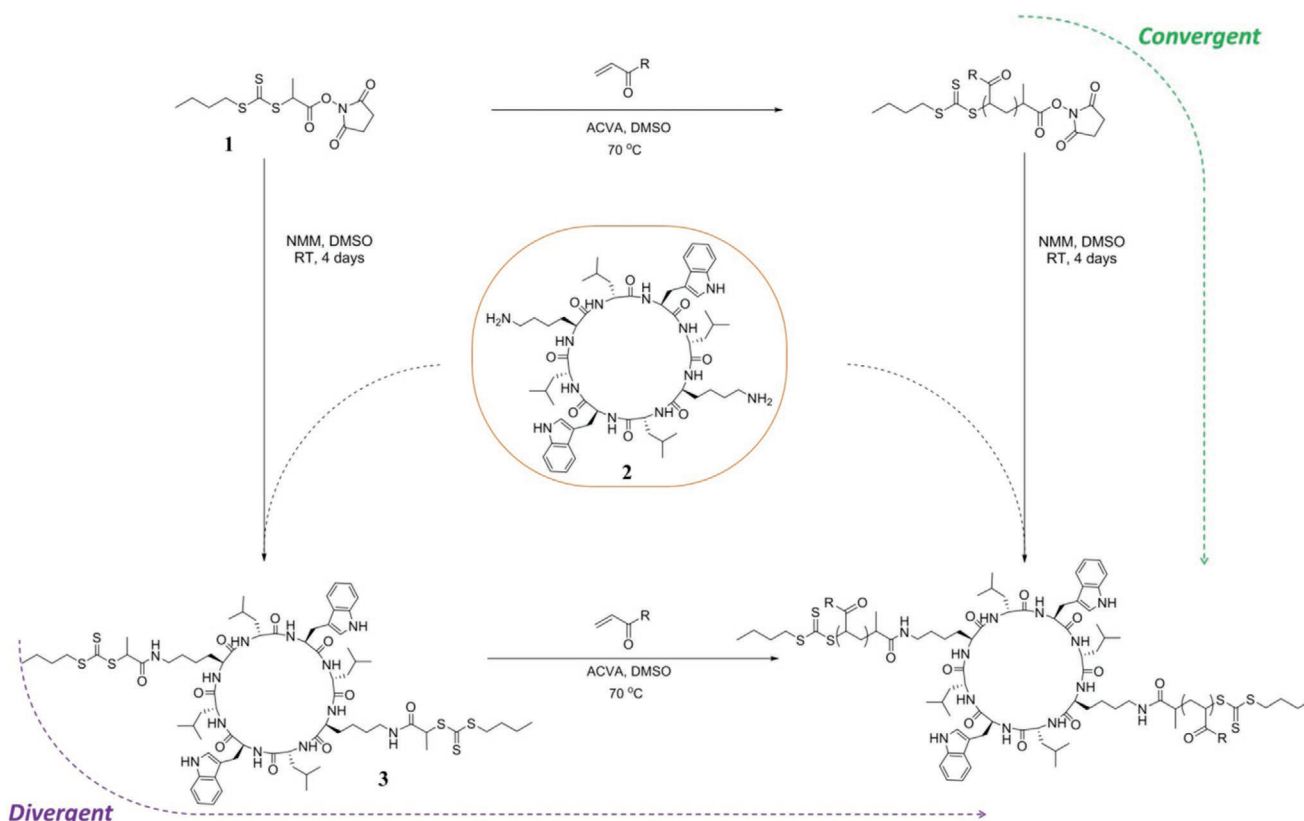
#### 4.4. Peptide Conjugates

Combination of monomer-sequence peptides and synthetic polymers via conjugation (as referred to as bioconjugation), gives rise to an advanced class of multifunctional block copolymers. Their specific properties inherited from peptides and polymers, their structural diversity and functionality of the

peptide–polymer conjugates makes them a very attractive material in diverse fields from biomedical to artificial intelligence. There are two synthetic approaches for peptide–polymer conjugations: 1) the direct coupling of peptides to synthetic polymers (grafting to), and 2) the polymerization from a modified peptide (macro-CTA) (grafting from). The direct coupling strategy works only well when the chain length of both segments (peptide sequence and the polymer chain) are relatively low as the chain end reactivity and accessibility decrease proportional to the increasing molecular weights.

Among the many polymerization techniques available, RAFT process is the most suitable techniques for the making peptide–polymer conjugates since RAFT polymerization is simple, tolerant to diverse synthetic conditions (temperature, solvent, monomers, etc.) and functionalities.

The literature on the synthesis of peptide–polymer conjugates is very rich. Countless different approaches could be taken to prepare peptide–polymer conjugates. Describing all these approaches and different chemistries used are outside the realms of this article. There are several detailed and tutorial reviews on the subject that interested readers could refer to refs. [205–211]. Here we would only focus on the latest work reported on the conjugates containing self-assembling peptides governing the self-assembly of the peptide–polymer conjugates. Self-organizing or self-assembling peptides are peptide sequences that are able to form structures using noncovalent bonds such as  $\pi$ - $\pi$  stacking and hydrogen bonding. The addition of covalently bonded polymer chains to these self-assembling peptides could either disturb their original organization or could be used to direct and control the original self-assembly of the peptidic block. One of the best examples of such peptide–polymer conjugates is the cyclic peptide–polymer conjugates. Cyclic peptides (CPs) are a type of flat ring-like configuration consisted of an even number of alternating D- and L-amino acids that can stack through antiparallel beta sheet hydrogen bonding to afford rigid tubular structures. Perrier and co-workers have



**Figure 20.** Grafting-to and grafting-from synthetic routes to a cyclic peptide–polymer conjugate. Reproduced with permission.<sup>[214]</sup> Copyright 2015, Wiley-VCH GmbH.

shown in a series of articles that different types of site-specific click chemistries could be used to conjugate polymer chains to CPs efficiently.<sup>[207,211–213]</sup> They also established the advantages and limitations of the two synthetic pathways to conjugate polymers to the peptide sequence: grafting to (convergent) versus grafting from (divergent) (Figure 20).<sup>[214]</sup> Using these two pathways an array of different (co)polymers have been conjugated to CPs. For example, conjugation of pH responsive poly (dimethyl ethyl methacrylate), PDMAEMA, resulted in formation of nanotubes with water-soluble supramolecular brushes. The self-assembly of the conjugates could be controlled by adjusting the charge density on the conjugated polymer arms.<sup>[215]</sup>

Assembly-disassembly of such structures were achieved using an amphiphilic block copolymer of poly(2-(diisopropylamino) ethyl methacrylate)/PDPA and poly(2-hydroxypropyl methacrylamide)/PHPMA where the tubular structure was stable at pH 7 but disassembles at acidic pH due to protonation of the PDPA functional groups.<sup>[216]</sup> Employing similar methods different types of polymer arms have been conjugated to CPs each endowing a certain properties to the resulting conjugate. From water soluble PEG arms containing disulphide bonds to make redox responsive conjugates<sup>[217]</sup> to functional arms able to form organometallic bonds<sup>[218]</sup> or directional hydrogen bonds sensitive to UV irradiation<sup>[219,220]</sup> for advanced drug delivery systems. As discussed CP–polymer conjugates results in formation of complex structures with diverse properties. However, complex hierarchical structures could be synthesized by simply attaching a self-organizing peptide sequence to the chain transfer agent.

For example, Binder and co-workers have reported that modifying the R group of a trithio RAFT agent with a beta amyloid sequence (LVFF, A $\beta$ 17–20). Using this macro-CTA, they prepared linear conjugates able to self-assemble into small micelles ( $D = 25$  nm). They also prepared physically cross-linked hydrogels with tuneable stiffness due to the presence of the LVFF peptide sequence.<sup>[221,222]</sup> Similarly Thang and co-workers modified the R group of a RAFT agent with a peptide sequence of ten, known as the cell-penetrating peptides. This modified CTA was able to control the synthesis of well-defined block copolymers (PEG and butyl acrylate) forming rods and vesicles in water. The cytotoxicity tests confirmed the biocompatibility of the conjugates and the semi quantitative cell uptake assay showed enhanced cellular internalization of the particles.<sup>[223]</sup> A different example was reported by Koga and co-workers. They prepared four different tetrapeptide sequences (RGDS, reverse SDGR, cationic KKKK, and anionic DDDD) known for their cell-binding ability. These sequences were covalently bonded to the CTA and used as macro-CTAs that were subsequently used for the polymerization of styrene. The amphiphilic conjugates self-assembled into peptide decorated spherical nanoparticles which were readily incorporated in to cells.<sup>[224]</sup> Aside from conjugating the peptide sequence to CTA, monomers bearing peptide sequence is also a way to prepare peptide–polymer conjugates. Chen et al. reported for the first time the synthesis of a methacrylamide monomer bearing peptide sequence of Phe–Gly–Arg–Gly–Asp–Ser as side group. This peptide monomer was then polymerized in acidic methanol to give well-controlled



polypeptide chains with narrow molecular weight distributions. Block copolymers prepared using this new monomer allowed for a good cell adhesion with no obvious toxicity thanks to the presence of the peptide sequence.<sup>[225]</sup> Recently Semsarilar and co-workers reported synthesis of two new acrylamide monomers with self-assembling tripeptides as side chains (MAM-Gly-Phe-Phe and MAM-Phe-Gly-Asp). They demonstrated that both monomers could be homo- and copolymerized with methacrylate monomers under RAFT conditions resulting in well-controlled (co)polymers. They also demonstrated that these two monomers could be used as both the stabilizing block and the core-forming block in a PISA process. The resulting morphologies were mainly long rigid rods and branched, leaf-like structures that are believed to be formed due to the presence of the tripeptide sequences bale to form H-bonding and  $\pi$ - $\pi$  stacking.<sup>[91,92]</sup>

## 5. Novel Applications of RAFT

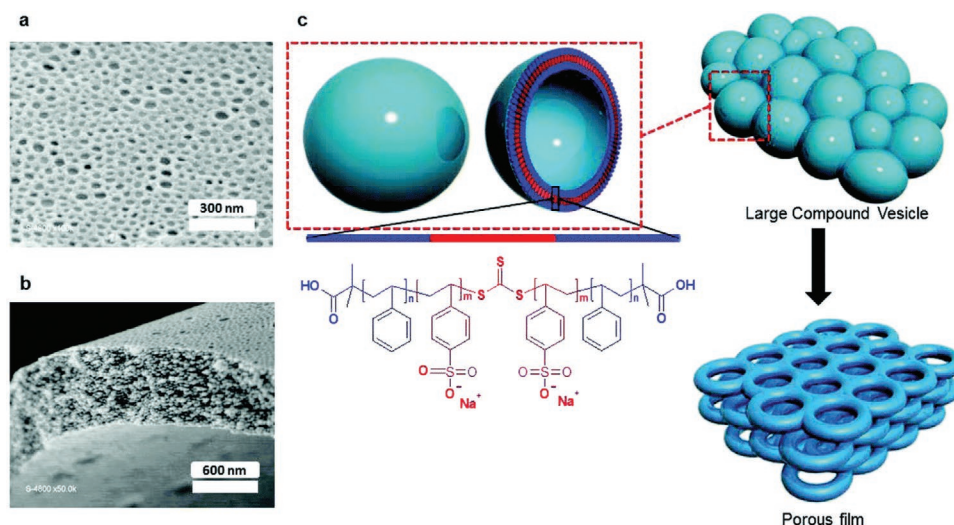
Polymers prepared by RAFT have been used in many different fields, notably in preparation of biomaterials (implants, scaffolds, coatings, drug, gene delivery, etc.),<sup>[226–230]</sup> sensing and detection,<sup>[231,232]</sup> coatings and patterning,<sup>[233–235]</sup> electronics,<sup>[236]</sup> nanocomposite,<sup>[235,237–240]</sup> and vitrimers.<sup>[241]</sup> One of the most recent and emerging applications of polymers and nanoparticles prepared by RAFT is membranes for separation. Here, we would like to focus on this novel application and bring it to the attention of the polymer community and material chemists as it is still in its infancy, awaiting further development.

### 5.1. Membranes

Polymers synthesized via RAFT polymerization have been used in a variety of different fields such as biomaterials, coatings, lubricants to name a few. RAFT is an excellent tool to design and synthesize tailored polymers with desired architecture and functionality crucial for the intended application. One of the most recent areas of application for such (co)polymers is in membrane science. Bespoke polymers could form thin porous films bearing functionalities that could be harnessed to fabricate stimuli-responsive thin film membranes that would outperform classical polymer membranes in terms of separation and energy consumption. The use of tailored (co)polymers in membrane fabrication is a relatively new line of research with the first work reported in 2007 by Abetz and co-workers. They demonstrated that isoporous asymmetric membranes could be prepared via phase inversion method using a block copolymer (PS-*b*-P4VP) synthesized via anionic polymerization with perfect control over molecular weight and composition.<sup>[242]</sup> This started a new branch of research on the use of tailored functional block copolymers in membrane science. However to date, very few articles have been published using RAFT synthesized (co)polymers for preparation of membranes. The very first report is by Ruokolainen and co-workers in 2007.<sup>[243]</sup> They synthesized a series of well-defined temperature-responsive polystyrene-*b*-poly(*N*-isopropylacrylamide)-*b*-polystyrene (PS-*b*-PNIPAM-*b*-PS) triblock copolymers using RAFT solution polymerization. These ABA triblock copolymers, either as pure

block copolymer or blended with PNIPAM homopolymer, were spin-coated on top of meso/macroporous polyacrylonitrile (PAN) support membrane in form of thin films. The composite membranes bearing active top layers exhibited classical lamellar, cylindrical, spherical, and bicontinuous double gyroid morphologies at dried state. Swelling the PNIPAM block in aqueous solution resulted in formation of open pores. Permeability tests as a function of temperature using PEG standards showed a temperature switchable on/off behavior, where the highest permeability was obtained at temperatures below the glass transition temperature of PNIPAM, and low molecular weight PEG standards (between 108 and 660 g mol<sup>-1</sup>). Despite the promising results presented in this article, the work was not picked up until 2014 where Phillip and co-workers reported preparation of membranes with tailored pore walls from polyisoprene-*b*-polystyrene-*b*-poly(*N,N* dimethylacrylamide) (PI-PS-PDMA) triblock copolymer.<sup>[244]</sup> The self-assembly of this triblock terpolymer under nonsolvent induced phase separation conditions resulted in formation of an asymmetric, porous structure. The top selective layer was formed by density packed PDMA-lined pores with average diameter of 8 nm. Hydrolysis of the PDMA block converted the pore lining to pH responsive poly(acrylic acid). It was also demonstrated that the pore size and the flux could be tuned via adjusting the pH. Later Mulvenna et al. showed that stimuli-responsive membranes could be prepared by simply incorporating functionality capable of forming noncovalent bonds. They synthesized an ABA block copolymer containing boronic acid moieties able to form weak or strong hydrogen bonds depending on pH.<sup>[244]</sup> The introduced H-bonding between the self-assembled chains could enhance the mechanical stability of the membranes while varying the solute pH could change the pore size due to extra H-bonding and the introduced negative charge. The same group also worked with a negatively charged ABA triblock copolymer, where the middle block contained a strong acid functionality (**Figure 21**). They synthesized a library of polystyrene-*b*-poly(sodium 4-styrenesulfonate)-*b*-polystyrene (PS-*b*-PNaSS-*b*-PS) with varying block lengths. Their systematic study, investigated the effect of solvent mixtures, solvent mixture ratios, molecular weights, block ratios, and polymer concentration.<sup>[245–247]</sup> It was shown that independent of the block ratios aggregates of different morphologies could be prepared depending on the solvent mixture ratios (THF/H<sub>2</sub>O). At constant polymer concentrations, different type of morphologies could be prepared (spheres, short worms, and vesicles). At low water ratios aggregates with PS shells (hydrophobic) were formed while at higher water contents hydrophilic particles with PNaSS shells were observed.<sup>[245,246]</sup> They also demonstrated that when the block ratios were even (PS<sub>5k</sub>-PNaSS<sub>5k</sub>-PS<sub>5k</sub>, PS<sub>10k</sub>-PNaSS<sub>10k</sub>-PS<sub>10k</sub>) depending on the choice of organic solvent (THF or DMF) hydrophobic LCVs or hydrophilic spheres could be prepared.<sup>[246,247]</sup> All these colloidal stable aggregates were used to make porous thin film membranes on a solid support via spin-coating. Image analysis and filtration tests suggested that the pore size of these porous thin films were in the range of 10–30 nm making these membranes suitable for ultrafiltration. Initially, the assumption was that in order to form more stable nanostructured membranes, symmetrical triblock copolymers were essential as polymer chains could act as a bridge between nanoaggregates.

However, Semsarilar and co-workers, in a series of articles demonstrated that PISA prepared diblock copolymer

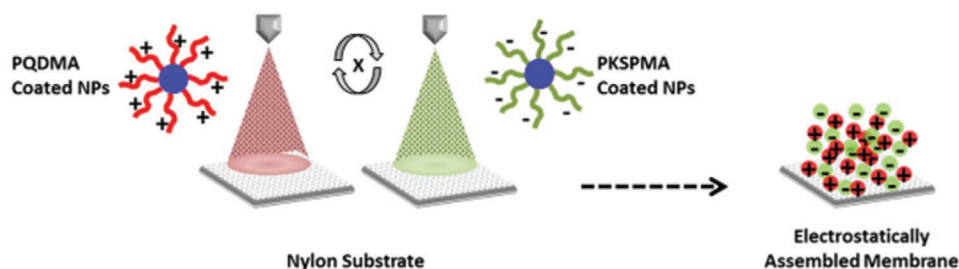


**Figure 21.** Porous thin film after spin-coating. a) Top surface showing honeycomb-like structure. b) Cross-section showing the superposition of layers of honeycomb-like morphology. c) Schematic illustration of the film preparation from an LCV fusion and bursting upon drying. Reproduced with permission.<sup>[246]</sup> Copyright 2017, The Royal Society of Chemistry.

nanoparticles could effectively form stable porous membranes provided that specific interactions (such as electrostatic charges) are introduced between the nanoparticles. For example, they have shown that acid decorated diblock copolymer nanoparticles of different morphologies could be simply spin coated on a mechanical support to form porous thin film membranes. The PISA synthesized poly(methacrylic acid)-*b*-poly(methyl methacrylate) (PMAA-*b*-PMMA) nanoparticles alone formed stable membranes under acidic conditions.<sup>[248]</sup> Due to pH-sensitivity of the PMAA chains at higher pH values (above pK<sub>a</sub> of PMAA ≈ 6.1) the repulsive forces introduced due to the deprotonation of the acid groups disturbs the integrity of the thin film membranes. To overcome this problem positively charged iron-oxide nanoparticles were blended with the PMAA-*b*-PMMA nanoparticles to equilibrate the negative charge and act as a binder between the negatively charged particles. This simple strategy worked really well as the authors demonstrated how varying the amount of iron-oxide nanoparticles and the morphology of the diblock copolymer nanoparticles lead to formation of pH-responsive membranes.<sup>[249]</sup> Besides pH-responsiveness these membranes exhibited magnetoresponsiveness as well since they contain magnetic iron-oxide cores. It was demonstrated that exposing the membranes to different strength magnetic fields causes both reversible and irreversible changes in the pore size of the membranes by altering the arrangement of the nanoparticles in the thin film layer. The (ir)reversibility depends to a large extent on the strength of the magnetic field and the time of exposure.<sup>[250,251]</sup> In a later work it was demonstrated that the pore size of such membrane could easily be tuned by varying the surface charge, size and the nature of the core-shell nanoparticles (both organic and inorganic).<sup>[252]</sup> In a different approach, instead of mixing the polymer nanoparticles with the inorganic iron-oxide nanoparticles, the PMAA-*b*-PMMA particles were decorated with iron-oxide cores through ligand exchange during nanoparticle synthesis. The membranes prepared from these decorated nanoparticles were stable and displayed similar properties to membranes prepared from

a mixture of iron-oxide and polymer nanoparticles discussed previously.<sup>[253]</sup>

Subsequently, the same group explored the possibility of preparing membranes from nanoparticles with different properties. In one example, the iron-oxide cores were replaced with silver-oxide particles. The resulting membranes showed antimicrobial properties when in contact with *Enterococcus hirae* due to the presence of silver-oxide cores.<sup>[254]</sup> Antimicrobial membranes were also prepared by employing polylysine-decorated nanoparticles. These particles were prepared via an aqueous one-pot PISA polymerization using a very short polylysine (only three lysine units) macro-CTA. The positive charge carried by the macro-CTA was enough to deactivate both Gram negative (*Escherichia coli*) and Gram positive (*Staphylococcus epidermidis*) bacteria.<sup>[90]</sup> Semsarilar and co-workers also prepared membranes from oppositely charged polymer nanoparticles through sequential depositing method. In this work nanoparticles bearing permanent positive and negative charge were prepared via aqueous PISA polymerization and were spray coated onto a mechanical support to form a thin film membrane with pores of ≈20 nm (Figure 22). The resulting membranes were stable under different conditions such as varying pH and pressure as well as in presence of concentrated salt solutions.<sup>[255]</sup> In a separate work the same group show that the pore size of membranes prepared via assembly of spherical nanoparticles in a thin film membrane could be tuned via coating the nanoparticles with a layer of silica while controlling its thickness. For this positively charged polymer nanoparticles were synthesized using PISA technique and the particles were coated a layer of silica via the classical sol-gel reaction using tetramethyl orthosilicate. The size of the silica coated nanoparticles was fine-tuned via controlling the thickness of the deposited silica layer. Membranes with different pore size and flow values were prepared using these nanoparticles. Unexpectedly, the presence of the silica layer not only altered the pore size but also enhanced the mechanical robustness of the prepared thin film membranes (as compared to the uncoated particles).<sup>[256]</sup>



**Figure 22.** Schematic representation of the sequential deposition of the thin film membrane using spray coating. Reproduced with permission.<sup>[255]</sup> Copyright 2018, Elsevier.

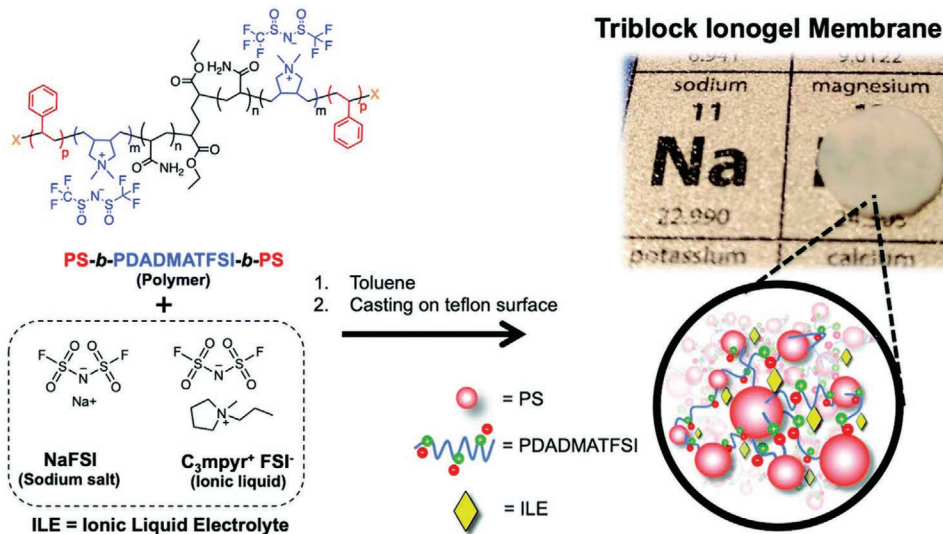
Recently, Mecerreyes and co-workers reported preparation of self-standing ionogel membranes from MADIX/RAFT controlled PISA polymerization of AB di and ABA tri block copolymers of poly(diallyldimethylammonium)-*b*-polystyrene with superior ionic conductivity values (**Figure 23**).<sup>[257]</sup> This is an excellent example to demonstrate how RAFT-controlled block copolymers could help the design of high performant advanced materials.

A more straightforward method to prepare functional membranes is via blending functional material with the polymer forming the body of the membrane. The blending method is a simple and cost effective approach however often the conferred functionality is not permanent due to incompatibility of the blended material. Also it makes the control over the nanostructure and the pore size of the membranes more complex. Up to present there are only a handful of studies on the incorporation of RAFT prepared polymers in membranes via blending. Majority of studies have been on enhancing the PVDF membrane properties such as hydrophilicity, antifouling, ion recognition, and pH sensitivity to name a few. The employed diblock copolymers almost always contained a PMMA block. This is because PMMA is actually the only polymer miscible with PVDF, ensuring a homogeneous mixing of the added polymer within the PVDF membrane matrix. The examples of the block copolymers used are poly(methyl methacrylate)-*b*-poly(4-vinylpyridine) P(MMA-*b*-4VP),<sup>[258]</sup>

poly(methyl methacrylate)-*b*-poly(2-(*N,N*-dimethylamino) ethyl methacrylate) P(MMA-*b*-DMAEMA),<sup>[259]</sup> poly(poly(ethylene glycol) methacrylate)-*b*-poly(methyl methacrylate)-*b*-poly(poly(ethylene glycol) methacrylate) P(PEGMA-*b*-MMA-*b*-PEGMA),<sup>[260]</sup> poly(methyl methacrylate)-*b*-poly(sulfobetaine methacrylate) P(MMA-*b*-SBMA),<sup>[261]</sup> and poly(methyl methacrylate)-*b*-poly(1-(2-(methacryloyloxy)ethyl)-3-butylimidazolium bromide) P(MMA-*b*-MEBIm-Br).<sup>[262]</sup> To improve the miscibility of the added block copolymer with the PVDF, Semsarilar and co-workers synthesized a PVDF-*b*-PEO-*b*-PVDF triblock terpolymer. The short PVDF segments in the triblock copolymer were able to cocrystallize with the bulk PVDF resulting in permanently locking the additive in the membranes matrix.<sup>[263]</sup>

## 6. Advantages, Limitations, and Future

Without any doubt, RAFT polymerization has shown a tremendous development after its initial discovery. While during the early days of RAFT, the polymers were rather limited in terms of controlled degree of polymerization, the situation has changed dramatically during the last years, at least for some of the MAM monomers. In addition, there have been significant improvements in the RAFT polymerization of LAM monomers such as isoprene. RAFT allows the possibility to synthesize



**Figure 23.** Ionogel membrane formation. Reproduced with permission.<sup>[257]</sup> Copyright 2020, The Royal Society of Chemistry.



polymers with different topologies, combination of different monomers as well as polymerization techniques such as living anionic polymerization. It also permits polymerization in the absence of hazardous or toxic solvents, photopolymerization (without radical initiators) enabling the polymerization at low temperatures, formation of well-controlled nanoparticles during polymerization using PISA strategies, and many more. These are very important aspects of RAFT, which have a high impact on the development of new functional polymers. The tailoring of molecular weight distributions is a strong advantage of RAFT, as not always, very narrow disperse polymers are useful and desired. For example, beneficial rheological properties may be obtained by well-controlled dispersities. Also the morphological properties can be influenced by controlling the dispersity of molecular weights and composition in the case of block copolymers. Another big advantage of RAFT polymerizations versus other controlled or living polymerizations is its tolerance to various functional groups, allowing different chemical postmodification pathways, thus such polymers may serve as a toolbox for different applications. Although RAFT shows a big potential, one of its present drawbacks is the lower rate of polymerization as compared to free radical polymerization, resulting in low production of polymers in large scale. On the other hand, the application of novel polymerization process designs, such as PISA, or microfluidics, offer not only the possibility to have faster polymerization rates, but also polymerization without hazardous solvents and radical initiators in many cases. These microfluidic reactors or a chain of such reactors (in case of synthesis of multiblock copolymers or other complex macromolecules) could be parallelized to make production at large scale in a safe manner possible. Also, it is possible to control the polymerization in situ, using a variety of analytical tools without interfering with the reaction. Besides large-scale polymer synthesis, RAFT polymerizations are also a very promising way to functionalize surfaces at specific sites to bind to a tailored RAFT agent. Depending on the system, water-based RAFT polymerizations could be carried out, which do not affect a water-insoluble substrate. This will offer possibilities to fabricate functionalized surfaces, such as in membranes and enable the production of membranes with different surface functionality or pore properties based on one basic membrane. In biomedical applications, RAFT polymerizations will have potential in the future, as there are monomers with low or no toxicity that could be used to make biocompatible polymers. Such polymerizations could also be performed in a biological matrix. This will offer useful opportunities in areas such as tissue engineering.

Similar to other controlled radical polymerizations, and different from living anionic polymerization, a drawback of the controlled radical polymerizations is the existence of a dormant end group, which is not “dead” as in the case of a terminated anionic polymerization. This may lead to degeneration of polymer chains as a function of time, if no deactivation step is carried out, such as heating up the polymer. Nevertheless, the end-functional group could be converted into other functional groups offering further possibilities to introduce or remove certain functionalities at the chain end specifically.

Given the above-discussed points, we consider RAFT as the imminent method to prepare tailor made polymers, copolymers, and block copolymers of various topologies and functionalities

from vinyl monomers by (rather) facile and green synthesis paths. These materials will be scalable and would find their way in many high-tech applications.

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## Conflict of Interest

The authors declare no conflict of interest.

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