Controlled/living radical polymerization in aqueous media: homogeneous and heterogeneous systems

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Abstract

Controlled/living radical polymerizations carried out in the presence of water have been examined. These aqueous systems include both the homogeneous solutions and the various heterogeneous media, namely dispersion, suspension, emulsion and miniemulsion. Among them, the most common methods allowing control of the radical polymerization, such as nitroxide-mediated polymerization, atom transfer radical polymerization and reversible transfer, are presented in detail. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Since Staudinger [1] proposed the concept of a chain polymerization and the basic structure of a polymer molecule eight decades ago, polymer science and technology has experienced an immense development that has revolutionized the look of the world and the life of human beings. Numerous polymeric materials have been created thanks to continuous progress in understanding the fundamentals of polymerization. One of the greatest contributions to this field from synthetic polymer chemists is the development of living polymerization methodology, which allows the preparation of macromolecules with the maximum degree of structural and compositional homogeneity. As a consequence, well-defined polymers with precise molar masses, compositions, topologies and functionalities can be tailor-made. This is a significant step toward the ultimate goal of polymer synthesis, when the design of novel materials is only limited by the imagination of human beings.

The terms of 'living polymerization' and 'living polymers' were introduced by Szwarc [2] in 1956, although prior to his classical work, Ziegler [3] and Flory [4] also described similar concepts. By definition, a living polymerization is a chain polymerization that proceeds without the occurrence of irreversible chain breaking processes, i.e. chain transfer and termination. For nearly 30 years after Szwarc reported his insightful work, living polymerization of vinyl monomers had been restricted to anionic polymerization systems. But in 1960s and 1970s, several cationic ring-opening polymerizations of heterocyclic monomers were found to proceed with most undesirable side reactions virtually absent [5–7]. It was discovered that if a dynamic equilibrium between an active and dormant species was formed, it allowed for fine tuning of the polymerization of tetrahydrofuran [8,9]. This concept of dynamic equilibrium was eventually extended to vinyl monomers in early 1980s, triggering the

Nomenclature

$(\tilde{n})$ average number of radicals per particle

$[I]$ initiator concentration

$[I]_0$ initial initiator concentration

$[M]$ monomer concentration

$[M]_0$ initial monomer concentration

AA   acrylic acid

ACPA   see V-501

AEROSOL-MA80   sodium dihexyl sulfosuccinate

AIBN   azobisisobutyronitrile

AN   acrylonitrile

ATRP   atom transfer radical polymerization

BPMOA   *N*,*N*-bis(2-pyridylmethyl)octylamine

BPMODA   *N*,*N*-bis(2-pyridylmethyl)octadecylamine

BPO   benzoyl peroxide

Bpy   2,2$'$-bipyridine

Brij98 $C_{12}H_{25}-(OCH_2CH_2)_{20}-OH$

CD   cyclodextrine

CLP   controlled/living polymerization

cmc   critical micelle concentration

CRP   controlled/living radical polymerization

CSA   camphorsulfonic acid

CTAB   cetyl trimethyl ammonium bromide

dAbpy   4,4$'$-dialkyl-2,2$'$-bipyridine, alkyl: mixture of pentyl and 5-nonyl

DCP   dicumyl peroxide

dHDbpy   4,4$'$-di(9-heptadecyl)-2,2$'$-bipyridine

DMAEMA   2-(dimethylamino)ethyl methacrylate

dNbpy   4,4-di(5-nonyl)-2,2$'$-bipyridine

DOWFAX8390   dihexadecyl disulfonated diphenyloxide disodium salt (Dow Chemical)

DP_n number average degree of polymerization

DP_w weight average degree of polymerization

DRI   differential refractive index detection

dTbpy   4,4$'$-di-*t*-butyl-2.2$'$-bipyridine

EB*i*B   ethyl 2-bromoisobutyrate

Forafac $C_8F_{17}CH_2CH_2COO^-K^+$ (Atofina)

HEA   2-hydroxyethyl acrylate

HEMA   2-hydroxyethyl methacrylate

HLB   hydrophilic-lipophilic balance

HV25   nonionic poly(ethylene oxide) ($DP_n = 25$) nonyl phenol surfactant (Witco)

$I_p = DP_w/DP_n = M_w/M_n$ polydispersity index

K activation/deactivation equilibrium constant (dimension depends on the system)

k_a rate constant of activation (dimension depends on the system)

k_d rate constant of deactivation (l mol^{-1} s^{-1})
k_p rate constant of propagation (l mol^{-1} s^{-1})
Kraton copolymer of ethylene and butylene
k_t rate constant of irreversible termination (l mol^{-1} s^{-1})
k_{tr} rate constant of transfer (l mol^{-1} s^{-1})
MALDI-TOF MS matrix-assisted laser desorption/ionisation — time-of-flight mass spectrometry
Me$_6$TREN tris[2-(dimethylamino)ethyl]amine
MEMA 2-(*N*-morpholino)ethyl methacrylate
MMA   methyl methacrylate
MMD   molar mass distribution
M_n number average molar mass (g mol^{-1})
M_w weight average molar mass (g mol^{-1})
N_A Avogadro's number
NaMA sodium methacrylate
NaSS   sodium styrenesulfonate
NaVBA sodium vinylbenzoate
n-BA   *n*-butyl acrylate
n-BMA *n*-butyl methacrylate
NMP   nitroxide-mediated radical polymerization
NMR   nuclear magnetic resonance
OEGMA oligo(ethylene glycol) methacrylate
OP-10 polyoxyethylene nonyl phenyl ether
P(NaSS) poly(sodium styrenesulfonate)
P(*n*-BA) poly(*n*-butyl acrylate)
P(*n*-BMA) poly(*n*-butyl methacrylate)
PMDETA *N*,*N*,*N'*,*N''*,*N''*-pentamethyldiethylenetriamine
PMMA poly(methyl methacrylate)
PRE   persistent radical effect
PS   polystyrene
PVA   poly(vinyl alcohol)
PVP   poly(*N*-vinylpyrrolidone)
RAFT   reversible addition-fragmentation transfer
R_p rate of propagation (mol l^{-1} s^{-1})
S   styrene
SDBS   sodium dodecylbenzene sulfonate
SDS   sodium dodecyl sulfate
SEC   size exclusion chromatography
SFRP   stable free-radical polymerization
SG1   *N-tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide
TEMPO 2,2,6,6-tetramethyl piperidinyl-1-oxy
tNtpy   4,4',4''-tris(5-nonyl)-2,2':6'',2-terpyridine
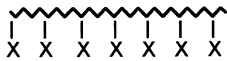Tween 80 sorbitane monooleate poly(ethylene glycol)
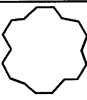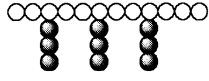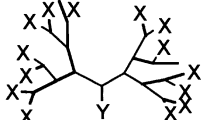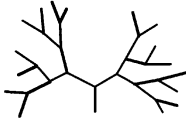
UV   ultra-violet detection
V-40   1,1′-azobis-(1-cyclohexane carbonitrile)
V-50   2,2′-azobis(2-methylpropionamidine) dihydrochloride
V-501   4,4′-azobis(4-cyanovaleric acid) (also called ACPA: 4,4′-azobis(4-cyanopentanoic acid))
VA-0442,2′-azobis[2-(2-dimidazolin-2-yl) propane] dihydrochloride
VA-0862,2′-azobis[2-methyl-*N*-(2-hydroxyethyl) propionamide]
x   monomer conversion

breakthrough discovery of cationic vinyl polymerizations that proceeded in a controlled fashion under certain restrictive conditions [10–12]. Since then, extensive investigations of various CLP mechanisms has been conducted [13,14]. The late 1980s and the entire 1990s witnessed a rapid expansion of the scope of CLP. To date, the major classes of chain polymerization, i.e. anionic [15–17], cationic [18,19], ring-opening metathesis [20,21], coordination [22] and radical polymerization [23,24], can become living or controlled under appropriate conditions. However, most of these polymerization techniques are not exempt from chain transfer or termination reactions. To differentiate these imperfect polymerizations from the ideal living polymerization, terms such as *controlled*, '*living*', *pseudo-living, quasi-living* and many others have been used in literature, which initiated an on going debate over nomenclature [25,26]. Until a uniform terminology is accepted, we will use the term 'controlled/living polymerization' to describe all the polymerization processes from which polymers with predetermined molar masses, low polydispersities and high chain-end functionalities can be obtained. The significance of controlled/living polymerization as a synthetic tool is widely recognized. With polymers having uniform and predictable chain length readily available, it provides the best opportunity to control the bulk properties by variations at a molecular level. Furthermore, a variety of novel polymer materials with predetermined composition, topology and functionality, as illustrated in Table 1, can be created.

Among the numerous polymerization techniques, free-radical polymerization is a widely used process from the viewpoint of industrial production and applications [27]. This technique is relatively easy to perform since it does not require stringent purification of the reagents, except the elimination of the dissolved oxygen. It generally leads to high molar mass polymers under relatively mild conditions. Polymerization temperatures can be usually set between room temperature and about 200°C. Many different processes can be applied such as bulk, solution, suspension or emulsion polymerizations. Moreover, a wide range of functional monomers can be polymerized by a radical mechanism and copolymerizations have provided a great variety of random copolymers with many structures and properties. The main limitations of radical polymerization are the lack of control over the molar mass, the molar mass distribution, the end-functionalities and the macromolecular architecture. This is caused by the unavoidable fast radical–radical termination reactions. Mainly for that reason, the recent emergence of many so-called 'living' or controlled radical polymerization (CRP) processes has opened a new area in this old polymerization method that had witnessed relatively small progress in the previous years.

Until now, CRP has been predominantly studied in homogeneous organic systems, i.e. bulk or solution polymerizations. With the rapid development of understanding of those controlled systems, one of the biggest present concerns is: can these methods be extended to the aqueous media? Indeed, the polymerizations carried out in aqueous media are receiving more and more attention and, in contrast to

Table 1
Polymers available by controlled/living polymerization techniques

Compositions	Topologies	Functionalities
Homopolymer	Linear	Side-functional groups
Periodic copolymer	Comb/brush	End-functional groups
Block copolymer	Star	Telechelic polymers
Random copolymer	Ladder	Site-specific functional polymers
Gradient copolymer	Cyclic	Macromonomers
Graft copolymer	Network/ Crosslinked	Multifunctional polymers
	Dendritic/ Hyperbranched	

the numerous controlled polymerization methods employed in organic media, aqueous polymerization is mainly focused on radical polymerization. Among the most important factors contributing to this trend are increased environmental concern and a sharp growth of pharmaceutical and medical applications for hydrophilic polymers. Another important reason is that in industry radical polymerization is widely performed in aqueous dispersed systems, and particularly, in emulsion polymerization. This technique offers many invaluable practical advantages over homogeneous polymerizations, such as the absence of volatile organic compounds, better control of heat transfer, and the possibility to reach high molar mass polymers with high conversion and a faster rate of polymerization than in bulk or solution systems. The

final water suspension of stable polymer particles (also called a latex) is easy to handle owing to a generally low viscosity, even at high solid content, and can be used directly for coating applications or as a dried polymer after removal of water.

Thus, it is obvious that a substantial progress in controlled free-radical polymerization would be achieved if this technique can be applied to either homogeneous or heterogeneous aqueous systems. The first, and main goal is to control the characteristics of the polymer in terms of molar mass, molar mass distribution, architecture, and function. The rapid and very recent development of this domain will be illustrated in this review article. Polymerizations in aqueous solution will be considered first, including the scope and limitations of the existing CRP systems. Then, the attention of the article will be focused on the application of CRP in aqueous dispersed media using the suspension, dispersion, emulsion and miniemulsion polymerization processes. The kinetics of polymerization and control over the polymer characteristics will be examined for each CRP technique used and a comparison with homogeneous polymerization will be made. The repercussions of CRP chemistry on the very mechanism of the heterogeneous polymerization systems will also be addressed with special attention.

2. General aspects of conventional radical polymerization in aqueous media

2.1. Homogeneous polymerization

One essential requirement for aqueous solution polymerization is that the monomer and the formed polymer should be sufficiently water-soluble. Some typical water-soluble monomers are listed in Table 2.

Various radical initiation techniques, including thermal, redox, photochemical, electrochemical and radiolysis, have been employed for aqueous solution polymerizations [28]. Basically, the polymerization follows the same principles as those in the organic systems. There are, however, a few unique features for aqueous solution polymerization. In particular, it is often observed that monomers with ionizable pendant groups polymerize much faster in aqueous solutions than in bulk or in the presence of organic solvents. The overall rate of polymerization for such monomers increases by 1.5–2 orders of magnitude in aqueous solution. This kinetic variance is caused by a remarkably enhanced k_p/k_t ratio, which is generally attributed to a number of factors: (i) solvation of the monomer molecules, particularly via hydrogen bond formation with water, alters the electron density in the double bond of the monomer and hence its reactivity [29]; (ii) increased ionic dissociation of the pendant group produces greater electrostatic repulsion between the two growing radicals [30]; (iii) the existence of polymer–water interactions that produce a strongly bound hydration shell also helps to protect the propagating radical center from termination [31]. Therefore, changes of pH and ionic strength exert a pronounced influence on the polymerization of these basic and acidic monomers. One of the consequences is that in copolymerization the reactivity ratios of two monomers, when one or both are ionizable monomers, vary with the degree of ionization. In contrast, monomers containing neutral hydroxy groups are less sensitive to pH and ionic strength variations. Such a stability of the water-structuring center makes the hydrogels derived from these monomers, such as 2-hydroxyalkyl (meth)acrylates, very attractive for biomedical applications.

2.2. Heterogeneous polymerizations

Although aqueous solution polymerizations are of considerable interest, the number of water-soluble

Table 2
Typical water-soluble monomers

Monomers with acidic functions	Monomers with basic functions
Acrylic acid	Acrylamide
Methacrylic acid	Methacrylamide
Itaconic acid	*N*-hydroxymethylacrylamide
Allenesulfonic acid	*N*,*N*-dimethylacrylamide
Ethylenesulfonic acid	*N*-isopropylacrylamide
Styrenesulfonic acid	*N*-acetamidoacrylamide
2-Sulfoethyl methacrylate	2-Aminoethyl methacrylate
	N,*N*-dimethylaminoethyl methacrylate
Monomers with heterocyclic functions	**Monomers with neutral hydroxyl functions**
N-vinyl-2-pyrrolidone	Allyl alcohol
2-Vinylpyridine	2-Hydroxyethyl acrylate
3-Vinylpyridine	2-Hydroxyethyl methacrylate (polymer is not water soluble)
4-Vinylpyridine	2-Hydroxypropyl methacrylate (polymer is not water soluble)
4-Methylenehydantoin	
4-Vinyl-3-morpholine	
1-Vinyl-2-methyl-2-imidazoline	

monomers available limits their applications. Heterogeneous polymerization processes, on the other hand, are applicable to a much wider range of monomers. Additionally, they offer many invaluable practical advantages in industrial applications. Presently, heterogeneous radical polymerization in aqueous media is one of the most important industrial processes for the production of synthetic polymers. A variety of systems can be used (Table 3). They differ from each other in the initial state of the polymerization mixture, in the mechanism of particle formation, in the size of the final polymer particles and in the kinetics of polymerization. The details of these differences have been well reviewed in literature [32–34]. The following is a brief introduction to three systems that are most relevant to the focus of this review. *Suspension polymerization* is a fairly common technique for industrial applications. *Emulsion polymerization* is the most widespread process of heterogeneous polymerization in aqueous medium and has been particularly studied in academic laboratories for many years. Finally, *mini-emulsion polymerization* which can be regarded as a derivative of emulsion polymerization, leads to the same type of final latex but presents additional advantages concerning the mechanism and the kinetics.

2.2.1. Suspension polymerization [35,36]

A water insoluble monomer is dispersed in the continuous aqueous phase as liquid droplets by vigorous stirring. An oil soluble initiator is employed to initiate polymerization inside the monomer droplets. During the course of polymerization, coalescence of the monomer droplets and adhesion of the partially polymerized particles are hindered by the presence of a small amount of stabilizers which may be either water soluble polymers, such as poly(*N*-vinylpyrrolidone) and poly(vinyl alcohol-*co*-vinyl acetate), or insoluble inorganic salts such as talc, calcium and magnesium carbonates, silicates and phosphates. The stabilizer can improve the dispersion by increasing the viscosity of the aqueous phase, but most often it acts by forming a film at the droplet/particle surface, thus preventing coalescence by steric effects.

Table 3

The different types of heterogeneous polymerization systems (from Ref. [32]; reproduced by permission of Academic Press Ltd, London, UK)

Type	Typical particle radius	Droplet size	Initiator	Continuous phase	Discrete phase (particles)
Emulsion	50–300 nm	≈1–10 μm	Water-soluble	Water	Initially absent, monomer-swollen polymer particles form
Precipitation	50–300 nm	Monomer usually water-soluble	Water-soluble	Water	As in ordinary emulsion polymerization, but monomer does not swell polymer
Suspension	≥ 1 μm	≈1–10 μm	Oil-soluble	Water	Monomer + formed polymer in pre-existing droplets
Dispersion	≥ 1 μm		Oil-soluble	Organic (poor solvent for formed polymer)	Initially absent, monomer-swollen polymer particles form
Microemulsion	10–30 nm	≈10 nm	Water-soluble	Water	Monomer, co-surfactant + formed polymer
Inverse emulsion	10^2–10^3 nm	≈1–10 μm	Water- or oil-soluble	Oil	Monomer, water + formed polymer
Miniemulsion	30–100 nm	≈30 nm	Water-soluble	Water	Monomer, co-surfactant + formed polymer

The average number of radicals per particle ($\tilde{n}$) is on the order of 10^{2-6}, therefore each particle behaves as an isolated micro reactor and the kinetics resembles that of bulk polymerization (or solution polymerization if the monomer phase contains diluent). Consequently, the droplet size and the amount of stabilizer do not affect the polymerization rate. The continuous aqueous phase serves only to decrease the viscosity and to dissipate heat generated by the polymerization. The diameters of the particles obtained from suspension polymerization are usually in the range of 20–2000 μm, depending on the stirring speed, volume ratio of the monomer to water, concentration of the stabilizer, the viscosity of both phases and the design of the reaction vessel. With a properly designed reactor and a well-stabilized suspension, monodisperse particles can be produced in agreement with theoretical predictions.

Another important property, one that is directly related to the target application, is the surface and bulk morphology of the individual particles. Particles with the polymer soluble (or swellable) in its own monomer have a smooth surface and a relatively homogeneous texture, such as polystyrene and poly(methyl methacrylate). However when the polymer is not soluble (or swellable) in its own monomer, the particles will have a rough surface and a porous morphology, like poly(vinyl chloride) and polyacrylonitrile. Crosslinked polystyrene beads with controlled degree of porosity and controlled pore structure are obtained by suspension polymerization using a diluent that properly dissolves the styrene and divinylbenzene comonomers but that is a poor swelling agent for the copolymer. These beads are of particular interest in the production of ion exchange resins and polymer supports.

Some typical polymers produced by suspension polymerization include polystyrene, poly(vinyl chloride), polyacrylates, poly(vinyl acetate) and their copolymers.

2.2.2. Emulsion polymerization [32,37,38]

In contrast to suspension polymerization, emulsion polymerization usually leads to particles with

submicron size that remain suspended in the aqueous medium, thus forming the so-called latex. A typical batch emulsion polymerization starts with water, hydrophobic monomer(s), surfactant and a water-soluble initiator, all the ingredients being incorporated at the beginning of the reaction. When compared with suspension polymerization, two ingredients are different. First, the stabilizer used to impart colloidal stability is a surface active agent (surfactant or emulsifier) composed of both hydrophilic and hydrophobic parts. It adsorbs at the interfaces and provides stabilization by either electrostatic effect (anionic and cationic surfactants), steric effect (nonionic surfactants) or both (polyelectrolytes). When its concentration is above the critical micelle concentration (cmc) it forms micelles, the core of which is swollen by the monomer. Second, the initiator is water-soluble. In the initial mixture of a batch emulsion polymerization the monomer is partitioned between three phases (at least two, when no micelle is present): the large monomer droplets (diameter > 1 μm) formed by stirring and stabilized by the surfactant adsorbed at the interface; the continuous water-phase (saturation concentration) which also dissolves the initiator and free surfactant molecules; the micelles (when [surfactant] $>$ cmc). As a result of the water-soluble character of the initiator, the radicals are produced in the continuous aqueous phase in which polymerization starts. This is an important feature of emulsion polymerization that affects both the process of particle formation and the kinetics of polymerization. Indeed, the monomer is not polymerized in the droplets but in particles, which are created early in the process when initiation starts. The droplets act only as monomer reservoirs, and provide monomer(s) to the polymerization loci via diffusion of the monomer molecules through the water-phase. Stabilization of the new particles is ensured by a redistribution of the surfactant between the various interfaces.

Formation of the particles follows complex nucleation mechanisms that can be either micellar or homogeneous depending on the surfactant concentration and the water-solubility of the monomer(s) [32,37]. In both cases, the primary radicals formed by decomposition of the initiator in the aqueous phase add a few monomer units, forming oligoradicals, which lose water-solubility upon further propagation. It is now well accepted that the final particles originate from these oligoradicals generated in the water-phase [32]. An accurate understanding of the particle nucleation mechanisms is not only interesting for fundamental knowledge, but is particularly useful to predict the final number of particles, N_p, to quantify the effect of the various parameters such as the type of surfactant and its concentration, the type of initiator and its concentration, the nature of the monomer(s), the temperature etc, and to predict the occurrence of continuous or secondary nucleation.

The unique feature of kinetics in emulsion polymerization results from the compartmentalization of the propagating radicals within separate particles. The polymerization kinetics is not simply depicted by initiation, propagation and termination as in a homogeneous radical polymerization. The situation is complicated by the existence of at least two phases for these events to take place. Continuous entry of oligoradicals from the water-phase into the particles, exit of propagating radicals out of the particles via transfer reactions to small molecules, transportation of monomer, etc. all have to be considered.

Emulsion polymerization kinetics is usually characterized by three intervals. *Interval I* is the particle formation stage, represented by the increase in both the number of particles and the polymerization rate. The end of *interval I* corresponds to stabilization of the value of N_p, which usually corresponds to the disappearance of micelles. The duration of *interval I* varies within the range of 2–10% conversion, depending on the type and the concentration of surfactants, the initiation rate, the degree of water solubility of monomers, etc. Polymerizations starting with *interval I* are called 'ab initio emulsion polymerizations'. To have a system with a perfectly known number of particles, it is often preferable to bypass *interval I* by starting an emulsion polymerization with preformed polymer particles. Such

polymerizations beginning directly with *interval II* are called 'seeded emulsion polymerizations'. *Interval II* corresponds to the main step of particle growth: propagation is permitted by the capture of oligoradicals generated in the aqueous phase and polymerized monomer is continuously replaced by new monomer molecules supplied from the droplets via diffusion through the water-phase. During *interval II*, both the number of particles and the monomer concentration inside the particles, $[M]_p$, remain approximately constant (providing the particle diameter is not too small, i.e. larger than 20 nm). Since monomer droplets are still present, the value of $[M]_p$ corresponds to the maximum concentration of monomer in a polymer particle. This maximum concentration, $[M]_p^{max}$, is the result of thermodynamic considerations and corresponds to the balance between opposing effects: decrease of the surface free energy by decreasing the surface area (i.e. the particle volume) and decrease of the free energy of mixing of polymer and monomer which tends to increase the particle volume (Morton equation [39]). Accordingly, the polymerization rate is relatively constant, as it reads:

$$R_p = k_p[M]_p N_p \tilde{n}/N_A \tag{1}$$

with k_p, the rate constant of propagation, $\tilde{n}$ the average number of radicals per particle and N_A, the Avogadro's number. Propagation thus obeys a zero internal order with respect to monomer concentration during *interval II* and not a first order as observed in homogeneous polymerizations and suspension polymerization. *Interval II* may extend from 5–10% to 30–70% conversion, ending with the disappearance of the monomer droplets. *Interval III* commences with a reduction of the polymerization rate, resulting from decreasing monomer concentration inside the polymer particles. Thus, a first-order kinetics is expected in this final stage until a gel effect takes over, and the polymerization rate can start to increase again. The various phases presented in each of the three intervals and the corresponding kinetics are depicted in Fig. 1.

Many theoretical descriptions concerning the kinetics of emulsion polymerization have been developed over the years [40–42]. The most commonly applied one was established by Smith and Ewart [40] who classified all emulsion polymerizations into three cases:

(i) Case 1, $\tilde{n} \ll 0.5$. This is applicable when radicals easily escape from the particles (i.e. significant transfer reaction) without re-entry (i.e. termination in aqueous phase), such as vinyl acetate and vinyl chloride radicals that have high chain-transfer constant to monomer. In this case, the polymerization rate is little affected by the number of particles.

(ii) Case 2, $\tilde{n} = 0.5$. This case is also referred to as the 'zero-one' system, and is applicable to most emulsion polymerizations. It corresponds to a situation where termination within the particles is instantaneous, the exit of radicals is negligible, and therefore the particles contain either 1 or 0 radicals. The polymerization rate shows strong dependence on the number of particles, hence the surfactant and initiator concentrations are of critical importance.

(iii) Case 3, $\tilde{n} \gg 1$. This occurs when the particle size is sufficiently large or the viscosity inside the particle is sufficiently high (at high conversion), so that two or more radicals can coexist within a single particle without instantaneous termination. This case leads to 'pseudo-bulk' kinetics, which is indistinguishable from that of the equivalent homogeneous system. It should be mentioned that pseudo-bulk kinetics can also be observed with $\tilde{n} \leq 0.5$ under certain circumstances.

The molar mass of the polymers obtained from emulsion polymerization (usually in the order of 10^6 g/mol) are significantly larger than those obtained from bulk polymerization, due to a longer lifetime of the propagating radicals resulting from compartmentalization. This is basically due to the fact that it is not the rate of chain termination that determines the lifetime of each growing chain, but the rate of entry of
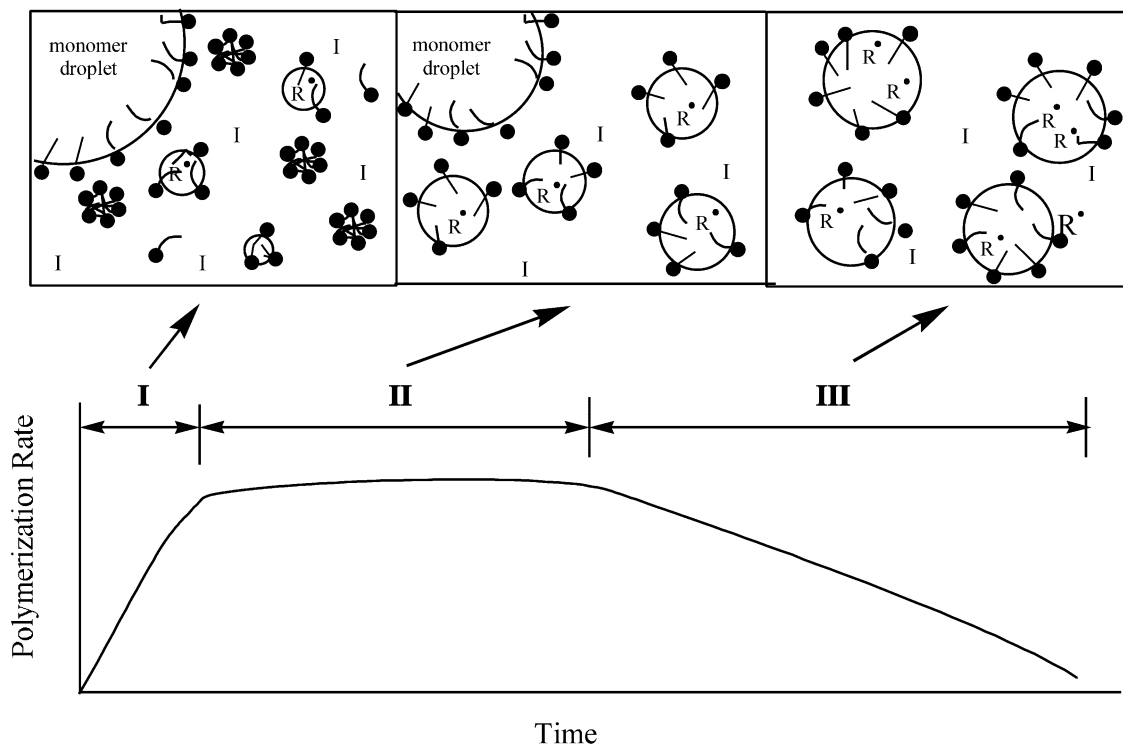
Fig. 1. The three intervals of an ab initio emulsion polymerization and their kinetics.

new radicals into the particles. It is therefore possible in an emulsion polymerization to increase simultaneously the molar mass and the polymerization rate by increasing N_p, whereas in bulk or in suspension polymerization, the molar mass decreases when the rate is increased (via an increase in the initiator concentration). The molar mass distribution is predicted to be broader in general compared with homogeneous systems.

Emulsion polymerization has been the dominant process used for the synthesis of poly(vinyl acetate), poly(chloroprene), poly(acrylic ester) copolymers, and polydiene-based synthetic rubbers. It is also widely used for the polymerization of monomers such as methacrylic esters, vinyl chloride, acrylamide, fluorinated ethylenes, etc. Various processes, other than a simple batch system, can be easily used, and offer advantages for the control of the polymerization (kinetics, number of particles, heat removal, stability, copolymer composition etc.). For instance, a semi-batch process with starved monomer feed allows control of the propagation rate and of copolymer composition, avoiding the composition drift observed in batch systems. A similar process is also used to create particles with unique morphologies, the core-shell structure being the most common. Numerous applications exist for polymers prepared in emulsion systems and their number will probably increase in the future owing to environmental regulations aiming at limiting the use of volatile organic compounds in the industry.

2.2.3. Miniemulsion polymerization [43,44]

Two possible loci of particle formation were identified in emulsion polymerization: the micelles

(micellar nucleation) and the water phase (homogeneous nucleation). Nucleation in the monomer droplets was not considered because of their large size and small number, resulting in a very low probability for capture of the water-phase-generated oligoradicals. Nevertheless, if droplet size becomes small enough, they can compete for the radical entry and become the primary locus of the polymerization. Ideally, such a concept as called *miniemulsion* aims at producing a latex which is a 1:1 copy of the original droplets thereby achieving a direct control over the number of particles, avoiding the complex nucleation step existing in conventional emulsion polymerization. This is accomplished by reducing the monomer droplets to submicronic size (50–500 nm) using a strong shear force such as ultrasonication. Enhanced stabilization of these tiny monomer droplets comes from the addition of a so-called 'co-surfactant' (such as hexadecanol) or a ultra hydrophobe (such as hexadecane). The function of the long-chain alcohol can be twofold: limiting the coalescence by forming a barrier at the surface of the droplets by combination with the surfactant and/or preventing the diffusion of monomer from small to large particles (Ostwald ripening) by building up an osmotic pressure within the monomer droplets. The ultra hydrophobe behaves exclusively according to the second mechanism. Other hydrophobes, such as decahydronaphtaline, octamethylcyclotetrasiloxane, tetraethylsilane, polymers, etc can be used [45]. Particularly, the presence of a few percent of added polymer has been shown to enhance nucleation and produce a latex particle from every monomer droplet [46–48]. The choice of a suitable hydrophobe is therefore a key issue for successful miniemulsion polymerization.

Technically, miniemulsion polymerization offers some unique advantages over an emulsion polymerization. The monomer droplets are the principal locus of polymerization, thus the nucleation step is not as complex as in emulsion polymerization, and the system is simplified to two phases throughout the polymerization process (a water phase and monomer/polymer particles). Micellar nucleation can be avoided because most miniemulsion polymerizations are carried out with a surfactant concentration below the critical micelle concentration. Homogeneous nucleation is still possible depending on the monomer, but can be limited by adjusting kinetic parameters to favor the capture of the oligoradicals before they reach their critical size. Both water-soluble and oil-soluble initiators can be used to generate stable latexes with small particles (50–500 nm). This process is especially useful for polymerizations involving a very water insoluble ingredient, which would transport slowly through the aqueous phase in an emulsion polymerization [49]. It is also a very powerful process for encapsulating various inert materials (such as dye or pigment) [50,51] in the final particles or for conducting copolymerizations of monomers with remarkably different water solubilities. In the final case, increased control over the copolymer composition can be achieved, since the composition is not affected by variations other than monomer reactivities.

An ideal miniemulsion polymerization (i.e. one in which every droplet is nucleated and transformed into a polymer particle, behaving as an individual nanoreactor), displays different kinetics from an emulsion polymerization, as studied for styrene by Bechthold et al. [52]. A particle formation (droplet nucleation) stage is initially observed accompanied by an increasing polymerization rate R_p and increasing $\tilde{n}$ (*interval I*). After the polymerization rate reaches a maximum and $\tilde{n}$ reaches a value of 0.5 this period is immediately followed by *interval III* (same definition as in emulsion polymerization) with a steadily decreasing rate and a constant value of $\tilde{n} = 0.5$. During this stage, the polymerization follows a first order kinetics with respect to monomer as in bulk, solution or suspension polymerizations. *Interval II* in emulsion polymerization, characterized by a constant polymerization rate, is missing in the ideal miniemulsion system. This is because the transport of monomer is negligible: there is no period of constant monomer concentration in the polymerization locus but an exponential decay. A last stage with

increasing R_p and $\tilde{n}$ is finally observed, typical of the gel effect. The polymerization rate is influenced by the surfactant concentration, which affects N_p, but not the initiator concentration, because the latter does not affect the number of particles.

Research on miniemulsion polymerization has been conducted for styrene, butyl acrylate, methyl methacrylate, vinyl acetate, vinyl 2-ethylhexanoate, as well as a number of copolymerization systems [43].

3. Controlled/living free-radical polymerization methods

Conventional radical polymerizations carried out in aqueous media encounter the same problems as their counterparts in organic media do, i.e. numerous chain breaking reactions occur, increasing the heterogeneity of the polymers and preventing a precise control of the polymer properties. Taking emulsion polymerization as an example, regulation of the molar mass is mainly achieved by adding chain transfer agents. The composition of a copolymer is manipulated to a large degree through polymerization processing. These rough strategies, however, do not satisfy the ultimate goal of tuning the polymer properties at the molecular level. Therefore, a more comprehensive approach to gain control over chain growth in aqueous media is needed, and the controlled/living radical polymerization techniques described in the following sections seem to be most promising routes.

3.1. General features and experimental criteria for controlled/living polymerization

Before various methods of controlled/living radical polymerization are described, it is necessary to take a brief look at the criteria that can be used to identify a controlled/living polymerization.

3.1.1. Feature 1: internal first-order kinetics with respect to monomer

The logarithmic monomer concentration, $\ln([M]_0/[M])$, is a linear function with time, provided that initiation is fast. This is due to the lack of termination, so that the concentration of propagating radical ($[P^{\cdot}]$) is constant. It should also be noted that in conventional radical polymerizations where termination occurs readily, pseudo first order kinetics could also be observed. The origin of the straight line, however, is that the loss of radicals by termination is compensated by continuous generation of radicals, with a rate equal to that of termination, so that the concentration of radicals remains constant (classical steady state). The main difference between conventional and controlled radical polymerizations is that the concentration of radicals in the latter case is established by an equilibrium between the activation and deactivation processes, allowing the rate of initiation (R_i) to be far greater than the rate of propagation (R_p). Regardless, the semilogarithmic plot is not sensitive to chain transfer process or slow exchange between different active species, as far as they do not affect the number of the active propagating species.

3.1.2. Feature 2: linear growth of degree of polymerization (DP_n) with conversion

The number average degree of polymerization is a linear function of monomer conversion.

$$\mathrm{DP_n} = \frac{\Delta[M]}{[I]_0} = \frac{[M]_0}{[I]_0} \text{ conversion} \tag{2}$$

This result comes from a constant number of chains throughout the polymerization, which requires the

following two conditions: (i) the initiation should be sufficiently fast so that all chains start to grow simultaneously; (ii) no chain transfer occurs to increase the total number of chains. Importantly, the evolution of molar masses is not very sensitive to chain termination, since the number of chains remains unchanged. Only when coupling reaction plays a significant role is the effect of termination observable by progressive reduction of the number of chains.

Features 1 and 2 can be combined into a single equation: [53]

$$\ln\left(1 - \frac{[I]_0}{[M]_0}DP_n\right) = -k_p \cdot [I]_0 \cdot t \tag{3}$$

The linearity of a plot of the left-hand side of Eq. (3) vs. time, t, becomes a sufficient criterion to exclude both chain termination and transfer reactions.

3.1.3. Feature 3: narrow molar mass distribution

Although this feature is desirable, it is not necessarily the result from a living polymerization, which requires only the absence of chain transfer and termination, but ignores the rate of initiation, exchange and depropagation. Substantial studies [15,18,54–56] indicate that in order to obtain a polymer with a narrow molar mass distribution, each of the following five requirements should be fulfilled. (i) The rate of initiation is at least comparable with the rate of propagation. This condition allows the simultaneous growth of all the polymer chains. (ii) The exchange between species of different reactivities is faster than propagation. This condition ensures that all the active chain termini are equally susceptible to reaction with monomer for a uniform growth. (iii) There must be negligible chain transfer or termination. (iv) The rate of depropagation is substantially lower than propagation. This guarantees that the polymerization is irreversible. (v) The system is homogeneous and mixing is sufficiently fast. Therefore all active centers are introduced at the onset of the polymerization.

Under the above conditions, a polymer with Poisson distribution may be formed, as quantified in Eq. (4), where DP_w (M_w) and DP_n (M_n) represent the weight and number average degree of polymerization (molar mass), respectively.

$$\frac{DP_w}{DP_n} = \frac{M_w}{M_n} = 1 + \frac{DP_n}{(DP_n + 1)^2} \cong 1 + \frac{1}{DP_n} \tag{4}$$

According to Eq. (4), polydispersity index ($I_p = DP_w/DP_n = M_w/M_n$) decreases with increasing molar mass. A polymerization that satisfies all five prerequisites listed above is expected to produce a polymer with a polydispersity less than 1.1 for DP_n greater than 10. In case of imperfect polymerizations such as those with slow exchange rate or with termination and transfer reactions, the polydispersity deviates from Poisson distribution, the dependency with conversion may be used as a mechanistic criterion to distinguish between various possible mechanisms [57].

3.1.4. Feature 4: long-lived polymer chains

This is a consequence of negligible chain transfer and termination in the polymerization. Hence, all the chains retain their capabilities of further growth after the full consumption of the monomer. Propagation resumes upon the introduction of additional monomer. This is a unique feature that allows the preparation of block copolymers by sequential monomer addition.

In radical polymerization, termination between radicals is a diffusion-controlled process, and hence reduction of its impact presents the biggest challenge to achieve the above controlled/living features.

While it is impossible to avoid termination completely, there are a number of ways to reduce the proportion of dead chains. The strategy is to introduce a dormant species that does not propagate by itself, but may convert reversibly to a radical and propagate. As long as the exchange between the dormant species and active radicals is rapid, each dormant species has an equal probability of being activated. Hence, both dormant species and free radicals should contribute equally to the total number of propagating chains. The instantaneous proportion of terminated chains can then be expressed in Eq. (5).

$$
\text{termination \%} = \frac{[\text{terminated radicals}]}{[\text{terminated radicals}] + [\text{growing chains}]}
$$

$$
= \frac{[\text{terminated radical}]}{[\text{terminated radicals}] + [\text{radicals}] + [\text{dormant species}]}
$$

(5)

According to this equation, the larger the proportion of the dormant species, the lower the percentage of terminated radicals. In conventional radical polymerization, the concentration of the dormant species can be regarded as zero. Hence each terminated radical makes a significant contribution to the fraction of the dead chains (which is very close to 1). When the concentration of the dormant species predominates, the overall impact of termination is largely suppressed even if the absolute number of terminated radicals remains the same as in the conventional radical polymerization. This is an important conclusion, indicating that well-controlled polymerization can be achieved without sacrifice of polymerization rate. Similarly, the contribution of chain transfer is also dramatically suppressed.

Among many available controlled/living radical polymerization methods [23,24], three approaches are presently successful and extensively studied.

3.2. Stable free radical polymerization (SFRP)

The first presented technique is to use a stable radical to couple with the active radical and reversibly form a dormant covalent species (Fig. 2).

This method is often called the stable free radical polymerization (SFRP) in literature. The stable radicals used include various nitroxides [58,59], triazolinyl radicals [60], dithiocarbamates [61], trityl [62,63] and benzhydryl derivatives [64], and organometallic species [65,66]. The nitroxide mediated polymerization (NMP) is usually more efficient than others are [23,24]. Cyclic nitroxides were initially used, the most common being TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy), however, they were only efficient in the high temperature polymerization of styrene. Quite recently, NMP has witnessed an important advance with the development of a new generation of acyclic nitroxides bearing a hydrogen

$$
\text{PX} \quad \underset{k_d}{\overset{k_a}{\rightleftharpoons}} \quad \text{P}^\bullet \quad + \quad \text{X}^\bullet
$$
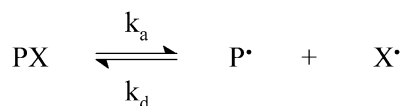
$$
\text{Equilibrium constant:} \quad K = \frac{k_a}{k_d} = \frac{[\text{P}^\bullet][\text{X}^\bullet]}{[\text{PX}]}
$$

Fig. 2. Activation/deactivation equilibrium in SFRP.

atom on the α-carbon. These novel nitroxides are able to control the polymerization not only of styrene at a lower temperature than the traditional nitroxides, but also of alkyl acrylates, acrylamides, and dienes [67–76]. This allows one to prepare complex copolymer architectures with blocks of different nature [74,77,78]. The polymerization can be carried out using either a unimolecular alkoxamine initiator (monocomponent system) [79] or a combination of a conventional radical initiator and a nitroxide radical (bicomponent system) [59].

3.3. Atom transfer radical polymerization (ATRP)

The second technique is a catalyzed reversible redox process (Fig. 3).

Control over the polymerization is realized based on the same principle as in SFRP. Since both activation and deactivation of the radicals involve an atom transfer reaction, this method was termed atom transfer radical polymerization (ATRP). Ru [80–82], Cu [83–88], Fe [89,90], Ni [91–93], and other transition metal complexes [94–97] are used as the catalysts. A variety of monomers can be polymerized using ATRP, ranging from styrenes, (meth)acrylates, acrylonitrile, (meth)acrylamides to methacrylic acid and includes some water soluble monomers such as 4-vinylpyridine [98–101]. Compared with SFRP, the equilibrium constant of ATRP is generally larger by an order of magnitude, and is more easily adjusted by choosing different initiator, transition metal and ligand. The larger equilibrium constant indicates that faster polymerization rates and milder reaction conditions are attainable [102]. Another unique advantage of ATRP comes from the use of many commercially available initiators (P–X), which include various alkyl halides as well as any compound with a weak halogen–heteroatom bond, such as sulfonyl halides. They provide the initial polymers with simple halogen as the end groups, which can be easily converted to other useful functionalities [103,104]. Presently the main limitations of ATRP is the employment of relatively high amount of transition metal complex (0.1–1% in reaction mixture) that has to be removed from the final polymer. This situation, however, can potentially be improved by enhancing the efficiency of the catalyst [102,105].

ATRP can also be conducted in an alternative way, i.e. in starting the polymerization with a conventional radical initiator and a metal complex at the higher oxidation-state (i.e. going from right to left in Fig. 3). This process is called *reverse ATRP* [106].

In both SFRP and ATRP, the stationary concentration of radicals is established through a balance between rates of activation and deactivation, rather than a balance between rates of initiation and termination, as in conventional radical polymerization. The polymerization kinetics are controlled by a process called the persistent radical effect (PRE) [107–109]. A pseudo-equilibrium between the

$$PX \; + \; M_t^n/L \; \underset{k_d}{\overset{k_a}{\rightleftharpoons}} \; P^\bullet \; + \; X\,M_t^{n+1}/L$$
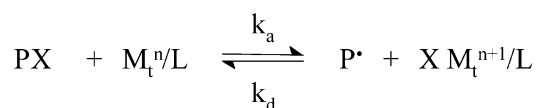
$$\text{Equilibrium constant:} \quad K = \frac{k_a}{k_d} = \frac{[P^\bullet][XM_t^{n+1}/L]}{[PX][M_t^n/L]}$$

Fig. 3. Activation/deactivation equilibrium in ATRP.

propagating radicals and the dormant species is established during the early stage of the polymerization, with the dormant species dominating. Because the propagating radicals can terminate with each other while the stable radical or the metal complex deactivator cannot, a continuous increase in the concentration of the latter is generally observed. It results in the self-regulation of the concentration of the active radicals in the presence of a deactivator. Thus, the value of the equilibrium constants in Figs. 2 and 3 is of great importance in manipulating the kinetics and the molar mass. The third controlled/living radical polymerization technique presented below, however, does not conform to this model.

3.4. Reversible/degenerative transfer reaction

In contrast to the previous techniques which behave according to a reversible termination reaction of the active macroradicals with small-molecule deactivators, the reversible transfer process is based on the reversible exchange of a labile end-group between a dormant chain and an active macroradical, as shown in Fig. 4. A direct exchange can take place in the same manner as in the case of degenerative iodine transfer, or the exchange can occur via an addition-fragmentation process.

The polymerization is made possible by the addition of a radical initiator in the system, which provides the propagating radicals as in a conventional radical process. The kinetics follows a classical steady state with slow initiation and fast terminations. The concept is not very different from telomerization except that the terminated chains act as a new species of transfer agent. Indeed, the transfer process takes place following two simultaneous steps: (i) transfer to the introduced chain transfer agent (transfer constant $C_{tr1} = k_{tr1}/k_p$), creating new chains with the fragments of the transfer agent at both ends; (ii) transfer to the newly created chains (exchange between an active and a dormant chain, transfer or exchange constant $C_{tr2} = k_{tr2}/k_p$) which contributes to the chain extension process. The large excess of transfer agent over the radical initiator provides the predominant dormant species. Provided the exchange between dormant species and radicals is much faster than propagation (high values of C_{tr1}

(A)
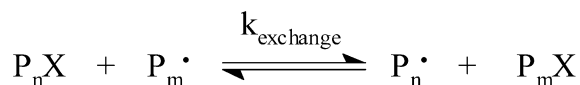
(B)

Fig. 4. Reversible transfer via (A) direct exchange (X = I) and (B) addition-fragmentation (X = S, CH$_2$).

and C_{tr2}), a linear increase of DP_n with monomer conversion can be achieved and the reaction yields end-functionnalized polymers exhibiting a narrow molar mass distribution.

The proper choice of the transfer agent is therefore the key to polymerization control. So far three types of transfer agents have been employed, alkyl iodides [110,111], unsaturated methacrylic esters [112], and thiocarbonylthio compounds [113–117]. The processes based on the latter two classes of compounds operate via addition-fragmentation chemistry, in particular, the one using thiocarbonylthio compounds is 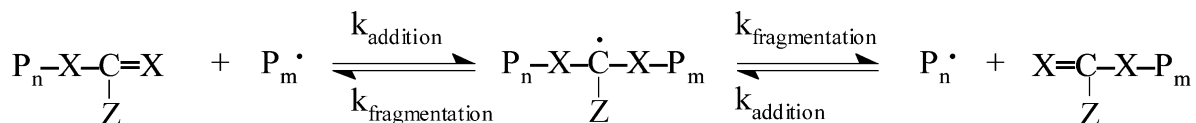called reversible addition-fragmentation chain transfer polymerization (RAFT). The reversible transfer systems can be potentially applied to any radical polymerizable monomer, especially those monomers with low reactivity such as vinyl acetate [118] that still remain a challenge for other controlled/living radical polymerizations. The drawback of this method, on the other hand, is that significant retardation may occur in some cases, particularly when targeting the synthesis of low molar mass polymers [119]. Moreover, the gel effect cannot be entirely avoided at high conversion due to the continuous supply of low molecular weight radicals. In ATRP and SFRP systems such a problem does not exist.

4. Controlled/living radical polymerization in aqueous solution

Although controlled/living radical polymerization (CRP) has been successful in organic bulk or solution systems, there are a number of challenges remaining in applying them to the aqueous media. In particular, the compatibility of the radical mediators with water, the solubility and partitioning of the radical mediators in different phases, as well as the stability of the dormant species in the presence of water, all of which may have significant influence on the control of the polymerization. Nevertheless, a considerable amount of exploration has been undertaken in this area. Nearly all water-borne systems have been investigated, ranging from homogeneous solution polymerization to heterogeneous dispersed polymerizations, such as dispersion, suspension, emulsion, and miniemulsion. The discussion in this section is focused on CRP in homogeneous aqueous solution.

To carry out polymerizations in homogeneous aqueous solutions, the radical mediator as well as the monomer and the polymer should be soluble in the medium. A number of water-soluble monomers have been polymerized via CRP in aqueous solutions. They include uncharged monomers such as 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, oligo(ethylene glycol) methacrylate, 2-(*N*-morpholino)ethyl methacrylate, 2-(dimethylamino)ethyl methacrylate and acrylic acid; as well as ionic monomers such as sodium styrenesulfonate, sodium methacrylate and sodium vinylbenzoate, etc. The chemical structures of these monomers are shown in Fig. 5.

Using TEMPO as the radical mediator, NaSS and NaVBA were polymerized in aqueous ethylene glycol mixture (75–80% ethylene glycol) [120–123]. The reactions were typically performed at 120–125°C, with potassium persulfate/sodium bisulfite as the initiator. While the P(NaSS) homopolymer was generally obtained in high yield, the homopolymerization of NaVBA only achieved relatively low conversion (<30%). Chain extension of P(NaSS) with NaVBA was reasonably efficient, yielding water-soluble block copolymers. Both homopolymers and block copolymers were obtained with narrow molar mass distributions. However, the acid form of the monomers was not polymerizable at all under identical conditions due to nitroxide decomposition in the acidic medium [74]. Employment of a water soluble Co(II) porphyrin complex has achieved the controlled polymerization of acrylic acid in aqueous solution, although detailed results were not provided [124].
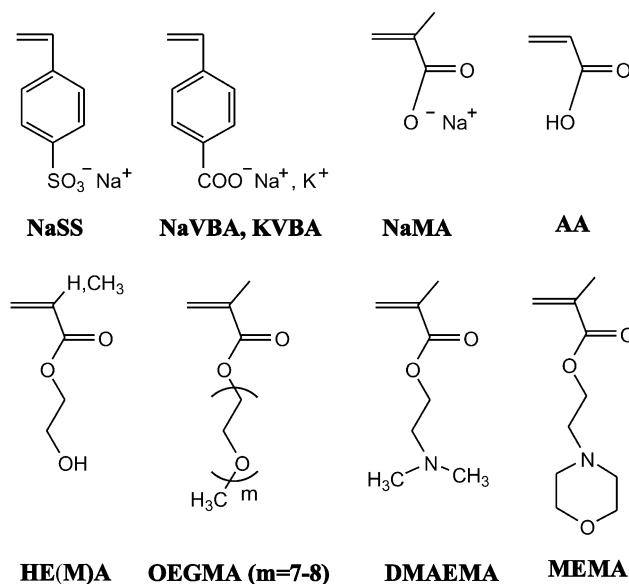
Fig. 5. Monomers polymerizable by NMP and ATRP in aqueous solution.

Most recently, Ladavière et al. were able to carry out the polymerization of AA in aqueous solution via RAFT [125]. The RAFT agents used are shown in Fig. 6. The polymerizations were initiated with 4,4′-azobis(4-cyanovaleric acid) (V-501) at 90°C in water (AA/water, w/w: 44/56 for A, 40/60 for B, 33/77 for C). Quantitative yields were obtained in less than 10 min. However, the molar masses of the polymers were low ($M_n \leq 3500$ g mol^{-1}), and the polydispersities were relatively high ($I_p \leq 1.9$).

More significant progress has been made in conducting ATRP in aqueous solution. The first monomer polymerized was HEA. After 12 h at 90°C in an aqueous medium (50 vol%), conversion reached 87%, and the resulting polymer had $M_n = 14\,700$ g mol^{-1}, $I_p = 1.34$ [126]. Following this pioneering work, polymerization of all the monomers shown in Fig. 5 except NaSS has been reported, with polydispersities of the polymers typically in the range of 1.1–1.3 [100,127–131]. The proper choice of the catalyst, the initiator, and the reaction conditions such as pH and temperature plays a critical role in the success of the polymerization.

Copper halide/2,2′-bipyridine complex is the most commonly used catalyst due to its commercial
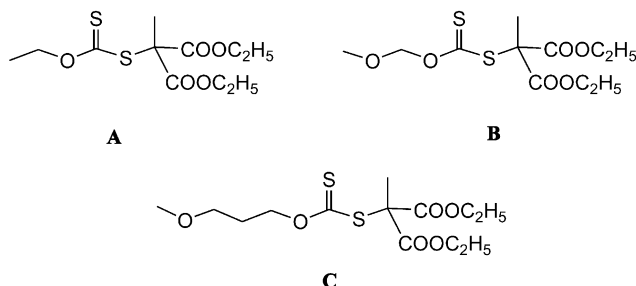
Fig. 6. RAFT agents for the polymerization of AA in aqueous solution.

availability and high water solubility. However, side reactions associated with this catalyst may readily occur in water, resulting in the loss of catalyst activity. An example is the polymerization of acidic monomers such as NaMA or NaVBA. The catalyst can be destroyed either by monomer coordination to the transition metal at high pH or by protonation of the ligand at low pH, resulting in a loss of the complexing ability. Hence it is not surprising that an optimum pH is required for a successful control of the polymerization [100,128]. The catalyst can also be involved in hydrolysis reactions, i.e. the ligand or the halogen coordinated to the metal center can be potentially replaced by water. It is a general observation that ATRP polymerizations in aqueous solution were remarkably faster than those carried out in organic media. Consequently, facile syntheses of well-defined hydrophilic polymers were achieved even at ambient temperature. Although this phenomenon is not yet fully understood, it is likely that subtle changes in the halogen substitution of the metal complex at the higher oxidation-state may partially contribute to the enhanced polymerization rate by reducing the deactivation rate. It was also suggested by some authors [129] that the formation of a more active Cu(I) catalyst in the presence of water may lead to the increased polymerization rate.

Pyridyl methanimines are cheaper ligands than bpy-based ligands, and are particularly useful for ATRP of methacrylates [87]. While they are generally expected to undergo hydrolysis easily in aqueous media, particularly at high temperature [132], two pyridyl methanimine ligands (Fig. 7) developed by Armes and Haddleton were found efficient in the polymerization of OEGMA in water at 20°C [133].

The reactions were performed at neutral pH. High conversion (>90%), polymers with good molar mass control, and low polydispersities ($I_p < 1.20$) were obtained with ligand L1. The performance of ligand L2 was inferior to that of ligand L1 but was still acceptable. The success was assigned to the remarkably high rate of OEGMA polymerization under aqueous ATRP conditions. Therefore, within the time scale of the polymerization, the catalysts were sufficiently stable against hydrolysis. Not surprisingly, when the polymerizations were carried out at higher temperatures they resulted in faster rates but provided materials with reduced molar mass control and higher polydispersities.

In addition to the catalyst, the end functionality of the initiator, or propagating chain end, can also be involved in side reactions. Typical initiators used for ATRP in aqueous solution are either alkyl chlorides or bromides. In the presence of water, these halides may undergo nucleophilic substitution by water, or elimination of hydrogen halide, particularly at high temperatures. Hence, choosing a low reaction temperature and an appropriate initiator is important to limit these side reactions. Pseudohalides such as azides that are less likely to be involved in these side reactions may be potentially used as ATRP initiators. Some preliminary results indicated that success with azide initiators depends on the nature of the monomer and the strength of the metal−azide bond [134]. The best result to date was achieved when charged monomers such as NaVBA were used, where the radical termination rate constant was dramatically reduced.

HEMA is different from other water-soluble monomers in Fig. 5 because its homopolymer is not soluble in water. Recently, Robinson et al. [130] reported a successful ATRP of HEMA in 50/50
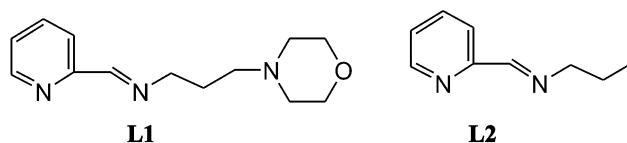

L1   **L2**

Fig. 7. Pyridyl methanimine ligands used for ATRP of OEGMA in aqueous solution.

methanol/water mixture using CuX/bpy as the catalyst. The polymerization attained more than 90% conversion within 1 h at 20°C, with molecular masses in excellent agreement with target and polydispersities in the range of 1.2–1.5. A block copolymer of OEGMA–HEMA was also obtained via sequential monomer addition.

5. Controlled/living radical polymerization in aqueous dispersed systems

Early attempts directed at control of chain-growth in emulsion polymerization can be traced back to 1974. Mikulasova and coworkers studied the polymerization of styrene initiated by heterogeneous polypropylene hydroperoxide with an amine activator in emulsion [135]. The molar mass of the polymer was found to increase linearly with conversion (although it did not pass through the origin), and the polydispersities remained very low ($I_p = 1.01$–1.13). The livingness of the polymerization was confirmed by the fact that after removal of the initiator from the emulsion via filtration, the polymerization still proceeded to 100% conversion and continued upon successive monomer addition. In this way, a number of diblock and triblock copolymers of styrene and ethylenic monomers such as methyl methacrylate, *p-t*-butylstyrene, acrylonitrile and maleic anhydride have been prepared [136–140]. Two factors account for the success of this system. Firstly, a system that provides for fast initiation is used. The peroxide groups attached to the surface of polypropylene decompose in the presence of styrene and an activator, generating radicals to initiate polymerization only from the surface. Therefore the initiation reaction ceases quickly (within 15 min at 35°C) and no additional initiating radicals are produced during the course of the polymerization. This can be assured by removing the heterogeneous initiator via filtration from the system a few minutes after the polymerization begins. This fast generation of radicals provides for the possibility of simultaneous growth of all the chains. Secondly, once the polymer particles are formed, the radicals inside the particles are protected by the compartmentalization effect. As long as new radical entry is absent, these radicals remain active and thus become long-lived. The high efficiency in block copolymer formation (>90%) indicates the lack of chain termination and transfer reactions. The drawback of this system, however, is the difficulty in obtaining polymers with predictable molar masses, because the number of initiating centers located on the surface of the heterogeneous initiator is hard to control. Moreover, homopolymerization has been limited to styrene and no information on the molar mass distribution of the block copolymers is available. The requirement for removal of the initiator from the system also increases the complexity of the reaction apparatus.

A recent study showed that a so-called 'micellar organized graft copolymerization' of styrene with poly(ethylene oxide) macromonomer also possessed a certain 'living' character, as a linear increase of molar mass with monomer conversion was observed up to 60% conversion [141]. This was ascribed to highly limited termination reactions between the compartmentalized propagating radicals. However, the polydispersities were high ($I_p > 1.4$) and significant termination was noticed at higher conversions.

These physical methods aiming at extending the lifetime of radicals can diminish the termination of polymeric radicals as well as the termination between polymeric radicals and small initiator-born radicals. It is generally unsuccessful, however, in limiting the occurrence of chain transfer and of termination originated from small radicals generated by chain transfer to monomer.

In order to manage all the factors leading to chain breaking and broadening of molar mass distributions at the same time, chemical methods such as SFRP, ATRP and RAFT would appear to be much more widely applicable than the physical methods.

5.1. Nitroxide mediated polymerization (NMP)

TEMPO and derivatives, as well as an acyclic nitroxide from the last generation (SG1) (Fig. 8) have been used as radical mediators to control polymerizations in aqueous alcoholic dispersion, aqueous suspension, seeded emulsion, ab initio emulsion, and miniemulsion. The systems are summarized in Table 4 and will be discussed below in more detail.

5.1.1. Precipitation and dispersion polymerizations

Dispersion polymerization can be considered as an intermediate technique between homogeneous and heterogeneous polymerizations. Indeed, all reagents are initially soluble in the polymerization medium while the polymer is not. Hence it precipitates as polymerization proceeds. In the absence of any stabilizer a macroscopic precipitate forms. When a soluble polymeric stabilizer is used, it adsorbs onto the surface of the polymer nuclei, thus favoring the formation of particles, the stability of which is ensured by steric effects. Only one example of CRP has been reported using this system and the control agent was TEMPO (N1) [142]. Because CRP initially produces low molar mass polymer, dispersion polymerization in a purely alcoholic medium (*n*-pentanol, *n*-butanol, *n*-octanol) did not operate and instead a solution polymerization was observed (no turbidity at the polymerization temperature) which produced a polymer that exhibited controlled characteristics. After changing the solvent to a water/ethylene glycol mixture in various proportions, genuine dispersion polymerizations were achieved. Although styrene was not soluble at room temperature, true solutions were obtained at the polymerization temperature. With the $K_2S_2O_8$/TEMPO bicomponent initiating system, the polymerization was quite slow, and the rate depended on the reflux temperature of the solvent mixture. Less than 45% conversion was usually reached within 24 h. TEMPO-capped polystyrenes were obtained exhibiting narrow molar mass distributions ($I_p < 1.3$) with M_n ranging from 2800 to 7200 g mol^{-1}. The experimental molar masses were found to be proportional to monomer conversion but were however larger than the predicted values, suggesting a low initiator efficiency. As expected, in the absence of PVP stabilizer a precipitation CRP was achieved; while in the presence of this stabilizer, dispersion polymerization took place, leading to the formation of particles with diameter in the range 0.73–1.50 μm. Both the average particle size and the particle size distribution were larger in the presence of TEMPO than in similar conventional radical polymerization systems. Nevertheless, it was shown that the presence of TEMPO did not prevent efficient grafting of the PVP stabilizer onto the polymer. When an alkoxyamine initiator was utilized instead of the bicomponent one, the polymerization proceeded with a faster rate leading to a controlled PS with M_n only slightly larger than expected. However, particle size was much larger, i.e. 3.64 μm compared to 0.53 μm obtained in a similar experiment initiated by persulfate.

5.1.2. Suspension polymerization

The very first publication [59] describing NMP in suspension concerned the copolymerization of styrene and butadiene (86/14 wt/wt). The reaction, initiated by BPO in the presence of TEMPO, yielded a copolymer with much narrower molar mass distribution than that prepared in the absence of nitroxide ($I_p = 1.36$ vs. 4.21). This example was given in order to demonstrate that controlled free radical polymerization could be applied not only to solution, or bulk polymerizations, but also to suspension. Recently, two more complete studies were reported [143,144]. The first one [143], was the TEMPO-mediated CRP of styrene and the second one [144] concerned the copolymerization of styrene with either *n*-butyl methacrylate or acrylonitrile, two monomers that presently cannot be controlled via NMP.
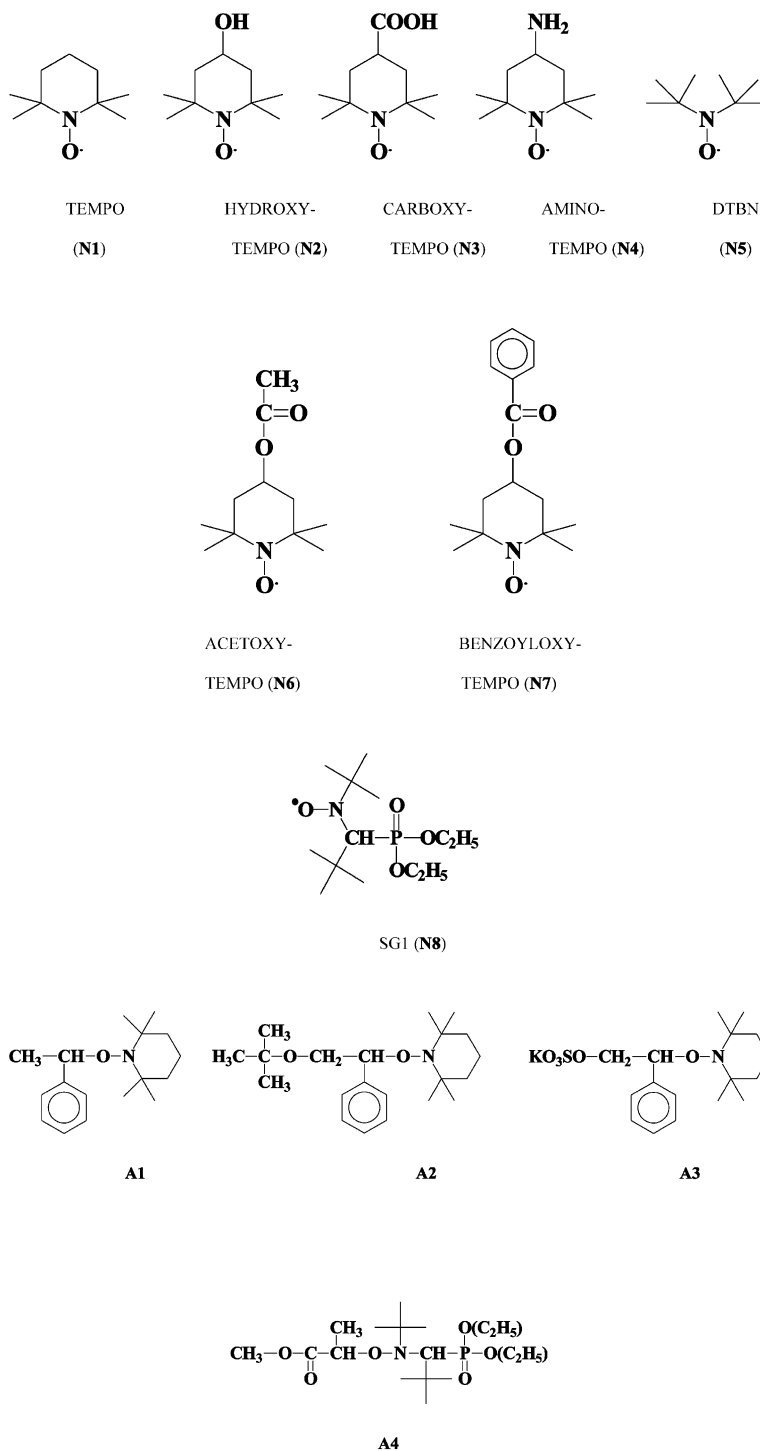
Fig. 8. Various nitroxides and alkoxyamines, respectively used as mediators and initiators in CRP in aqueous dispersed systems.

Table 4
Nitroxide-mediated CRP in aqueous dispersed media: various systems reported in the literature (see Fig. 8, for the structure of the nitroxides and alkoxyamines)

System	Nitroxide	T (°C)/P (bar)	Monomer	Initiator	Surfactant	Reference
Dispersion	N1	112–130	S	$K_2S_2O_8$ or alkoxyamine A1	PVP	[142]
Suspension	N1	120–135	S	PS–N1 macroinitiator (+DCP)	PVA + SDS	[143]
	N1	125	S, AN, *n*-BMA			[144]
Seeded emulsion	N1	125 (15 bar)	S	Alkoxyamine A2	AEROSOL-MA80	[145]
Ab initio emulsion	N1–N5	130	S	$K_2S_2O_8$, V-50, alkoxyamine A3	SDS	[146]
	N1,N2, N6, N7	120	S	$K_2S_2O_8$	SDS	[147]
	N8	90	S	$K_2S_2O_8/Na_2S_2O_5$	SDS	[148]
Miniemulsion	N1	125	S	BPO	DOWFAX8390	[150,153]
	N1	125	S	PS–N1 macroinitiator	DOWFAX8390	[156]
	N1	135	S	$K_2S_2O_8$	SDBS	[151,154]
	N1	135	S, BA	PS–N1 macroinitiator	SDBS	[157]
	N8	90	S	AIBN	SDS	[148,152]
	N8	90	S	$K_2S_2O_8/Na_2S_2O_5$	SDS	[148,152,155]
	N8	115	BA, S	Alkoxyamine A	SDS/Forafac DOWFAX8390	[158,159]

Initiation was performed by a TEMPO-capped polystyrene macroinitiator. Suspension polymerizations were carried out at 120–135°C using sodium dodecylsulfate, poly(vinyl alcohol) and stearic acid as a stabilizing system. Polymer beads were obtained with diameter in the range 1–3 mm. Particle stability during synthesis was a challenge as polymerization temperature was above the glass transition temperature of the (co)polymers. Nevertheless, the tendency towards agglomeration was overcome by a high stirring speed (>1000 rpm). The rate of polymerization was not found to be different from that in bulk and was regulated by the thermal self-initiation of styrene. When styrene was polymerized alone, homopolymers with molar masses following the theoretical values were obtained, with polydispersity index below 1.5. The percentage of dead chains was estimated from model calculation; it increased from 27% at 41% conversion to 36% at 72% conversion. This proportion could however be reduced through a decrease of the polymerization time either by the addition of a radical initiator (such as DCP, which decomposes slowly) or by an increase in the polystyrene macroinitiator concentration. In the copolymerization reactions, the molar mass increased linearly with monomer conversion but the polydispersity indices also increased as a result of termination reactions; control was improved when the proportion of styrene was increased. As in emulsion polymerization, the partial solubility of acrylonitrile in the water-phase had an effect on the copolymer composition and modified the apparent reactivity ratios.

5.1.3. Emulsion polymerization

The very first description of nitroxide-mediated CRP of styrene in emulsion concerned a seeded system [145]. Such a system was selected in order to avoid the complex nucleation step existing in an ab initio emulsion polymerization. For this purpose, a PS seed latex was designed with particle diameter of 90 nm and narrow particle size distribution. The dialyzed latex was allowed to swell with styrene in such an amount that apparently no droplet should form, in the presence of the oil-soluble alkoxyamine A2 and a few percent of free TEMPO. Upon heating to 125°C, polymerization proceeded, reaching 99% conversion within 36 h. Transmission electron microscopy showed the absence of secondary nucleation, agregation or coagulation of the particles. The M_ns increased with conversion but remained below the theoretical values. Simultaneously, the polydispersity index increased from 1.41 to 1.54. The low values of M_n and the observed broadening of the molar mass distribution on the low molar mass side were assigned to the occurrence of thermal self-initiation of styrene, creating new chains. An enhancement of the thermal Diels–Alder reaction of styrene in emulsion as compared to bulk was proposed, due to a possible hydrophobic effect. The authors concluded that CRP in emulsion would considerably improve with the development of new systems, operating at ambient temperature.

Despite the limitations put forward by the previous authors, a study performed by Marestin et al. [146] was devoted to nitroxide-mediated CRP of styrene in an ab initio emulsion polymerization, carried out at 130°C. Among the various nitroxides tested (N1–N5), only amino-TEMPO (N4) gave satisfying results. With the others, extremely low conversions were observed before complete coagulation of the system. Polymerization proceeded further in a living fashion inside the separated organic phase. Amino-TEMPO, in conjunction with SDS surfactant and persulfate, or V-50 initiators, led in contrast to emulsions that remained stable even after long polymerization times (a few days). Solids content was however maintained quite low (5 wt%) and typical particle diameters were between 400 and 600 nm with broad distribution. Owing to the hydrolysis of SDS, dodecanol was shown to form in the system and was believed to improve stability. This was confirmed by the better results obtained when a fatty alcohol

such as hexadecanol was purposely added. It was then suggested that the system actually offered similarities with a miniemulsion process, the high shear usually needed to divide the organic phase being unnecessary at elevated temperature. The better result obtained with amino-TEMPO was initially assigned to the ability to protonate the amino-group (pH was between 4 and 8), improving latex stability by an electrostatic effect (effect of the charge of the initiator used in association with this nitroxide-negative for persulfate and positive for V-50-was however not discussed). A second advantage put forward by the authors, comes from the most favorable partitioning of this nitroxide between the aqueous and the organic phases: in comparison, TEMPO and hydroxy-TEMPO respectively, display too low and too high water-solubility. Polymerizations were however particularly slow as conversions in the range 37–69% were obtained after a long reaction time (from 36 to 109 h). However, they yielded low molar mass polystyrenes ($M_n < 6000$ g mol^{-1}), growing with conversion and exhibiting poly-dispersity indices in the range 1.2–1.8 depending on the experiments.

The effect of hydrophilicity of TEMPO-based nitroxides was examined in more details by Cao et al. [147] for batch emulsion polymerizations of styrene conducted at 120°C with persulfate as an initiator and SDS as the surfactant. Among the nitroxides studied (N1, N2, N6 and N7), only the acetoxy derivative (N6) achieved controlled polymerization. This result was ascribed to an optimized balance between the hydrophilic and the hydrophobic character of the nitroxide, favoring an optimal partitioning between both the aqueous and the organic phases. The rate of polymerization and the quality of control depended on the [nitroxide]/[K$_2$S$_2$O$_8$] initial molar ratio. With a 1.1/1 ratio, 81.4% conversion was achieved within 12 h, yielding a polystyrene with $M_n = 17\,900$ g mol^{-1} and $I_p = 1.29$. In addition, stable latexes with small particle size (below 100 nm) and good regularity were obtained.

When the bicomponent initiating system was replaced by the negatively charged water-soluble alkoxyamine A3 [146], a stable latex could be obtained without any added surfactant, providing that polymerization was carried out at low solids content (<2 wt%). The addition of SDS or SDBS surfactant considerably improved the stability, allowing the formation of a stable latex with 10 wt% solids, but with bimodal particle size distribution. Polymerization was faster than with the bicomponent initiating system and the formed polymer had a M_n of 42 000 g mol^{-1} with $I_p = 1.7$. This polydispersity index could be reduced to 1.2 upon the addition of 0.3 equivalent of free amino-TEMPO, however, at the expense of the polymerization rate, which dropped significantly.

Ab initio emulsion polymerizations of styrene were also conducted at 90°C, using the stable acyclic phosphonylated nitroxide radical SG1 (N8) as a mediator [148]. Owing to a significantly higher equilibrium constant of activation–deactivation ($K = 1.9.10^{-8}$ mol l^{-3} at 125°C) [71,72] than that of TEMPO for styrene polymerization ($K = 2.10^{-11}$ mol l^{-3} at 125°C) [149], this stable radical can successfully be used as a mediator at a lower temperature, i.e. from 90 to 130°C. Polymerization kinetics was thoroughly studied in a system containing 20 wt% of styrene, utilizing K$_2$S$_2$O$_8$/Na$_2$S$_2$O$_5$ as a water-soluble redox initiator and SDS as a surfactant. A long induction period was observed, which was assigned to the formation of water-soluble alkoxyamines and to the existence of the nucleation step. In this system, the molar mass of the polymers increased with conversion, following the theoretical line, but their distribution was rather broad (I_p between 2.0 and 2.5) and systematically broader than in the corresponding miniemulsion polymerization (see Section 5.1.4). Rather small particles were obtained (average diameter was 120 nm), with a large distribution in particle size. One of the disavantages of the emulsion process was the lack of stability with respect to the miniemulsion system, as a few percent of coagulum usually formed. The authors concluded that a better understanding of the nucleation step in a controlled radical emulsion polymerization would be necessary to improve the system.

5.1.4. Miniemulsion polymerization

The majority of the studies concerning NMP in aqueous dispersed media have been devoted to miniemulsion polymerization [150–159]. There are many reasons for this trend. The first goal was to skip the nucleation step, as in seeded emulsion polymerization. The direct, quantitative nucleation of the small monomer droplets presents additional advantages. For instance, oil-soluble initiators can be employed, which opens the door to the use of any type of preformed alkoxyamine (monomer-based, macroinitiators, etc.) and allows thermal self-initiation in the case of styrene, without provoking the formation of very large unstable particles. In addition, the system contains only two phases. The absence of a monomer phase that serves only as a reservoir, favors the optimal location of the nitroxide within the polymerization locus. Finally, the miniemulsion system displays improved stability, as stated above, in comparison with emulsion polymerization.

As shown in Table 4 and in Fig. 8, various initiating systems have been selected and used with either TEMPO or SG1 nitroxides. The oil-soluble BPO and the water-soluble $K_2S_2O_8$ radical initiators were both used in conjunction with TEMPO. With the former system, Prodpan et al. [150,153] performed the miniemulsion polymerization of styrene at 125°C. They also studied the controlled thermal autopolymerization of styrene in miniemulsion, i.e. without added BPO. In both cases, the miniemulsion system was well suited to produce stable latexes containing 20 wt% polystyrene with controlled molar mass and narrow molar mass distribution. The parameters that usually affect the kinetics and molar mass distribution in bulk were found to be the same in miniemulsion. Under identical conditions the miniemulsion polymerization was however slightly slower than the corresponding bulk polymerization. The latexes obtained in the presence of TEMPO exhibited large particles with a broad particle size distribution. In addition the number of particles in the system continuously increased with monomer conversion. With $K_2S_2O_8$, polymerizations were performed at 135°C [151,154] and required a good adjustment of the surfactant and hydrophobe respective concentrations, to get stable latexes with small particle diameter (50 nm). The [TEMPO]/[$K_2S_2O_8$] initial molar ratio was crucial in achieving a well-controlled polymerization. With a ratio of 2.9/1, conversion reached 87% within 6 h, much faster than the usual bulk polymerizations. The fast polymerization was ascribed to the partial solubility of TEMPO in the aqueous phase, hence reducing the build up effect in the organic phase. Polymer samples taken during the polymerization had a narrow molar mass distribution ($I_p = 1.1$), with the expected shift of molar mass with monomer conversion. It was shown however [157], using chain extension in bulk as a proof, that a large proportion of dead chains existed in the system, most probably formed in the latter part of the polymerization.

Because bicomponent initiating systems do not allow accurate control over the number of active chains, TEMPO-capped polystyrenes were used as macroinitiators [156,157]. They were prepared in bulk using BPO as the radical initiator. In one case, the macroinitiator was isolated by precipitation from a bulk polymerization that had been conducted up to 71% conversion [156]. In the other case, the styrene solution in which it was prepared was directly emulsified after 5% conversion, without further purification [157]. Although all other experimental conditions used for the miniemulsion polymerization were quite similar and the features of a controlled polymerization were expectedly observed, rather different results concerning kinetics and the final proportion of dead chains in the system were reported. Pan et al. [156] showed that the experimental molar masses were systematically below the theoretical ones and that the polydispersity index continuously increased with monomer conversion. This behavior was ascribed to thermal autopolymerization of styrene leading to the creation of new chains throughout the reaction period, and to concomitant irreversible terminations. The polymerization

rate was independent of the initiator concentration, conversion reaching 70–80% after 22 h. In contrast to these observations, Keoshkerian et al. [157] claimed that with the monocomponent initiating system they used, they could reach 99.6% conversion within 6 h, resulting in a living polymer with narrow molar mass distribution ($I_p = 1.15$). As a proof of livingness, this polystyrene was chain extended either with styrene in bulk after isolation or with *n*-butyl acrylate, the latter being directly added in the polystyrene latex. In the first case, a large majority of the chains were able to reinitiate polymerization, demonstrating the presence of a very low proportion of dead chains. In the second case, continued polymerization proceeded up to 99.4% conversion, yielding a well defined block copolymer with I_p remaining as low as 1.18. This was the first block copolymer completely prepared in miniemulsion via NMP. The reasons for the faster kinetics and better control obtained in miniemulsion with respect to bulk polymerization were however not understood.

Nitroxide-mediated polymerizations in miniemulsion were also reported using SG1 as the mediator instead of TEMPO (see Fig. 8). The first examples concerned the miniemulsion polymerization of styrene at 90°C, using either an oil-soluble radical initiator (AIBN) [148,152] or a water-soluble redox initiator, the persulfate/metabisulfite system [148,152,155]. With AIBN, incomplete polymerizations were observed even after 24 h. The slow down of the polymerization rate was assigned to the increase in nitroxide concentration owing to the persistent radical effect, which was not compensated for by thermal self-initiation of styrene at 90°C. The experimental molar masses followed the theoretical values but the molar mass distribution remained broader than in bulk as I_p reached 1.6 at final stage, vs. 1.3 for the same polymerization carried out in bulk. Similarly to the previous systems using TEMPO, when the initiator was changed to the water-soluble initiator, polymerizations became much faster. Some of them reached more than 90% conversion within 8 h. The plots of conversion vs time systematically displayed an induction period, corresponding to the time required for generation of the primary radicals in water and trapping of the formed oligoradicals by free SG1, initially in high concentration. Because of partitioning of SG1 between the two phases, deactivation could initially occur in the water phase, preventing excessive aqueous phase irreversible termination and hence favoring a high initiator efficiency. Another consequence of the reaction conditions also assigned to partitioning was that the rate of polymerization was found to be significantly larger than in bulk. A complete study of this system was undertaken and the important parameters affecting the rate of polymerization and the control over molar masses were identified and varied. The most important one was pH. The redox couple used to initiate the polymerization leads to the formation of acidic byproducts. When carefully buffered, the miniemulsion polymerizations allowed a good control over the molar masses, M_n following the predicted values, I_p decreasing with monomer conversion, although remaining larger than in bulk owing to the faster propagation. Under acidic conditions however, the polymerization did not follow this trend anymore. The polymerization went faster and the molar masses were larger than expected. Both results were assigned to side reactions of the SG1 nitroxide with the initiator that were particularly enhanced in acidic conditions. These side reactions led to an uncontrolled consumption of both species and hence to a decrease of the concentration of formed alkoxyamines (and thus of living chains) accompanied by a decrease in the concentration of free nitroxide (explaining the fast polymerizations). For the same reason, changing the initiator concentration to target different molar masses need to be accompanied by a careful adjustement of the buffer concentration in order to maintain the pH close to 7. Another important parameter was the monomer/water ratio. Indeed, increasing the ratio from 1/9 to 3/9 led to a very significant reduction of the polydispersity index of the final polymer. For instance, a polystyrene exhibiting $M_n = 17\,500$ g mol^{-1} was obtained with $I_p = 1.22$, while I_p was never below 1.5 when the

monomer/water ratio was 1/9. This trend was explained by the more favorable location of the free nitroxide in the organic phase, resulting also in a reduction of the polymerization rate. Successful chain extensions with styrene were directly performed in the aqueous dispersed system, demonstrating the living character of the polymerization, although the existence of dead chains could not be excluded. Like evidenced by most authors applying CRP in aqueous dispersed systems, broad particle size distributions were usually observed. Nevertheless, the latexes did not contain any coagulum and were perfectly stable.

In addition to styrene, the new acyclic nitroxides such as SG1, were also shown to control the polymerization of acrylic esters. Experiments were performed in bulk and well-defined poly(*n*-butyl acrylate) homopolymers and derived block copolymers were produced [72,74,77]. A limitation, however, is that the polymerization temperature cannot be below 100°C because of a lower activation–deactivation equilibrium constant than for styrene [72]. To date, the only example on *n*-butyl acrylate CRP in miniemulsion was reported by Farcet et al. using an oil-soluble alkoxyamine initiator, the SG1-based adduct of methyl acrylate at 115°C [158]. The results were in perfect agreement with those obtained in bulk: fast polymerization, good control over the molar masses and narrow molar mass distribution. The chains were extended in situ by the shot addition of styrene after more than 80% conversion in the first step. This two-stage reaction yielded a block copolymer with high blocking efficiency and narrow molar mass distribution (M_n = 49 900 g mol^{-1}; I_p = 1.27; 49 mol% of styrene) (see Fig. 9). When polymerizing mixtures of styrene and *n*-butyl acrylate in miniemulsion, well-defined gradient copolymers were obtained exhibiting a narrow molar mass distribution and a narrow composition distribution [159]. In both cases, stable latexes were obtained but the final particle size was not reproducible, and the distribution was broad. Those recent results are thus very promising for the preparation of more complex architectures via NMP in miniemulsion. Work has to be done however to improve the colloidal properties of the latexes.

5.2. Atom transfer radical polymerization (ATRP)

A number of early studies indicated that ATRP using Ni [91], Ru [91], Pd [160], Rh [96,161], and Re [97] complexes as the catalysts could survive the presence of a significant amount of water. Subsequently, Lecomte et al. [94] investigated the 'suspension' polymerizations of MMA with a palladium catalyst. When the polymerization was carried out without stabilizers, a bimodal molar mass distribution was observed for high molar mass polymer, although the average molar mass obtained was in good agreement with the theoretical value. This was attributed to the poor stirring of the system. The addition of a nonionic surfactant overcame this problem and led to a polymer with relatively narrow molar mass distribution (I_p = 1.55 at 100% conversion). Nevertheless, the aqueous suspension did not remain stable even in the presence of the surfactant, and the molar mass of the polymer obtained was nearly twice the expected value. Another approach to 'suspension' polymerization was reported by Nishikawa et al. [162] who used ruthenium-based catalysts for the polymerization of MMA. The suspension was prepared by mixing the monomer with toluene/water mixture or pure water without any stabilizers. The biphasic system was maintained under vigorous and continuous stirring. Good control over the molar masses and polydispersities was realized, although the MMDs were broader in the absence of toluene ($I_p \sim 1.4$) than those obtained in the presence of toluene (I_p = 1.1–1.3). The latter also achieved finely dispersed particles without forming larger flocculates or precipitates. In both cases, the controlled/living polymerization proceeded even without activator such as Al(O*i*–Pr)$_3$, which was an improvement from their counterparts in the organic media.
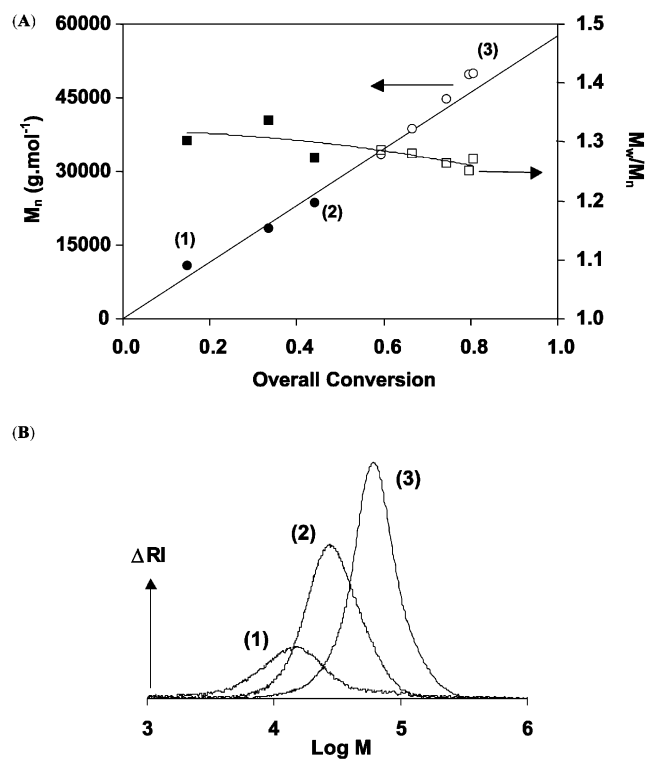
Fig. 9. SEC chromatograms and molar mass evolution for the nitroxide-mediated sequential copolymerization of *n*-butyl acrylate and styrene in miniemulsion at 115°C. (A) M_n (circles) and M_w/M_n (squares) vs. overall conversion for the CRP of *n*-BA (black symbols) and for the second polymerization of styrene (white symbols); (B) Size exclusion chromatograms of three selected samples. Experimental conditions: water = 298 g; *n*-BA = 74 g (0.58 mol); S = 60 g (0.58 mol); SDS = 2.446 g; Forafac® = 1.497 g; NaHCO$_3$ = 0.326 g; [alkoxyamine initiator A4] = 0.032 mol l^{-1} with respect to BA (from Ref. [158]; reproduced by permission of the American Chemical Society, Washington DC).

Among all ATRP systems, those mediated with copper complexes have been most extensively studied in the heterogeneous aqueous media. The following discussions are therefore focused on copper-based ATRP. Analogous to the polymerizations carried out in the organic system, the atom transfer equilibrium was approached in both directions (Fig. 3) in the aqueous dispersed media. Starting with an alkyl halide and a copper(I) complex, the system is named *direct ATRP*; while beginning with a conventional radical initiator and a copper(II) complex, the polymerization is called *reverse ATRP*.

5.2.1. Direct ATRP

The first copper-mediated ATRP under micellar conditions was reported in early 1998 [163]. Ethyl 2-bromoisobutyrate, CuBr/bpy and SDS were employed as the initiator, catalyst, and surfactant, respectively. The polymerization of MMA was performed at 60–80°C. In spite of the relatively high yield (72% at 60°C and >80% at 80°C in 2 h), the MMDs of the polymers obtained were quite broad ($I_p >$ 1.5). This exploration was followed later by more comprehensive studies carried out by other groups [164–167], which resulted in the identification of some crucial experimental conditions for conducting successful ATRP in a multiphase environment.

Table 5

Cu-mediated ATRP of BMA with different ligands in aqueous dispersed media. BMA/water $= 1.5$ ml/10 ml, $[BMA]_0:[EBiB]_0:[CuBr]_0:[Ligand]_0 = 200:1:1:2$ (for 1–5) or 200:1:1:1 (for 6–10)

	Ligand	Brij 98[a] (%)	T (°C)	Time (h)	Conv. (%)	$M_{n,th}$	$M_{n,sec}$	I_p
1	bpy	5	70	3	100	28 400	272 000	3.27
2[b]	dTbpy	2	50	2.2	80	22 750	37 610	1.45
3	dNbpy	2	70	4.2	96	27 300	33 230	1.25
4	dAbpy	2	70	1.8	88	25 030	33 980	1.25
5	dHDbpy	2	90	2.2	83	23 680	27 750	1.21
6	tNtpy	2	70	1.7	84	23 890	37 190	1.38
7	PMDETA	5	70	3.0	100	28 400	380 000	6.70
8	Me$_6$TREN	3	20	1.3	73	20 800	928 700	2.20
9	BPMOA	2	70	2.5	94	26 700	48 300	1.97
10[c]	BPMODA	2	20	7.5	83	23 610	36 760	1.43

[a] Weight percentage vs. water.

[b] 8% of CuBr$_2$ (vs. Cu total) added.

[c] 30% of CuBr$_2$ (vs. Cu total) added to the aqueous phase.

In order to establish and maintain the atom transfer equilibrium during the polymerization, it is essential to have both the radical activator and deactivator available in the organic phase where the polymerization takes place. Otherwise either no polymerization or uncontrolled polymerization would occur. One of the roles the ligand plays is adjusting the partitioning behavior of the metal complexes. A suitable ligand should have sufficient binding affinity towards the metal in order to compete with water as a potential coordinating molecule. At the same time, it should also bring enough metal complexes (at both higher and lower oxidation states) in the organic phase to mediate the polymerization. Several common ATRP ligands, including bipyridyl and terpyridyl derivatives, picolyl amines and aliphatic amines, were examined for the polymerization of *n*-butyl (meth)acrylate in aqueous dispersed media [168]. The results are compared in Table 5. It was found that not every ligand that worked in bulk or solution ATRP continued to be successful in water-borne systems. Only those ligands that display sufficient hydrophobicity, as shown in Fig. 10, can bring at least some activator and deactivator into the organic phase, and therefore maintain a fast equilibrium between the growing radicals and the
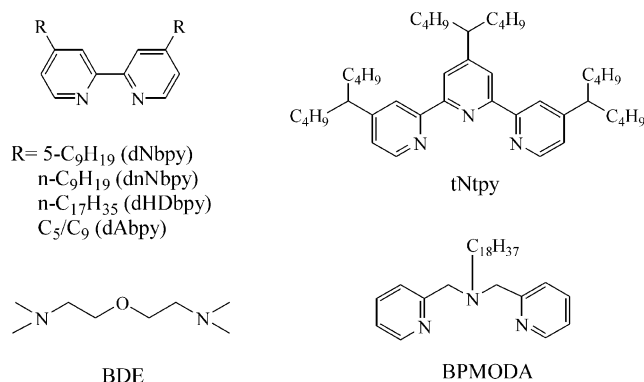

Fig. 10. Ligands successful for copper-based ATRP in aqueous dispersed media.

dormant species. Ligands such as bpy, PMDETA, etc., that form water-soluble complexes with copper halide are not effective, due to a failure in establishing the atom transfer equilibrium in the polymerization loci.

The partitioning behavior of a few copper complexes, particularly $Cu^{II}Br_2$/dNbpy and Cu^IBr/dNbpy, between the monomer (*n*-BMA, *n*-BA or styrene) and water was studied in detail using UV–vis spectroscopy [169,170]. The results showed that even with a very hydrophobic ligand such as dNbpy, neither the Cu^I nor the Cu^{II} complex were restricted to the organic phase. In a mixture of *n*-BMA/water (1.5/10 v/v), about 5% of the initial Cu^I and 40–90% of Cu^{II} (depending on the initial concentration of Cu^{II}) would partition into the aqueous phase at room temperature. The percentages increased to 20–30% for Cu^I and 80–99% for Cu^{II} at 90°C. This indicates that a certain degree of catalyst transportation through the aqueous phase is possible. It was proposed that the aqueous partitioning of $Cu^{II}Br_2$/dNbpy complex was caused by the dissociation of both dNbpy and Br ligands. As a result, the majority of the Cu^{II} species in the aqueous phase remained as $CuBr_2$ without coordination with dNbpy. In a separate study using atomic absorption spectroscopy, Wan et al. [166] compared the partitioning behavior of CuCl complexed by bis(*N*,*N*′-dimethylaminoethyl) ether (BDE, Fig. 10) and bpy, respectively. In the mixture of styrene/water (50/50 v/v), the partition coefficient of Cu^{II}/BDE ($K_p = [Cu]_{aq}/[Cu]_{sty} = 72.5$) was found to be three times less than that of Cu^{II}/bpy ($K_p = 230.0$) in the aqueous phase at 80°C. While these partitioning studies provided valuable information, they were undertaken in the absence of any surfactants, thus the results may not fully represent the partitioning behavior of the metal complexes, particularly the dynamics of the partitioning, in real polymerization systems. For example, the observed 'living' nature of the polymerization can be hardly explained by the seemingly low percentage of the deactivator remaining in the organic phase indicated by the partitioning measurements, unless either of the following three occurs. (i) The presence of the surfactant enhances the partitioning ratio of the metal complexes in the organic phase. (ii) The surfactant reduces the diffusion rate of the metal complexes between the two phases; hence, more deactivators are trapped by radicals before they diffuse into the aqueous phase. (iii) Cu^{II} species rapidly transfer from the aqueous phase back to the organic phase. In the first two cases, it is expected that the nature of the surfactant would also affect the polymerization control.

Consequently, surfactant is the second parameter to be considered. The most critical requirement is that it should not affect the equilibrium between the radical and the dormant species. The use of SDS led to high molar mass polymers with large polydispersities, indicating uncontrolled polymerization [164]. This was attributed to the facile interaction of the surfactant with the catalytic system. The unsuccessful polymerization using SDS, however, does not preclude the possibility of using other anionic surfactants in aqueous dispersed ATRP as long as the surfactant has a weak coordinating hydrophile to the metal. The surfactant also functions to stabilize the dispersed system throughout the polymerization. Although it was demonstrated that the stability of the latex was not related to the control of the molar mass and the polydispersity [164,170], a system with a reasonable colloidal stability is not only easy to handle but also provides convenience to study kinetics. Both cationic and nonionic surfactants did not interfere with the livingness of the polymerization. However, only nonionic surfactants having HLB values within a suitable range resulted in stable latexes without significant coagulation [170,171]. For example, *n*-BMA polymerization was well stabilized by Brij98 (HLB = 15.3) and Tween 80 (HLB = 15.0); and MMA polymerization was reasonably stabilized by HV25 (HLB = 16.6). On the other hand, it was also realized that HLB was not the only property responsible for the latex stability [171]. Other factors, such as the size (total molar mass), the chemical nature of the hydrophobic and hydrophilic moieties, and the

structural features of the latter (degree of branching and chain length distribution, etc.) in the nonionic surfactants may also play important roles. These are expected to be subjects of future studies.

Direct ATRP usually yielded particles with average size larger than micron [171]. Owing to the oil-soluble initiators used such as EB*i*B, a (micro)suspension mechanism is most likely to operate in direct ATRP, i.e. the polymerization takes place in the monomer droplets. As a result, the kinetics of direct ATRP in the aqueous dispersed system is very similar to that of the organic homogeneous system [164]. From the point of view of colloid, however, the large particles usually lead to an unstable dispersion, and therefore large amount of stabilizers (5–20 wt% relative to monomer) are required to prevent coagulation. To improve the colloidal stability, a miniemulsion process was applied. In the polymerization of *n*-BMA using EB*i*B as the initiator at 70°C, the particle size was reduced from 1.5 μm without sonication to 300 nm with sonication and use of a hydrophobe [172]. Consequently, the latex obtained was highly stable.

Direct ATRP in aqueous dispersed media has been successful for the homopolymerization of acrylates, methacrylates, and styrenes [164–166,170,171]. Typical reaction temperatures were 60–90°C, with solids content around 15%. An example of *n*-butyl acrylate polymerization using Tween 80 as the nonionic surfactant is shown in Fig. 11.

In aqueous dispersed systems the synthesis of block copolymers, however, is more complicated than
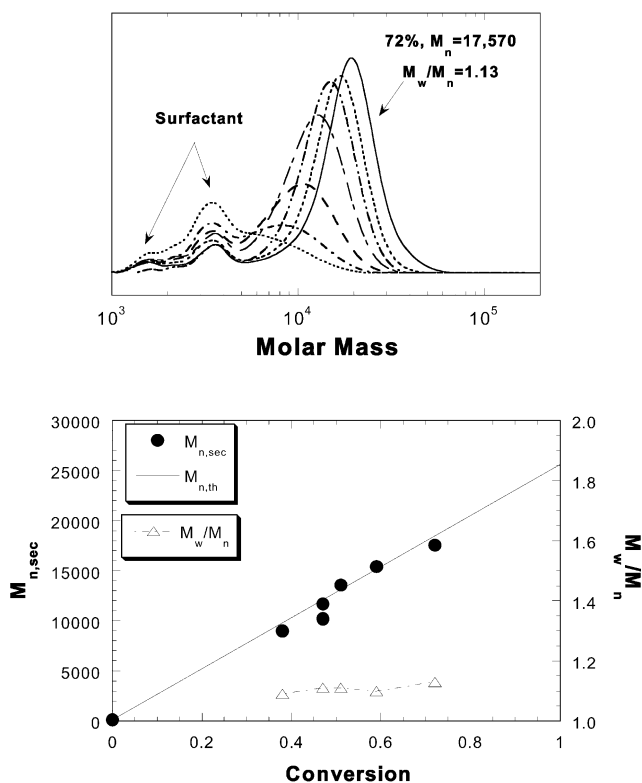

Fig. 11. SEC chromatograms and molar mass evolution of the polymerization of *n*-BA in aqueous dispersed media using dAbpy as the ligand. *n*-BA/water = 1.5/10 (v/v), surfactant: Tween 80 (2 wt% vs. water); [*n*-BA]$_0$:[EB*i*B]$_0$:[CuBr]$_0$:[dAbpy]$_0$ = 200:1:1:2, with 10 vol% of decane (vs. *n*-BA) added; 90°C. (From Ref. [167]; reproduced by permission of Wiley–VCH, Germany.)

for bulk or solution systems. This difficulty can be attributed to two possible causes. First, it is more challenging to maintain a high end-functionality of the polymers in an aqueous dispersed system. The loss of end-functionality may arise from the increased radical termination during the polymerization, particularly when the deactivator concentration in the organic phase is reduced. A loss of terminal functionality may also occur as a result of side reactions with water, such as the substitution or elimination of the halogen group. Whether it arises in either way it would result in incomplete block copolymer formation. The second problem is associated with the cross-over reaction of the growing radicals between chain segments and differences in deactivator concentration required when using different monomers. In the equilibrium established between the active and the dormant species, some monomers (styrene, methacrylates) generate more deactivator (Cu^{II}) than other monomers (acrylates) [173,174]. Although this situation also occurs in homogenous polymerizations, it is much more pronounced in the water-borne systems due to the variation of the deactivator partitioning behavior with different monomers [170]. Therefore the presence of higher amounts of deactivator when going from polystyrene/ PMMA to polyacrylates would result in very slow polymerization of the acrylic monomers. In solution or bulk polymerization systems, the strategy of a 'halogen-switch' [175], i.e. the use of a bromine-containing initiator and $Cu^{I}Cl$ as the catalyst, is often applied to ensure efficient cross-propagation or initiation of the second block. In a water-borne system, however, the use of the halogen switch turned out to be much more difficult. This problem may be associated with the compartmentalization of the media, which might lead to insufficient halogen exchange for physical reasons. Due to the aforementioned limitations, the direct synthesis of block copolymers by sequential monomer addition in the aqueous dispersed media still remains a challenge for preparation of certain block copolymers by ATRP at the current stage. Nevertheless, successful block copolymerizations were accomplished by using a poly(*n*-butyl acrylate) macroinitiator prepared in bulk to initiate the polymerization of styrene in the aqueous dispersed media. Clean block copolymers were obtained with varying end groups and ligands [176], as exemplified in Fig. 12.

Other applications of ATRP in aqueous dispersed systems include the combination of latex with aqueous homogeneous ATRP. Well-defined polymer chains were grafted from the surface of synthetic latex particles. A cross-linked polystyrene latex was functionalized at the surface by a monomer bearing an alkyl halide group. Activation of this group by CuBr/bpy complex in the presence of various
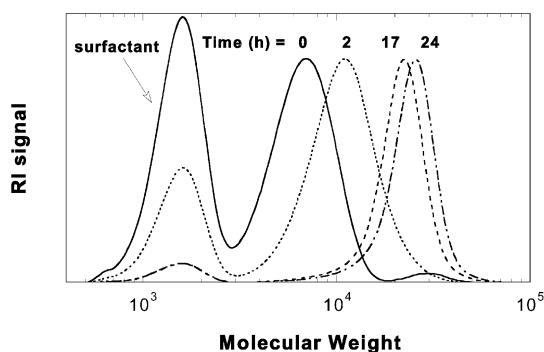
Fig. 12. Chain extension of P(*n*-BA) by styrene via ATRP in aqueous dispersed media. $[S]_0:[P(-nBA)-Cl]_0:[CuBr]_0:[dAbpy]_0 = 223:1:1:2$; 3% Brij98 vs. water, S/water $= 1.5/10$ ml, 90°C. (From Ref. [176]; reproduced by permission of the American Chemical Society, Washington, DC.)

water-soluble monomers led to the formation of hairy particles [177]. The same type of surface modification was performed on colloidal silica particles dispersed in water [178].

Precipitation polymerization by ATRP in aqueous medium was also practiced in a novel way [179]. Instead of using a water-soluble monomer, Storsberg et al. used a randomly methylated β-cyclodextrin (m-β-CD) to complex the hydrophobic monomer, MMA; the hydrophobic initiator, EBiB; and the hydrophobic catalyst, CuBr/dNbpy. The complexes became highly water-soluble. During the polymerization, water-insoluble PMMA precipitated from the reaction medium. First-order kinetics were observed after a slight induction period. The molar mass of the polymer increased almost linearly with the monomer conversion, and the polydispersities remained relatively narrow ($I_p = 1.3$–1.8). After isolation and redispersion in water with sonication, the PMMA was able to initiate the polymerization of styrene in the presence of CD-complexed CuBr/dNbpy, resulting in formation of a block copolymer. However, the yield of the block copolymer (5–10%) as well as the initiation efficiency of the PMMA macroinitiator (~12%) were both very low, and the polydispersity of the block copolymer was large ($I_p \gg 2$).

5.2.2. Reverse ATRP

Reverse ATRP was applied to aqueous dispersed system with high expectation of success because of the following two reasons: first, many water-soluble initiators used in conventional emulsion polymerization can be utilized; second, the initial system is easy to handle, since Cu^{II} species that are stable in air are used in place of Cu^{I} species. The fundamental requirements for a successful polymerization are the same as those for direct ATRP, i.e. a sufficiently hydrophobic ligand should be used in the presence of a nonionic or cationic surfactant. Most studies were focused on the polymerization of n-BMA, using $CuBr_2$/dN(A)bpy as the deactivator, and Brij 98 as the surfactant [169,170,180].

Typical water-soluble initiators evaluated include potassium persulfate, 2,2′-azobis(2-methylpropionamidine) dihydrochloride (V-50), 2,2′-azobis[2-(2-dimidazolin-2-yl) propane] dihydrochloride (VA-044), etc. A successful ATRP was initiated with $K_2S_2O_8$ when pH was carefully adjusted with a buffer solution. When azo initiators were employed, no pH adjustment was necessary [180]. The most effective temperature for control over the polymerization was 70–90°C. In contrast to direct ATRP, reverse ATRP usually displayed an induction period that lasted from a few minutes to more than half an hour, depending on the temperature and the ratio of the deactivator to the initiator. Accompanying this induction period was a remarkable color change in the system, indicating transformation of Cu^{II} to Cu^{I} species. Therefore the induction period was due to the time required for deactivation of the radicals before reaching the atom transfer equilibrium. Despite the linear increase of the molar mass with conversion and the narrow molar mass distributions observed in reverse ATRP, the initiation efficiency was usually below 50%, calculated from the radical initiator added to the system (initiation efficiency $f = M_{n,th}/M_n = M_0 \cdot ([M]_0/2[I]_0) \cdot X/M_n$, with M_0, the molar mass of the monomer). This was mainly attributed to irreversible radical termination reactions in the aqueous phase where there was insufficient radical deactivator [169]. Consequently, both temperature and the concentration of the initiator affected the molar mass of the polymer, while the concentration of the copper complex and the surfactant had little influence.

In a reverse ATRP reaction the final latex was usually very stable. Particles of 150–300 nm diameter were obtained, and the particle size varied with the concentrations of the initiator, the copper complex, the surfactant and the temperature. Despite the similarity in particle size with classical emulsion and miniemulsion polymerizations, the kinetics of the reverse ATRP were fundamentally different. The

polymerization rate was found to be insensitive to the particle size and was entirely controlled by the atom transfer equilibrium. Further discussions will be given in Section 5.4.

Miniemulsion polymerization was also employed for reverse ATRP of *n*-BMA [172]. Although a very hydrophobic ligand, dNbpy, was used, addition of a hydrophobe such as hexadecane was still necessary to stabilize the tiny monomer droplets generated by sonication. Both an oil-soluble initiator such as AIBN and a water-soluble initiator such as V-50 were able to produce highly stable latexes with submicronic particles (~300 nm). The molar mass control was better with V-50 than with AIBN as the initiator, due to the faster decomposition rate of the former, thus affording a more rapid initiation. In addition, miniemulsion polymerization initiated by AIBN was slower than in bulk. This phenomenon was attributed to the lower initiation efficiency resulting in a smaller number of growing chains. The low initiation efficiency might originate from increased primary radical termination in the organic phase because of preferential partitioning of the deactivator to the aqueous phase, or from the radical termination in the aqueous phase. In the latter case, even if a water-soluble alkyl halide was generated via the reaction between a radical and a Cu^{II} species in the aqueous phase (with or without coordination to the ligand), an effective activation–deactivation cycle could hardly continue due to the absence of the activator from the aqueous phase (Cu^I species is much less soluble in water) [169]. This is a major difference between ATRP and NMP. In NMP no activator is needed in the aqueous phase to break the alkoxyamine C–O bond. Therefore, in SG1 mediated miniemulsion polymerization, the partitioning of SG1 actually enhanced the initiation efficiency due to the suppression of the radical termination in the aqueous phase (see Section 5.1.4)

5.3. Reversible transfer radical polymerization

5.3.1. Degenerative iodine transfer

Degenerative transfer process based on iodine atom exchange has been applied to the polymerization of styrene in emulsion and miniemulsion [181,182]. Perfluorohexyl iodide ($C_6F_{13}I$) was used as the transfer agent. It had been employed previously by Yutani et al. for the polymerization of fluorinated monomers [183] in batch and semi-batch emulsion polymerization processes. This molecule exhibits a rather small chain transfer constant of $C_{tr1} = k_{tr1}/k_p = 1.4$ in the bulk polymerization of styrene at 70°C [181]. Hence, a non-linear increase of DP_n with monomer conversion was expected and was actually observed in bulk [181]. In a batch emulsion system, addition of various concentrations of $C_6F_{13}I$ were shown to disturb neither the polymerization kinetics nor the colloidal characteristics of the latexes. However, a low transfer efficiency (50%) was observed with DP_n values being always above the theoretically ones and twice as large as $[M]_0/[C_6F_{13}I]_0$ at final conversion. This problem was ascribed to the slow diffusion rate of the hydrophobic transfer agent from the monomer droplets to the active particles, through the aqueous phase. This situation had already been encountered in classical emulsion polymerization when a very hydrophobic transfer agent was used such as dodecanethiol [184]. To check this hypothesis and overcome the problem, a batch miniemulsion approach was used. Since the transfer agent is initially located in the polymerization locus, no transport through the aqueous phase is required. A very classical recipe was used with sodium dodecylsulfate as the surfactant and ultrasonication to strongly shear the initial monomer-in-water emulsion. The perfluorinated transfer agent was considered as sufficiently water-insoluble to play the role of the hydrophobe, preventing Oswald ripening [181]. In one of the reported examples [182], the authors stated that only an oil-soluble initiator should be used. A water-soluble initiator provided no control over the molar masses of the polymer and this was ascribed to

the possible contribution of homogeneous nucleation. Nevertheless, the specific type of the failed water-soluble initiator was not mentioned. Contrary to this result, in another contribution [181], both oil-soluble (AIBN) and water-soluble (ACPA) radical initiators were successfully employed. As a consequence of the change from an emulsion to a miniemulsion system, the control over the molar masses was remarkably improved. As expected, the molar masses of the polymer increased with monomer conversion; although larger than theoretical at the beginning, they reached the predicted value at final conversion, just like in bulk system. The polydispersity index continuously decreased from approximately 2.0 to 1.5, indicating that the molar mass distribution resulted from an effective although slow exchange reaction. Polystyrene with molar mass as high as 60 000 g mol^{-1} could be obtained with relatively narrow molar mass distribution ($I_p = 1.5$). When polymerization was carried out with slow monomer addition instead of a pure batch process, the proportionality of M_n with conversion was obtained from the beginning but a continuous increase in DP_w/DP_n was observed [181]. The proportionality of DP_n with conversion was explained by the enhanced rate of transfer with respect to propagation owing to a high polymer/monomer ratio. The broadening of the MMD was ascribed to the high viscosity of the system (*interval III*) leading to reduced dynamics of exchange between the growing macromolecular species [181], or to polymerization preferentially occurring at the particle/water interface, resulting in the same effect [185]. Another source of broadening could be the existence of a secondary nucleation reaction which, because the absence of transfer agent in the newly created particles, would yield an uncontrolled polymerization. However, no evidence of secondary nucleation was observed in the described experiments.

The existence of iodine-terminated dormant chains was established by successful chain extension experiments performed by slowly adding a new charge of styrene after 90% conversion in the first miniemulsion step. A linear augmentation of DP_n with conversion was observed together with a shift of the SEC peaks. Under these experimental conditions, the DP_n values followed the theoretical line, but again a continuous increase of the polydispersity index was found (final values close to 2.0). Changing from styrene to *n*-butyl acrylate for the second step resulted in exactly the same behavior and led to the synthesis of polystyrene-*b*-poly(*n*-butyl acrylate) and polystyrene-*b*-poly(*n*-butyl acrylate-*co*-styrene) block copolymers [185].

One of the advantages of the polymerization in a dispersed system is the possibility of reaching high conversions in a short time. This feature was confirmed in both emulsion and miniemulsion polymerizations in the presence of $C_6F_{13}I$. Indeed, in the reported miniemulsion polymerizations, complete styrene conversion was usually achieved within 3 h [181,182]. The miniemulsion polymerizations led to stable final latexes with average particle diameter ranging from 90 to 150 nm and polymer content of 10–20 wt%.

5.3.2. Reversible addition-fragmentation transfer

5.3.2.1. CRP employing poly(methacrylic ester) macromonomers as transfer agents. Macromonomers of general structure $CH_2=C(Z)CH_2P$ (P: polymeric leaving group, Z: activating group) have been used as efficient chain transfer agents to control the polymerization of methacrylic esters in emulsion at 80°C, using a water-soluble initiator (ACPA or potassium persulfate) and an anionic surfactant (SDS) [186,187]. The first step consisted in the synthesis of a latex of poly(methacrylic ester) macromonomer by emulsion polymerization in the presence of a catalytic chain transfer agent, such as alkyl cobalt(III) complexes. Various macromonomers were prepared, namely poly(methyl methacrylate), poly(*tert*-butyl

methacrylate) and poly(phenyl methacrylate). Polymerizations were run to complete conversion and the resulting macromonomers exhibited a molar mass ranging from 1000 to 15 000 g mol^{-1} with a polydispersity index in the range 1.6–2.0. The second step was the slow addition of a new methacrylic ester monomer under starved-feed conditions. This second step led to chain extension (same monomer) or block copolymer formation (different monomers) by a reversible transfer reaction to the macromonomer via an addition-fragmentation mechanism (Fig. 4). Molar masses increased linearly with monomer conversion, remained close to the theoretical values, and I_p simultaneously decreased to reach typical values of 1.4–1.5. The molar concentration of terminal double bond remained constant throughout the polymerization indicating negligible copolymerization with the macromonomer. Owing to a very low transfer constant to the macromonomer (k_{tr}/k_p is 0.21 for PMMA macromonomer in the polymerization of MMA) [112], the higher the [macromonomer]/[monomer] ratio was maintained, the faster the transfer reaction was with respect to propagation. For this reason, and because of slow termination reaction, the authors stated that emulsion polymerization is probably the process best suited to achieve narrow polydispersities. However, no information on the latex colloidal properties was reported. Application of this technique to styrenic or acrylic monomers in the second step was not straighforward because of extensive copolymerization with the macromonomer, which could be minimized at higher temperature and/or lower conversions.

5.3.2.2. CRP employing dithiocarbonates (xanthates) as transfer agents. Among the dithio compounds which can be used as reversible addition-fragmentation transfer agents (Table 6), the dithiocarbonates (or xanthates) exhibit rather small transfer constants (see Tables 7 and 8, which summarize the values for C_{tr1} (RAFT agent) and C_{tr2} (polymeric RAFT agent formed), respectively). This can lead to polymerizations exhibiting the same features as observed in degenerative iodine transfer: M_n does not increase linearly with conversion, but eventually matches the predicted value (providing the transfer constant is larger than 1), and the polydispersity index is quite far above 1.

As with the dithioesters, the quality of the control can be tuned by properly selecting the leaving and activating groups [116]. A few xanthates have been employed in emulsion polymerization. For instance

Table 6

Dithio compounds of general formula Z–C(=S)S–R used as transfer agents in aqueous dispersed systems

Activating group Z	Leaving group R		Reference
C_2H_5O-	$-CH(CH_3)-C(=O)OC_2H_5$	X1	[116]
C_2H_5O-	$-CH(CH_3)-C_6H_5$	X2	[119,188,189]
C_2H_5O-	$-CH_2-C_6H_5$	X3	[119]
C_6H_5-	$-C(CH_3)_2-C_6H_5$	R1	[119,193,194]
C_6H_5-	$-CH(CH_3)-C_6H_5$	R2	[119]
C_6H_5-	$-CH_2-C_6H_5$	R3	[119]
CH_3-	$-CH_2-C_6H_5$	R4	[119]
C_6H_5-	$-CH_2-COOH$	R5	[196,197]
C_6H_5-	$-C(CH_3)_2-C(=O)NH_2$	R6	[196,197]
C_6H_5-	$-C(CH_3)_2-C(=O)OC_2H_5$	R7	[193,194]
C_6H_5-	$-C(CH_3)_2-CN$	R8	[194]
C_6H_5-	$-C(CH_3)(CN)-CH_2CH_2-$ $C(=O)O-$–poly(ethylene-*co*-butylene)	R9	[194]

Table 7
Transfer constants for some of the dithio compounds of general formula Z–C(=S)S–R used as transfer agents in aqueous dispersed systems (composite values including both the addition and fragmentation steps)

	C_{tr1}	Monomer	T (°C)	Reference
X2	1.5	*n*-BA	70	[188]
R1	10	MMA	60	[119]
R2	0.16	MMA	60	[119]
R3	26	S	110	[119]
	0.03	MMA	60	[119]
R4	10	S	110	[119]
R5	6	S	110	[197]
R7	2	MMA	60	[119]
R8	13	MMA	60	[119]

X1 (Table 6) has been tested for the emulsion homopolymerizations of styrene and *n*-butyl acrylate at 85°C, using sodium persulfate as the water-soluble radical initiator and SDS as the surfactant [116]. A semi-batch process was implemented. An oil phase composed of a small fraction of the monomer and all of the xanthate was dispersed in an aqueous solution of the surfactant and the buffer. The polymerization was started by addition of the initiator, and the remaining part of the monomer was continuously fed into the reactor, along with a second stream of initiator solution. The final latexes were stable with 30 wt% solid content and the particle diameter ranged from 40 to 112 nm. Importantly, no retardation was observed and neither the kinetics nor the particle size were affected by the addition of the xanthate transfer agent. For both styrene and *n*-butyl acrylate the final M_ns were in good agreement with the expected values (extending, respectively, from 17 000 to 10^5 g mol^{-1}). Poly(*n*-BA) exhibited narrower MMD that polystyrene, I_p being in the range 1.4–2.3 while it was systematically larger than 2.0 for polystyrene, typical of a slow exchange reaction. The chosen process, with continuous slow monomer addition, forced the system to remain in the *interval III* of emulsion polymerization. The high polymer/ monomer ratio enhanced the transfer reaction over propagation. Hence, in contrast to batch polymerization, M_n increased linearly with monomer conversion from the beginning, i.e. the transfer agent was incorporated in the polymer early in the reaction. Kinetic modeling showed that this situation of high polymer/monomer ratio should have two opposing effects: a decrease of I_p, but also an increase in the proportion of dead chains. Identical experimental conditions were implemented with the xanthates X2

Table 8
Transfer constants for some polymeric dithio compounds [192] (composite values including both the addition and fragmentation steps)

Structure of Z–C(=S)S–P	Monomer	C_{tr2}	
Z = CH$_3$; P = PS	S	3.1	exp(+11.5 kJ mol^{-1}/RT) 180 at 60°C
Z = C$_6$H$_5$; P = PS	S	6000 ± 2000 at 40°C (preliminary result)	
Z = C$_6$H$_5$; P = PMMA	MMA	140 at 60°C	

and X3 [119]. Styrene was polymerized at 80°C in the presence of SDS surfactant and ACPA initiator. Good control over the molar masses was obtained but MMD was broad ($I_p \approx 2.0$).

The dithiocarbonate X2 was also employed as a reversible tranfer agent for the batch emulsion polymerization of *n*-butyl acrylate [188] and styrene [189] and further use of the formed latexes as a seed for the growth of a second block. In the batch process, in contrast to the previous starved–feed conditions, the polymerization was strongly affected by the presence of the xanthate: all reactions exhibited an inhibition time of a few minutes. This retardation, not observed in bulk or solution, was assigned to the exit of the $R^{\cdot}$ radical from the particles and subsequent termination either in the water phase or in another active particle after re-entry [188]. This result is not typical of controlled emulsion polymerization using the RAFT technique but was also observed in emulsion polymerization employing a classical chain transfer agent [190,191]. In the batch homopolymerization of *n*-BA [188], owing to a rather slow consumption of the transfer agent because of low transfer constant ($C_{tr1} = 1.5$ in the *n*-BA polymerization), this effect operated over most of the conversion range. As a result of this slow transfer, M_n increased over the whole conversion range, but reached the theoretical value only at complete monomer conversion. The rather good agreement between the final experimental M_n and the theoretical value showed that the xanthate X2 did not exhibit the same slow diffusion effect observed for $C_6F_{13}I$. P(*n*-BA) with a M_n as large as 140 000 g mol^{-1} could be obtained and I_p displayed a continuous decrease with conversion, from approximately 2.0 to 1.6. Kinetics of the batch emulsion polymerization of styrene in the presence of X2 was studied as a function of the respective concentrations of initiator ($K_2S_2O_8$), surfactant (SDS) and RAFT agent [189]. In particular, the fate of the $R^{\cdot}$ radical after it exits from the particles was shown to depend on the initiator concentration. Indeed, at low initiator concentration, $R^{\cdot}$ might participate in the nucleation step (reentry in micelles) and increase N_p, while at high initiator concentration, irreversible termination in water might dominate. For styrene, differently from *n*-butyl acrylate, the efficiency of the transfer reaction was not always 1. This result was not attributed to a slow diffusion process or to side reactions affecting the concentration of X2, but by the possible surface-active character of X2 in this system, leading to a modification of its local concentration.

The P(*n*-BA) latexes were stable with particle diameter ranging from 38 to 58 nm and were subsequently used as a seed for the second-stage emulsion polymerization of styrene, which was carried out either batchwise or semi-batchwise at 70°C. When the second step was performed under batch conditions, the polymerization rate was not affected by the concentration of dormant chains in the seed (acting as transfer agent), most probably because it was impossible for the polymeric radicals to exit the particle after being produced by transfer. Block copolymers were formed, starting either with P(*n*-BA) [188] or with PS [189] as the first block. The blocking efficiency was improved when the second step was performed under starved–feed conditions instead of batch conditions.

5.3.2.3. CRP employing dithioesters as transfer agents. Dithioesters usually exhibit larger transfer constants in the polymerization of styrenic, acrylic and methacrylic monomers than dithiocarbonates (Tables 7 and 8, [192]). The dithioester R1 was the first one reported to be an efficient transfer agent for the emulsion polymerization of *n*-BMA at 80°C, using ACPA as the radical initiator and SDS as the surfactant [113]. A semi-batch process was employed, yielding 95% P(*n*-BMA) within 2 h, with $M_n = 57\,700$ g mol^{-1} (theoretical $M_n = 60\,000$ g mol^{-1}), $I_p = 1.22$. No additional information on the colloidal characteristics of the latex were presented.

Later, the same group reported the use of a set of four RAFT agents (R1–R4; in addition to the two xanthates presented above) for the emulsion polymerization of styrene, methyl methacrylate and for the

preparation of block copolymers [119]. Again, the semi-batch process was applied, with slow introduction of the monomer into the emulsion containing a small part of the monomer and the overall amount of the RAFT agent. The instantaneous conversion was maintained in the range 90–99% by a proper adjustment of the addition rate. In the emulsion polymerization of styrene carried out at 80°C, the best results were obtained with R3 and R4 leading to polymers displaying good control over the molar mass, with polydispersity indices below 1.4. The MMD was therefore narrower than with either of the two xanthates X2 and X3. With the cumyl dithiobenzoate R1, retardation was observed in the early stages of the polymerization and the final polydispersity index was very large (7.09). R1 afforded much better control in the emulsion polymerization of MMA, which was also performed at 80°C, since the polydispersity index was 1.54 at 85% conversion. To minimize retardation, the reaction conditions were however slightly changed with respect to styrene polymerization: the RAFT agent, dissolved in part of the monomer, was not introduced to the reaction in one shot, but continuously over a period of 10 min, in order to produce low molar mass PMMA transfer agent. However, this modification was not sufficient to reach the level of control exhibited in solution polymerization.

Both the PS and PMMA homopolymer latexes were used as a seed for chain extension with the other monomer (MMA and S, respectively), to synthesize the corresponding block copolymers by a one-pot procedure. When S was polymerized first, the addition of MMA yielded a block copolymer displaying the expected molar mass throughout the polymerization, despite a continuously increasing polydispersity index (from 1.35 to 1.57). In solution, the same order of monomer addition failed to produce a well-defined block copolymer, because of the low transfer constant of the PS RAFT agent in MMA polymerization. The success in semi-batch emulsion was assigned to the high polymer/monomer ratio, enhancing transfer over propagation. In the reverse experiment (MMA first), a linear increase of M_n with conversion was achieved in the second step, but again I_p increased continuously to reach values slightly larger than 2. Interestingly, the authors mentioned that batch conditions systematically gave poor results in emulsion, while a significant improvement was observed when polymerization of styrene was performed in a batch miniemulsion system. This process did not eliminate retardation however, but conversion reached 25% in 4 h yielding a narrowly distributed PS with M_n below the theoretical value. No indication on the colloidal characteristics was given.

Monteiro and co-workers [193] employed the RAFT agents R1 and R7 in a seeded emulsion polymerization recipe, in order to eliminate the nucleation step and set the number of particles. In contrast to the previous studies performed under *interval III* of emulsion polymerization, these reactions were performed in the presence of monomer droplets (*interval II*) and the purpose was to gain a better insight into the polymerization mechanism under such conditions. In particular, the effect of primary radical $R^{\cdot}$ desorption from the particles and the influence of the droplets were examined. The retardation effect, already observed by the same authors when using the xanthate RAFT agent X2 under batch conditions [188], was thoroughly examined here with dithioesters using seeded emulsion polymerization of S. Both transfer agents R1 and R7 are very similar regarding the transfer reaction: they exhibit similar transfer constant values as RAFT agents and both lead to the incorporation of the dithiobenzoate group at the chain-end. Therefore, no difference in polymerization rates was expected. However differences could arise since they have a different leaving group that should behave differently in an aqueous dispersed system because the probability of exit into water of the leaving radical after the first addition-fragmentation reaction strongly depends on its water-solubility. Hence the 2-(ethoxycarbonyl)prop-2-yl radical from R7, being more water-soluble than the cumyl radical from R1, has a greater probability to escape, once formed. This trend was expected to affect the polymerization kinetics in the early stage of the

reaction, before complete conversion of the RAFT agent. Indeed, retardation was observed for both transfer agents, and was more pronounced with R7. This retardation effect was not only observed at the beginning of the polymerization but over the entire conversion range. This result was quite unexpected since the transfer agents should be rapidly consumed owing to large transfer constants. Thus, it was suspected that a continuous slow transport of the transfer agent from the droplets to the particles was operating during *interval II*. This was also the reason for the broad molar mass distributions observed. Nevertheless, the authors proposed that the diffusion of the transfer agents R1 and R7 should be fast on the polymerization timescale and suggested that oligomeric RAFT agents were initially formed outside of the particles and that diffusion of these oligomeric agents should be very slow. This assumption was based on the observation that a red layer formed on top of the emulsion, immediately at the onset of the polymerization. This organic layer was ascribed to short dormant polymers swollen with monomer during *interval II*, further forming a red coagulant after disappearance of the monomer droplets. The slow and incomplete delivery of the transfer agent into the polymerization locus and the high initiator concentrations needed to compensate for the retardation effect were thus the main parameters which led to the strong deviation of M_n from theory.

In a subsequent work, de Brouwer et al. reported the use of a batch miniemulsion process to avoid monomer transport problems and employed various dithioesters such as R1, R7, R8 and polymeric RAFT agents (R9 and PMMA with dithiobenzoate end-group) [194]. The polymerizations were very successful regarding the control over molar masses. Various homopolymers were prepared at 70°C: poly(2-ethylhexyl methacrylate), poly(methyl methacrylate), poly(*i*-butyl methacrylate), poly(*n*-butyl methacrylate) and polystyrene. In all cases, the experimental M_ns were in good agreement with the theoretical ones and the polydispersity indices were usually below 1.2 and never above 1.4. Poly(2-ethylhexyl methacrylate)-*b*-polystyrene), poly(2-ethylhexyl methacrylate)-*b*-poly(methyl methacrylate) and poly(2-ethylhexyl methacrylate)-*b*-poly(methyl methacrylate-*co*-methacrylic acid) block copolymers were also synthesized. When MMA was added in one shot in the second step, a secondary nucleation was evidenced leading to the formation of a latex with two different types of particles: the expected block copolymer particles and a crop of particles containing uncontrolled PMMA, resulting most probably from homogeneous nucleation. Finding the proper conditions for the preparation of a stable latex was however not straightforward. The usual recipe to prepare the initial miniemulsion was applied with various ionic surfactants and various hydrophobes in different combinations. While the monomer-in-water miniemulsion was always stable before the onset of polymerization, as soon as the reaction started, destabilization occurred with formation of an organic red layer on the top of the system [194,195]. This organic layer was composed of monomer and low molar mass polymer. This situation was observed with every initiator used (water-soluble potassium persulfate; oil-soluble AIBN, V-40 and VA-086) and for all the monomers. The only way to avoid this destabilization was the use of a non-ionic surfactant of relatively high HLB (in the range 15.3–17.8) in conjunction with hexadecane or Kraton. Under these conditions a polymerization initiated with potassium persulfate at 70°C proceeded in the absence of the formation of the separate organic layer, leading to stable latexes with particle diameters in the range 220–340 nm. The phase separation phenomenon was however not clearly understood.

Dithioesters with structures different from those designed in the group of Rizzardo et al. have been used by Claverie et al. [196,197] in batch emulsion polymerization. The commercially available S-thiobenzoyl-thioglycolic acid (R5) did not prove to be a very efficient RAFT agent in styrene emulsion polymerization. In the acidic form, efficiency was low because of poor water-solubility and the latex exhibited extensive coagulation whereas use of the sodium salt of R5 led to uncontrolled behavior. The

proposed explanation relies on the high water-solubility of R5 salt in conjunction with a low transfer constant: water-phase generated oligoradicals can enter the particles without undergoing transfer. A new and supposedly more efficient RAFT agent was prepared in situ by reacting R5 in aqueous solution with a large excess of a water-soluble azo initiator (V-50) at 95°C for 2–8 h. In the presence of triethylamine, hydrolysis of the amidine group into amide could be observed, yielding the molecule R6. When used in situ in the batch emulsion polymerization of styrene stabilized with CTAB, this RAFT agent led to a well controlled polymerization with a linear increase of M_n with conversion, a good match between experimental and theoretical values and final I_p between 1.5 and 2.0. The latex was stable with 17 wt% solids content and no observable floc. With other monomers such as MMA and vinyl acetate, the control was however more problematic. Preparation of a triblock copolymer of styrene, *n*-butyl acrylate and acrylic acid was also achieved using the same system, in spite of a slow polymerization rate and high polydispersity (2.42) of the final polymer [196].

5.4. Peculiarities of kinetics in controlled/living emulsion and miniemulsion polymerizations

Because of radical segregation, conventional emulsion and miniemulsion polymerizations usually exhibit slow termination reactions (long-lived radicals) resulting in much faster polymerization than in the homogeneous systems under similar conditions. This kinetic behavior, however, has not yet been systematically observed in controlled/living radical polymerizations. Instead, CRP systems display a few unique features.

5.4.1. Nucleation step

First, the difference in particle formation processes between conventional emulsion polymerization and CRP systems with water-soluble radical initiator such as bicomponent NMP, reverse ATRP and RAFT (with large transfer constant for the transfer agent) should be emphasized. The particle formation step is very complex in conventional radical polymerization. Particles are formed from oligoradicals generated in water, which grow by adding monomer, then reach a critical size at which point they exclude themselves from the aqueous phase (involving micelles if present). This exclusion step is generally accompanied by a fast growth of the radical before termination (because of the much higher monomer concentration in the so-formed organic locus than in water and as a result of the segregation effect). Therefore, this step is irreversible and the new chain cannot desorb from the nuclei to the water-phase. The situation should be completely different in CRP, as the large majority of the chains are created early in the reaction and grow quite slowly throughout the polymerization process. In these systems, the short dormant chains formed initially are sufficiently small and hydrophilic (they contain a charged initiator fragment at one end) to partition between the aqueous and the organic phases. In other words they are not irreversibly trapped in the organic phase as in conventional emulsion polymerization, and redistribution can be expected until they reach a critical size. Thus, well-defined small nuclei cannot form and the so-called nucleation step is delayed and prolonged. For this reason, colloidal stability as well as narrow particle size distribution become a challenge.

In emulsion polymerization, to ensure good control of the polymerization occurring in the particles during *intervals II* and *III*, the control agent should be hydrophobic. However, with occurrence of propagation in the aqueous phase before nucleation as well as transport from the droplets to the active particles during *interval II*, the control agent should also exhibit a certain degree of water-solubility. Success therefore depends on attaining a good balance between the hydrophobic and the hydrophilic

character of the control agent. Miniemulsion polymerization simplifies the nucleation process and allows the use of very hydrophobic control agents and/or hydrophobic unimolecular initiators (for direct ATRP and NMP with an alkoxyamine initiator), therefore providing a more direct pathway from bulk to aqueous dispersed medium. Indeed, better control of (co)polymer characteristics has been obtained from miniemulsion polymerization rather than from true emulsion systems.

5.4.2. Kinetics

Depending on the polymerization method and the nature of the control agent, the kinetics of different CRP systems display altered characteristics. Those operating via a reversible termination reaction (NMP and ATRP) do not follow the same kinetics as a conventional radical polymerization. They are governed instead by the activation–deactivation equilibrium (Figs. 2 and 3). The transient and persistent radical concentrations are regulated by the persistent radical effect [107–109] rather than by a steady state resulting from an initiation/termination balance. As a consequence, reversible termination is favored due to the large concentration of deactivator, which continuously increases with conversion. A steady state holds only in styrene polymerization when thermal self-initiation continuously produces radicals ($T > 100°C$) [198], or when a radical initiator with slow decomposition is purposely added [199,200].

5.4.2.1. CRP via reversible termination (NMP and ATRP). A theoretical kinetic analysis based on the persistent radical effect (no other source of radical generation than the activation reaction) was applied to miniemulsion systems [201]. The instantaneous rate of polymerization is proportional to $[P^\cdot]$ and inversely proportional to the concentration of deactivator at a given time (as shown in Figs. 2 and 3). In a NMP miniemulsion system, the concentration of released nitroxide owing to the PRE at a given monomer conversion x is equal to the concentration of irreversibly terminated chains, and is given by:

$$[X^\cdot]_{(ME)} = -A + \sqrt{(A + [X^\cdot]_0)^2 - B\cdot\ln(1 - x)}$$

with $[X^\cdot]_0$ representing the initial concentration of nitroxide in the system,

$$A = \frac{k_t}{N_A \cdot v_p \cdot k_c}$$

and

$$B = \frac{4\cdot K\cdot [P - X]_0 \cdot k_t}{k_p}.$$

In a bulk polymerization the same relationship leads to:

$$[X^\cdot]_{(BULK)} = \sqrt{[X^\cdot]_0^2 - B\cdot\ln(1 - x)}$$

From simple mathematics, $[X^\cdot]^2_{(BULK)} = [X^\cdot]^2_{(ME)} + 2\cdot A\cdot([X^\cdot]_{(ME)} - [X^\cdot]_0)$, so that $[X^\cdot]_{(BULK)} \geq [X^\cdot]_{(ME)}$. Therefore, the difference between the concentrations of free nitroxide released at a given conversion in bulk and miniemulsion is to a large extent determined by the value of parameter A, which is dependent on the size of the particles (V_p: particle volume) for a given monomer and a nitroxide. When the particles are very small, A is large and $[X^\cdot]$ is larger in bulk than in miniemulsion, indicating

the greater degree of irreversible termination. As a consequence, the polymerization should be faster in miniemulsion than in bulk, the proportion of dead chains should be smaller, but the molar mass distribution should be broader. The polydispersities can be reduced by addition of free nitroxide. However, when particle volume is larger, A becomes smaller and the concentration of released nitroxide is nearly the same in both systems. Consequently, the compartmentalization effect does not operate any longer. This conclusion, although derived from consideration of NMP systems, can be applied to ATRP systems as well.

The critical diameter at which the polymerization rate becomes significantly faster, or the proportion of terminated chains generated at the same rate becomes significantly lower (for instance, 50% improvement in miniemulsion than in bulk) is influenced by the target degree of polymerization (DP_n), k_t, k_c, k_p and k_a. Nevertheless, it appears from simulations that a large rate enhancement is not expected, with the usual nitroxides, for the range of particle size usually obtained in emulsion and miniemulsion (from 50 to 500 nm). This results from the typical small k_t/k_c ratio (from 1 to 20 approximately), except in the case of the SG1-mediated polymerization of styrene, for which $k_t/k_c \gg 100$. As a consequence, the overall concentration of propagating radicals (relative to the organic phase volume) is not much larger in a miniemulsion system than in the corresponding bulk polymerization. Therefore, the average number of radicals per particle is simply inversely proportional to N_p and usually far below 1, while the average number of deactivator molecules per particle is much larger than 1 (typically from a few tens to a few hundreds). Indeed, most of the nitroxide-mediated and atom transfer miniemulsion polymerizations initiated with an oil-soluble species (monocomponent or bicomponent systems) exhibit the same polymerization rate as in bulk. They were sometimes slower, but this could be caused by side reactions and low initiator efficiency. In other words, a pseudo-bulk kinetics operates and polymerization rate is independent of N_p.

Therefore, decreasing the particle size does not seem to be the simplest and most efficient way to increase the rate. On the other hand, partitioning of the control agent between the aqueous and organic phases, as well as a slow decomposition of the radical deactivator in the organic phase, may affect the polymerization rate more significantly, but these possibilities have not yet been examined carefully. NMP systems using a water-soluble radical initiator ($K_2S_2O_8$ in conjunction with TEMPO or $K_2S_2O_8/Na_2S_2O_5$ in conjunction with SG1) exhibited faster propagation than in bulk [148,152,154,155,157]. While partition of the nitroxide between the aqueous and the organic phase was considered as the main cause, it now seems more reasonable to suspect a slow degradation of the nitroxide during the course of the polymerization, either because of acidic conditions or by side reactions with the initiator components. Only one group described a propagation faster than in bulk with the use of an organic alkoxyamine macroinitiator, although particle size was rather large (200 nm); the reasons for this unexpectedly fast reaction, however, were not explained [157]. The influence of partitioning of the control agent on the polymerization rate in ATRP system is also noteworthy, but unfortunately, the effect is often shadowed by low initiation efficiency [172]. When the metal complexes are highly hydrophilic, the polymerization usually displays a higher rate than in bulk under otherwise identical conditions, but the control of the molar mass and MMD is lost [170].

5.4.2.2. CRP via reversible transfer. When controlled/living radical polymerization is performed via a reversible transfer method, the systems is maintained in a classical steady state because of continuous radical generation. Thus, kinetics should not differ from that observed in a conventional radical polymerization: in emulsion polymerization, the zero/one kinetics should apply, R_p should depend on N_p etc.

Nevertheless, when the hydrophilicity and the reactivity of the transfer agent are taken into account, differences are observed in emulsion and miniemulsion polymerization and one of the following three cases is generally encountered.

(i) Very hydrophobic transfer agent with a low transfer constant, such as $C_6F_{13}I$ [181,182,185]. The transfer agent has almost no effect on the polymerization kinetics. In emulsion polymerization the nucleation step is not affected, and the same number of particles are obtained with and without the transfer agent. This situation is a consequence of the formation of chains with large DP_n at the onset of the polymerization as a result of the low transfer constant. Thus, the nucleation step, requiring the fast formation of hydrophobic nuclei, is similar to conventional radical polymerization. In addition, the hydrophobicity of the transfer agent prevents the exit of the small radical formed upon primary transfer, hence avoiding retardation through subsequent termination in water. However, in this case, only the miniemulsion process allows for high transfer efficiency thereby achieving relatively good control of the polymerization.

(ii) Transfer agents with a low transfer constant and intermediate hydrophilicity, such as xanthates and some dithioesters [116,119,188,189]. In batch systems a retardation effect is observed owing to the possible exit of the radical, $R^{\cdot}$, from the particle. Controlled polymerization can be achieved in emulsion and not necessarily in miniemulsion. Semi-batch conditions with starved monomer feed (forced *interval III*) are preferred to avoid the retardation effect and to enhance the transfer reaction over propagation.

(iii) Transfer agents with a high transfer constant and intermediate hydrophilicity, such as dithioesters [119,193–195]. Retardation in emulsion and miniemulsion occurs and stability of the latex is strongly affected. This phenomenon most probably arises from the very fast transfer reaction that can lead initially to very short oligomers that cannot properly participate in the nucleation step. Conditions of the miniemulsion process have to be carefully adjusted so as to form stable latexes.

In summary, for all CRP systems in aqueous dispersed media, the nature of the radical mediator (nitroxides, transition metal complexes, reversible transfer agents) plays a particularly important role. Its functions are not limited to participating in the equilibrium between radical and dormant species, and hence achieve the control over molar mass, MMD, functionality as well as control over the polymerization rate. The difference between CRP in aqueous dispersed media and their homogeneous organic counterparts is that additional control over the kinetics is also expected from partitioning of the radical mediator in aqueous/organic phases in the former systems. Furthermore, the radical mediator also affects the stability of the latex by producing a large concentration of short polymers in the initial stage of the polymerization, hence changing the nucleation step. On the other hand, particle size, one of the most important parameters affecting polymerization rate in conventional emulsion and miniemulsion, has different impact on CRP kinetics depending on the method used, with the influence being much less noteworthy for NMP and ATRP than for reversible transfer.

6. Conclusions

Several controlled/living radical polymerization systems have been examined in the presence of water. They include polymerizations carried out in both the homogeneous aqueous solutions and the various heterogeneous media, i.e. dispersion, suspension, emulsion and miniemulsion. The most

commonly used methods allowing control of radical polymerization have been represented such as nitroxide-mediated polymerization, atom transfer radical polymerization and reversible transfer. Application of these techniques to aqueous systems that had been well developed in homogeneous organic phases is far from straightforward. The control agents have to be carefully selected so that they are stable and efficient in the presence of water. The existence of at least two phases in dispersed aqueous systems complicates considerably the mechanisms employed for control. The field is however of great interest and is undergoing a fast evolution. The aim is to reach the same level of control that will allow the preparation of materials with the same complex architectures in aqueous systems, as it is now possible in the polymerizations conducted in organic media. Additional work is still required to accomplish this task, but success can be predicted in the near future.

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