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POLIMERY

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Progress in controlled/living polymerization (CLP) in aqueous media

Part III. CONTROLLED/LIVING POLYMERIZATION IN AQUEOUS MEDIA***)

Summary — A review with 69 refs. covering ionic polymerizations, coordination polymerizations ROMP, radical polymerizations such as degenerative transfer radical polymerization (DTRP) including iodine transfer polymerization and reversible addition-fragmentation chain transfer (RAFT polymerization), nitroxide-mediated polymerization (NMP) and atom transfer radical polymerization (ATRP). CLP in aqueous media, though developing rapidly, is still in its infancy. Precise manipulation of the polymerization process in aqueous dispersed media should enable various polymers with tailored properties to be prepared in the near future.

Key words: controlled/living polymerization, water, aqueous medium, living cationic polymerization, living coordination polymerization, living ring opening metathesis polymerization (ROMP), degenerative transfer radical polymerization, reversible addition-fragmentation chain transfer (RAFT) polymerization, nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP).

Conventional polymerizations carried out in aqueous media encounter the same problems as their counterparts in organic media, *i.e.*, numerous chain breaking reactions occur, increasing the heterogeneity of the polymers and preventing a precise control of polymer properties (*cf.* Part II). Taking radical emulsion polymerization as an example, the molecular weight is controlled mainly by adding chain transfer agents. The composition of a copolymer is manipulated to a large extent by controlling the very polymerization process. These rough strategies, however, fail to secure the ultimate goal of fine tuning the polymer properties at the molecular level.

With the rapid development of CLP in organic homogeneous systems, one of the major concerns is: can these methods be extended so as to include the aqueous media? A significant amount of research that has been conducted toward this goal in the decade is summarized below.

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IONIC POLYMERIZATIONS

The facile interaction between water and ionic species requires strictly anhydrous conditions to prevail in CLP. However, in the controlled/living systems based on a rapid equilibrium attained between a small amount of active ionic species and a dominating dormant covalent species, the influence caused by chain transfer or termination of the ionic species with water should become diminished. Nevertheless, so far no controlled/living anionic polymerization has been achieved in aqueous media, probably because even the dormant species at the equilibrium is unstable in water.

Recently Sawamoto *et al.* [1] have reported that controlled/living cationic polymerizations of styrene and substituted styrenes (*p*-alkoxy, hydroxy, methyl, chloro) can be accomplished in the presence of water, or even in aqueous media (with or without a surfactant). The molecular weights rose as the monomer conversion was increased and the polydispersities were low (<1.5 in most systems). The cationic nature of the polymerizations was determined by ^{1}H NMR as well as by adding ionic and radical terminators. Random and block copolymers of *p*-hydroxystyrene and *p*-methoxystyrene were also prepared under appropriate aqueous conditions. The success of these polymerizations lies in the following factors:

(*i*). Relatively water-resistant Lewis acids were used, such as BF_3OEt_2 or triflates of Ln (Ln = Yb, Sc, Sm, Nd, Dy), Sn, Cu, and Zn. The triflate group acted as a strong electron-withdrawing group to increase the acidity of the Lewis acids.

(*ii*). Relatively stable dormant species in water were formed. The end groups C-Cl, C-OH and C-OEt attached to styrenes were reluctant to enter into side reactions in water, which provided the nearly constant concentration of the growing polymer chains if the end groups were able to be re-activated (even so, loss of end group was still observed) In contrast, the polymerization of isobutyl vinyl ether (IBVE) was uncontrolled, because the C-Cl end group bound to IBVE easily reacted with water to form an unstable hemiacetal and this reaction was followed by elimination of β-hydrogen.

(*iii*). When surfactants were used, polymerization occurred in the interior of droplets which helped to protect the active cations from contact with water, and thus reduced the chances of chain transfer and termination. Nevertheless, at conversions exceeding 30% in the polymerization of *p*-methoxystyrene catalyzed by $Yb(OTf)_3$, the actual molecular weights deviated considerably from the calculated values, thereby indicating the occurrence of extensive transfer reactions in this system. The transfer product bearing the C-OH terminus could not be re-activated by $Yb(OTf)_3$.

(*iv*). When BF_3OEt_2 was used as the catalyst, the C-OH terminus formed by chain transfer to water could be re-activated and continue propagation. Thus, water actually served as a reversible chain transfer agent. Consequently, the polymerization rate and the polydispersities were influenced by the amount of water in the system. The larger amount of water, the slower the polymerization and the narrower the molecular weight distribution due to the decreased concentration of active cations. The maximum amount of water added to the system was 1.6 equivalents relative to BF_3OEt_2.

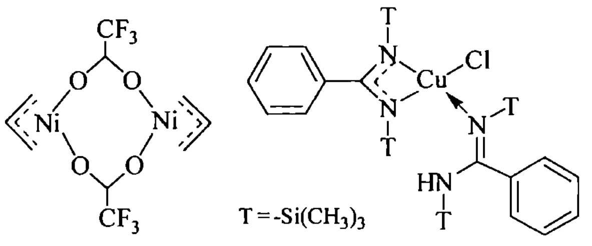
The livingness of the polymerizations was not interrupted by the addition of surfactants, regardless of their nature (ionic or nonionic). The colloidal properties were not reported, however.

Nomura *et al.* [2] have also reported on the cationic living ring-opening polymerization of lactones in the presence of water. The catalyst, $Sc(OTf)_3$, remained active when 20 equivalents of water (or 2 mol % *vs.* monomer) was added. The polymerization presumably proceeded *via* an activated monomer mechanism.

COORDINATION POLYMERIZATIONS AND ROMP

So far no controlled/living coordination polymerization has been conducted entirely in water. But a few polymerizations have been reported that display the living character and proceed with a significant amount of water in the system. Their common feature is the use of late transition metal complexes that remain robust in the presence of water.

Deming and Nowak [3] have reported on the polymerization of isocyanides catalyzed by $[(\eta^3\text{-}C_3H_5)Ni(OC(O)CF_3)]_2$ (1 in Fig. 1) in toluene at room temperature to remain living upon exposure to water and air. This result was achieved by using carefully designed water-resisting catalysts. In order to weaken the influence of the side reaction that involves reducing the active catalyst Ni(II) to a much less active Ni(I) by the isocyanide monomer, a highly electron-withdrawing trifluoroacetate group was introduced to activate Ni(I) by removing the electron density from the metal center. To accelerate the initiation rate, an allyl group which is known to undergo migratory-insertion reactions with isocyanides, an essen-



1 2

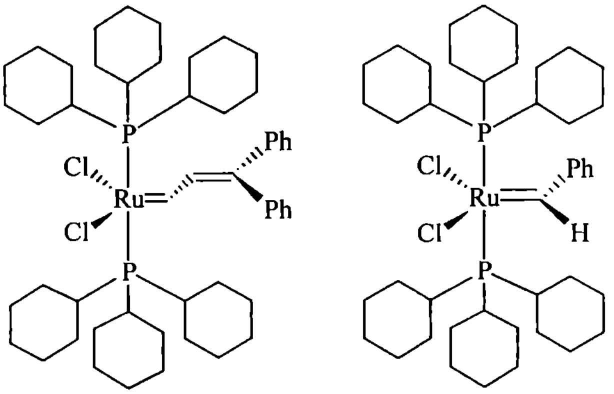
Fig. 1. Catalysts in controlled/living coordination polymerizations in the presence of water

tial step in the initiation of isocyanides, was also incorporated into the catalyst structure. As a result, molecular weights increased in direct proportion to monomer conversion, and polydispersities ranged on average from M_w/M_n = 1.1 to 1.6. Block copolymers have also been synthesized by sequential monomer addition.

The livingness of norbornene polymerization catalyzed by $[Pd(CH_3CN)_4][BF_4]_2$ was also found unaffected when water was added in excess (mole ratio of H_2O/norbornene/Pd^{2+} = 1000/200/1) [4].

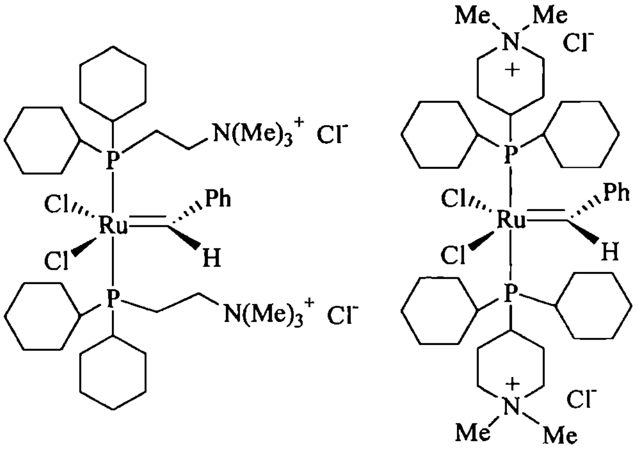
Another example of controlled/living system is the polymerization of carbodiimides initiated by a copper amidinate complex (**2** in Fig. 1) [5]. In this case, however, water actually deteriorated slightly the living character of the polymerization by acting as a mildly effective terminating agent. Therefore, both molecular weights and yields in wet solvents were lower than those in dry solvents, but the polydispersities were slightly higher.

For ROMP in aqueous media (*cf.* Part II), a number of late transition metal complexes were found effective as catalysts. Although the initiation rates of these polymerizations were shown to have been enhanced by water, apparently they were still incomparable with the propagating rates and no living polymerization was achieved. In 1996, Grubbs *et al.* [6] reported on the first living ROMP of functionalized norbornenes and 7-oxanorbornenes to run in aqueous media in the presence and in the absence of a surfactant. The structures of the two well-defined ruthenium carbene complexes are shown in Fig. 2.



1 **2**

Fig. 2. Grubbs catalysts for living ROMP in aqueous media



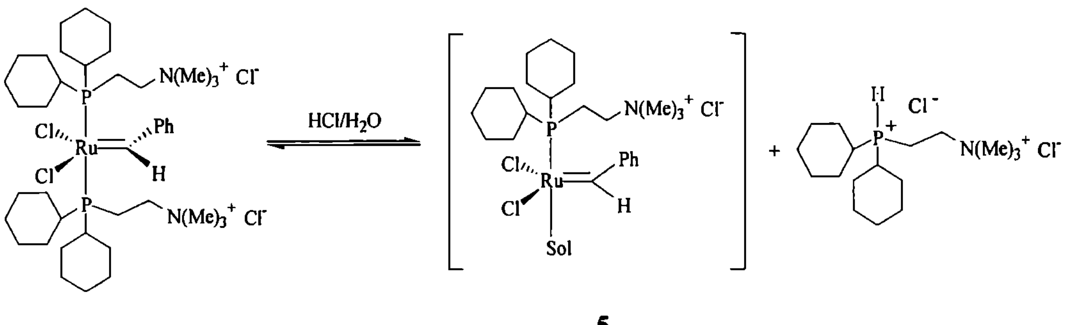
3 **4**

Fig. 3. Water soluble Grubbs catalysts for living ROMP

Both catalysts are insoluble in the aqueous phase. In order to increase the initiation efficiency, the catalyst was introduced into the polymerization system as a solution by using a small amount of organic solvents. The polymerizations took place in the organic phase and satisfied all the criteria for a controlled/living system, with or without a surfactant (stirring was necessary in either case). The success of these polymerizations is due to the fast and complete initiation relative to propagation, especially with **2** employed as the catalyst, partly because of the preferential coordination of water to the propagating species, which slows down the rate of propagation relative to the rate of initiation.

Later, the structures of the ruthenium catalysts (Fig. 2) were further modified to incorporate hydrophilic moieties so as to make the catalysts water soluble [7]. The new structures are shown in Fig. 3.

In combination with a Brønsted acid such as HCl, both catalysts quickly and quantitatively initiate the living polymerization of water-soluble monomers in a pure water solution. The Brønsted acid is essential to achieve livingness of the polymerization. It not only eliminates hydroxide ions that would decompose the cata-



3 **5** (1)

lyst, but also enhances the catalyst activity by protonating the phosphine ligands. Two long-lived propagating alkylidenes in equilibrium, corresponding to bisphosphine and monophosphine with the latter generated according to eq. 1, were directly observed by ^{1}H NMR. Their constant concentrations during the course of the polymerization confirm the absence of chain termination in these systems.

RADICAL POLYMERIZATIONS

Early attempts at controlling the chain growth in emulsion polymerization can be traced back to 1974. Mikulasova *et al.* [8] have studied the polymerization of styrene initiated by heterogeneous polypropylene hydroperoxide with an amine activator in emulsion. The molecular weights of the polymer were found to increase linearly with the degree of conversion (although missing the origin), and the polydispersities remained very low (M_w/M_n = 1.01—1.13). The livingness of the polymerization was confirmed by the fact that after the initiator had been removed from the emulsion by filtration, the polymerization still proceeded to 100% conversion and continued upon a successive addition of the monomer. In this way, a number of diblock and triblock copolymers of styrene and vinyl monomers such as methyl methacrylate, *p-t*-butylstyrene, acrylonitrile and maleic anhydride have been prepared [9].

Two factors are seen to account for the success of this system. First, a fast initiation system has been used. Only the peroxide group attached to the surface of polypropylene decomposes in the presence of styrene and an activator, generating radicals to initiate the polymerization at the surface. Therefore, the initiation ceases quickly (within 15 min at 35°C) and no more initiating radicals are produced during the remaining course of the polymerization. The latter is even assured by removing the heterogeneous initiator from the system *via* filtration a few minutes after the polymerization has begun. This fast radical generation provides the possibility of a simultaneous growth of all the chains. Secondly, once polymer particles are formed, the radicals inside the particles are protected by the compartmentalization effect. As long as there are no new radicals to enter the particles, these radicals remain active and thus become long-lived. The high efficiency in block copolymer formation (>90%) indicates to the absence of chain termination and transfer, the latter may be due to the low monomer concentration in the particles.

The drawback to this system, however, is the difficulty to get polymers with predictable molecular weights, because the number of the initiating centers located on the surface of the heterogeneous initiator is hard to control precisely. Moreover, homopolymerization has been limited to styrene only and no information on the distribution of molecular weights of the block copolymers is available. The removal of the initiator from the system also increases the complexity of the reaction apparatus.

A recent study showed the so-called "micellar organized graft copolymerization" of styrene with a poly(ethylene oxide) macromonomer to be also fairly "living" in character, as the molecular weights were found to rise linearly with monomer conversion up to 60% conversion [10]. This direct relation was ascribed to highly limited terminations between the compartmentalized propagating radicals. However, the polydispersities were high (M_w/M_n > 1.4) and a significant termination was noticed to occur at higher conversions. A similar result was obtained for the block copolymerization of *N*-isopropylacrylamide onto poly(ethylene glycol) in water triggered by a redox initiation system [11].

These physical methods aiming at extending the lifetime of radicals can diminish the termination of polymeric radicals as well as between polymeric radicals and small initiator-born radicals. However, they are in general unsuccessful in limiting the occurrence of termination originating from small radicals generated by chain transfer to monomer. Recently, a more comprehensive approach to gain control over chain growth in aqueous media has been practiced employing the strategies described in Part I. Since all the factors leading to chain breaking processes and broadening of *MWD*, such as slow initiation, termination and transfer, are treated at the same time, these chemical methods proved to be much more widely applicable than the physical methods.

Degenerative transfer radical polymerization

This can be regarded as a conventional radical polymerization occurring in the presence of a reversible chain transfer agent. Therefore, the kinetics in either homogeneous or heterogeneous system is similar to that of a classical radical polymerization proceeding under the corresponding conditions.

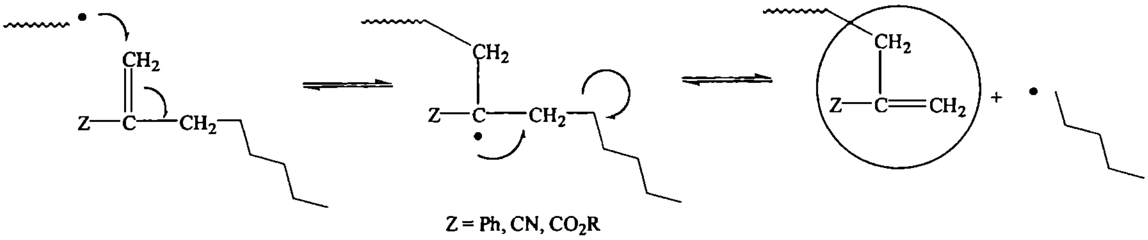
Iodine transfer polymerization

Degenerative transfer processes based on iodine atom exchange have been applied to the polymerization of styrene in emulsion and miniemulsion [12, 13]. Perfluorohexyl iodide ($C_6F_{13}I$) was used as the transfer agent. In an emulsion system, low transfer efficiency (50%) was observed, leading to doubled molecular weights as compared with those predicted by the Mayo equation. This problem, caused by a slow diffusion rate of the hydrophobic transfer agent through the aqueous phase, was overcome *via* miniemulsion approach. The transfer agent in the latter system was initially located in the polymerization locus, therefore, no transportation through the aqueous phase was necessary. As a consequence, the control over the molecular weights was remarkably improved, except that the plot of the molecular weights *vs.* conversion did not pass through the origin. This miss was due to the low transfer constant of $C_6F_{13}I$, which also explained the relatively broad distribution of molecular weights ($M_w/M_n > 1.5$) of the polymers obtained. Using a starved feed of the monomer, the consumption rate of transfer agent relative to propagation was forced to enhance, and a linear increase in molecular weights with the rising conversion was obtained [12]. This system has been successfully applied to prepare block copolymers of styrene and *n*-butyl acrylate [14].

Stable latexes with particle sizes ranging from 90—150 nm were obtained in miniemulsion. The polymerization rate was significantly faster than that in the bulk, presumably resulting from the compartmentalization effect, as normally observed in classical emulsion and miniemulsion polymerizations.

Addition-fragmentation polymerization

Macromonomers of the general structure $CH_2{=}C(Z)CH_2(A)_n$ (where $(A)_n$ — radical leaving group; Z — activating group) have been used as efficient chain transfer agents to control the polymerization of methacrylic monomers in emulsion, using water soluble initiator and anionic surfactant [15]. The process is based on a reversible addition-fragmentation mechanism (Scheme 1).



Scheme 1. Reversible addition-fragmentation polymerization

Provided the exchange rate of the end group (the structure within the circle in Scheme 1) between polymer chains is fast, homo- and copolymers with narrow molecular weight distributions can be prepared (M_w/M_n = 1.3—2.3). The major side reaction is the transfer to monomer and initiator. Therefore, a starved feed process in emulsion, which maximizes the transfer event to macromonomer, and a low concentration of initiator are helpful in achieving low polydispersities and high purity of block copolymers.

Not only methacrylic but also acrylic and styrenic monomers can be attained under proper conditions. However, no information on the latex properties has been reported.

RAFT polymerization

Moad *et al.* [16, 17] reported on the polymerizations of *n*-butyl methacrylate and styrene by RAFT in emulsion (batch, seeded, or continuous feed) or miniemulsion, using dithioesters (**1**—**3** in Fig. 4) as the chain transfer agents. A water-soluble initiator (4,4'-azobis(4-cyanopentanoic acid)) and an anionic surfactant (sodium dodecyl sulfate, SDS) were employed. Under mild conditions (80°C), the polymerizations reached high conversions (95—100%) in 2 hours or less, resulting in polymers with low polydispersities (M_w/M_n < 1.4). Block copolymers of MMA and styrene were synthesized by sequential monomer addition, and polydispersity was found to increase as the degree of conversion was raised. Other dithioesters were also tested, but the results were not satisfactory owing to low transfer constants, retardation effect, or poor solubility [17]. No other kinetic information and latex properties were available.

Claverie *et al.* [18] have utilized another dithioester (**4** in Fig. 4) generated *in situ* from the corresponding acid to control the polymerization of styrene and MMA in emulsion. Although molecular weights increased in direct proportion to monomer conversion, polydisperisties were relatively high (>1.5 for styrene, >3 for MMA), indicating a low transfer rate between propagating and dormant chains. Triblock copolymer of styrene, butyl acrylate and acrylic acid was also achieved in spite of a slow polymerization rate and high polydispersi-

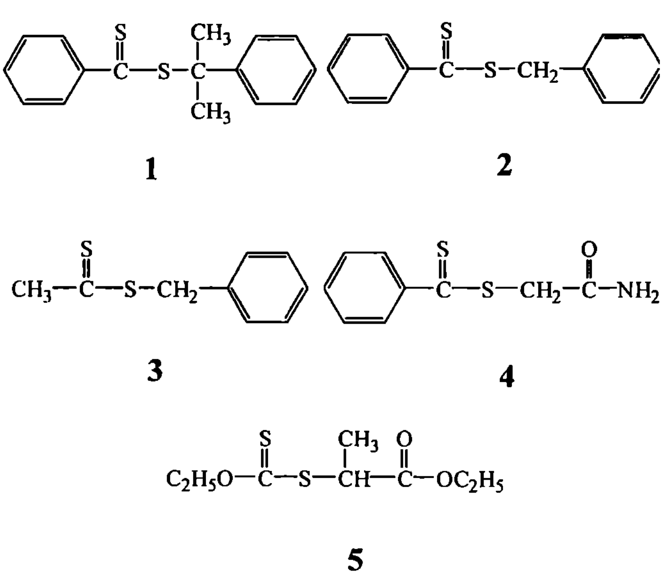
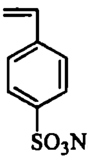
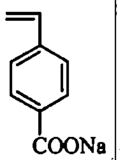
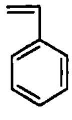
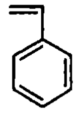
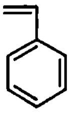
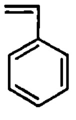
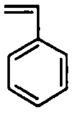
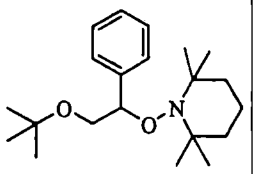
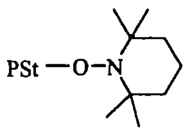


Fig. 4. Structure of chain transfer agents in RAFT

ty (2.42) of the final polymer. The latex particle size ranged from 120 nm to 350 nm, depending on the nature of the monomers. Broad particle size distribution was observed.

Table 1. TEMPO-mediated polymerizations in aqueous media

Media	Solution[1]	Seeded emulsion	*ab initio* emulsion[2]	Miniemulsion		Suspension	Dispersion[3]
Monomer	 						
Surf/Cosurf	—	anionic/none	anionic/hexadecanol	anionic/hexadecane		anionic/none	PVP[4]/none
Initiator	$K_2S_2O_8/Na_2S_2O_5$		$K_2S_2O_8$ or V-50[5]	BPO, or TEMPO-oligo(sty)	$K_2S_2O_8$		$K_2S_2O_8/$ $Na_2S_2O_5$
Temp., °C	120—125	125	130	125	135	120—135	112—130
M_w/M_n	1.12—1.33	1.41—1.54	1.14—1.78	1.4—1.9	~1.1	/	1.12—1.31
Latex property	—	unavailable	5% solid content, 500 nm, broad distribution	20% solid, 60—190 nm broad *MWD*	20% solid, 50—160 nm broad *MWD*	>1 mm	500 nm—3 μm broad *MWD*
Ref.	[45]	[46]	[21]	[47]	[48]	[49]	[50]

[1] Aqueous ethylene glycol solution, water/ethylene glycol = 1/4 ~ 1/3.
[2] 4-Amino TEMPO used as the radical trap.
[3] Aqueous ethylene glycol media, water = 5%, 15%, 25 wt %.
[4] PVP: poly(*N*-vinylpyrrolidone).
[5] V-50: 2,2'-azobis(2-methylpropionamidine) dihydrochloride.

Xanthates can also be used in RAFT [19]. The compound **5** in Fig. 4 was found to be consumed rapidly (within 5% monomer conversion) in the emulsion polymerization of styrene and *n*-butyl acrylate, giving excellent fit between the experimental and the theoretical molecular weights. Again, the distributions of molecular weights were relatively broad (M_w/M_n > 1.4), suggesting a slow xanthate exchange between polymer chains against propagation. The level of control was independent of the particle size, which ranged within 40—110 nm for styrene latexes.

It is noteworthy that, when the emulsion polymerization procedure is used, a good control of the polymerization requires a rapid diffusion rate of the RAFT agent from droplets to particles, so that all the polymer chains grow simultaneously. However, a fast diffusing RAFT agent also prompts a fast exit rate of the radical derived from the RAFT agent upon transfer, especially when the particle size is small. This might be the main reason for the drastic retardation of the polymerization observed in some aqueous dispersed systems [20].

Nitroxide-mediated polymerization (NMP)

TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) and derivatives have been used as radical mediators to control polymerizations in aqueous alcohol solution, seeded emulsion, *ab initio* emulsion, miniemulsion, suspension, and aqueous alcoholic dispersion (Table 1).

There are several common features of these polymerizations, especially in the heterogeneous systems. Firstly, only styrene and derivatives are polymerized successfully. Secondly, even if conducted at high reaction temperatures (>120°C), the polymerizations are generally slow, which originates from the small equilibrium constant in eq. 7 (*cf.* Part I). With oil soluble initiators, high polymer yields are obtained easily; however, only moderate monomer conversions are reached with water soluble initiators. The latter seems to be related to the solubility of the radical trap. Hydrophobic trap such as TEMPO mostly resides within the organic particles; therefore, when a water-soluble initiator is used the chain growth in the aqueous phase is uncontrolled and many radicals die. Thus, the stoichiometry between the radical trap and the radicals entering the organic phase is changed and ultimately the maximum conversion is limited. To improve the conversion, a balance between the aqueous and organic solubility of the nitroxide is critical. Claverie *et al.* [21] have studied the structural influence of several TEMPO derivatives on the polymerizations in emulsion (Fig. 5). Only amino-TEMPO that has appropriate solubility in both phases resulted in latex with reasonable conversion, other nitroxides gave conversions less than 1%.

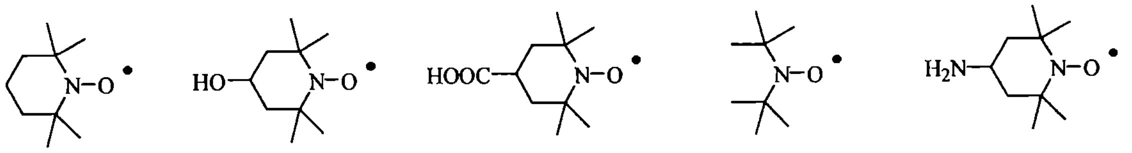
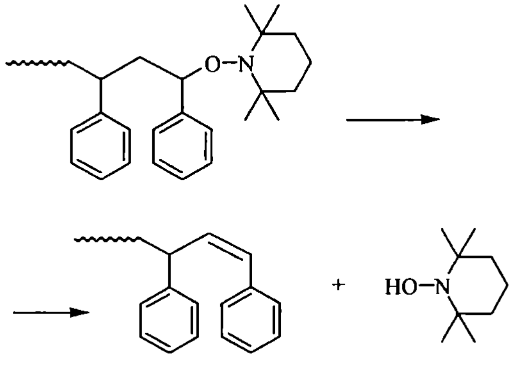


Fig. 5. Different nitroxides studied in emulsion [21]

The high temperature required for these polymerizations imposes many negative effects on the aqueous systems. First of all, the polymerization needs to be conducted under pressure since the temperature is above the boiling point of water. The harsh condition also causes problems in stabilizing the latex, as a result of an increase in Brownian movements of the particles as well as the decomposition of most commonly used surfactants at high temperature combined with long reaction periods. This probably explains the large particle size and broad particle size distribution (PSD) observed in all the heterogeneous systems (significant thermal autopolymerization of styrene may also contribute to the broad PSD in emulsion due to the initiation inside monomer droplets). Furtherome, many side reactions, such as the irreversible decomposition of the polymeric alkoxyamine (eq. 2), termination and transfer, thermal initiation of styrene, are enhanced at elevated temperatures, leading to increased polydispersities and dead chains. Finally, high temperature also prohibits the employment of monomers that are susceptible to hydrolysis.



(2)

To overcome these problems, polymerizations need to be performed at a reduced temperature; the use of a nitroxide is required, that enables a higher activation-deactivation equilibrium constant to be achieved than that obtained with TEMPO for styrene polymerization. *N-tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1, Fig. 6) has thus been applied in miniemulsion and batch emulsion systems [22]. Owing to a significantly higher equilibrium constant (K = 1.9 · 10^{-8} mol L^{-1} at 125°C as compared with the 2 · 10^{-11} mol L^{-1} for TEMPO at the same temperature), SG1 successfully accomplished CLP of styrene in these aqueous dispersed systems at 90°C.

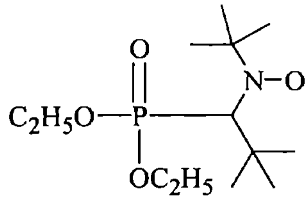


Fig. 6. Structure of SG1

Both oil-soluble (AIBN) and water-soluble ($K_2S_2O_8/Na_2S_2O_5$) initiators were employed in miniemulsion systems, the latter being used only in batch emulsion systems. Under each circumstance, molecular weights increased linearly with monomer conversion. In contrast to bulk polymerizations conducted under otherwise identical conditions, where the experimental and theoretical molecular weights matched very well, values higher than calculated were observed at a low conversion in the dispersed system. This was attributed to the heterogeneity of the dispersed system, which caused an apparent slow initiation due to the slow entry rate of radicals. Polydispersities decreased with conversion but remained systematically larger in a dispersed medium than in the bulk. This is presumably a consequence of a lower concentration of SG1 in the organic phase after partitioning. The polymerization rate was insensitive to the initial concentration of the surfactant, but significally affected by pH. Broad particle size distribution was observed in both miniemulsion and emulsion systems.

Atom transfer radical polymerization (ATRP)

2,2′-Bipyridine (bpy) forms a water-soluble complex with copper(I) halide (CuCl or CuBr), and has been used to catalyze the ATRP of hydrophilic monomers such as 2-hydroxyethyl acrylate (HEA) [23], oligo(ethylene oxide) methacrylate (OEGMA) [24, 25], sodium methacrylate [26], sodium 4-vinylbenzoate (NaVBA) [27], and 2-(dimethylamino)ethyl methacrylate [28], in aqueous solutions. Acidic monomers are generally challenging for the ATRP system, because the catalyst may be destroyed by either monomer coordination to the transition metal or by the protonated ligand that loses the complexing ability. It is hence not surprising that in the polymerizations reported above, pH plays a critical role. The optimum pH depends on the balance between the reduced propagation at a high pH, owing to the charge density built up on the polymer backbone, and the competing protonation of the ligand at a low pH. In addition, the choice of an appropriate initiator is also important. Under suitable conditions, facile synthesis of well-defined hydrophilic polymers can be achieved even at ambient temperature *via* ATRP in an aqueous solution. Compared with similar polymerizations in organic media, the aqueous polymerizations often display remarkably fast rates [25], which might correspond to the change of catalytic structures in different solvents.

ATRP of hydrophobic monomers has also been effectively conducted in heterogeneous aqueous media. A number of early studies indicated that polymerizations using Ni [29], Ru [30], Pd [31], Rh [31, 32], and Re [33] complexes as the catalysts could survive the presence of a significant amount of water. Suspension polymerizations of MMA with palladium and ruthenium catalysts, and with or without stabilizers have been investigated [34, 35]. In spite of the poor colloidal stability, moderate to good control over the molecular weights has been achieved.

As one of the most successful controlled/living radical polymerization systems, copper-based ATRP in aqueous dispersed media has attracted much attention [36—38]. However, the extension from organic homogeneous media is not straightforward and requires a suitable choice of many components in order to suit the new multiphase environment. The following points are considered the key to the success.

(*i*). 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 polymerization takes place. It is acceptable that the various components may change phase dynamically, as long as the system still allows for rapid activation and deactivation of all chain ends. The role of adjusting the partitioning behavior of the metal complexes is mainly played by the ligand. A proper ligand should have a sufficient binding affinity for the metal in order to compete with water as a potential coordinating molecule. At the same time, it should bring enough metal complexes (at both higher and lower oxidation states) in the organic phase. Not every ligand that works in the solution ATRP continues to be successful in water-borne systems. Only those ligands that display sufficient hydrophobicity [38, 39] (Fig. 7) can bring at least some activator and deactivator into the organic phase, and therefore maintain a fast equilibrium between the growing radicals and the dormant species. Whereas ligands such as bpy, *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA), *etc.*, that form water-soluble complexes with copper halide, are ineffective owing to the failure to establish the atom transfer equilibrium in the polymerization loci [39].

(*ii*). The surfactant is critical, too. A good surfactant does not effect the equilibrium between the radical and the dormant species and meanwhile affords a stable dispersed system throughout the polymerization. It has been demonstrated that the use of anionic surfactants such as sodium dodecyl sulfate (SDS) should be avoided due to their facile interaction with the catalytic system [37]. Both cationic and nonionic surfactants do not interfere with the livingness of the polymerization, however, only nonionic surfactants having HLB (hydrophile-lipophile balance) values within a suitable range result in stable latexes [40].

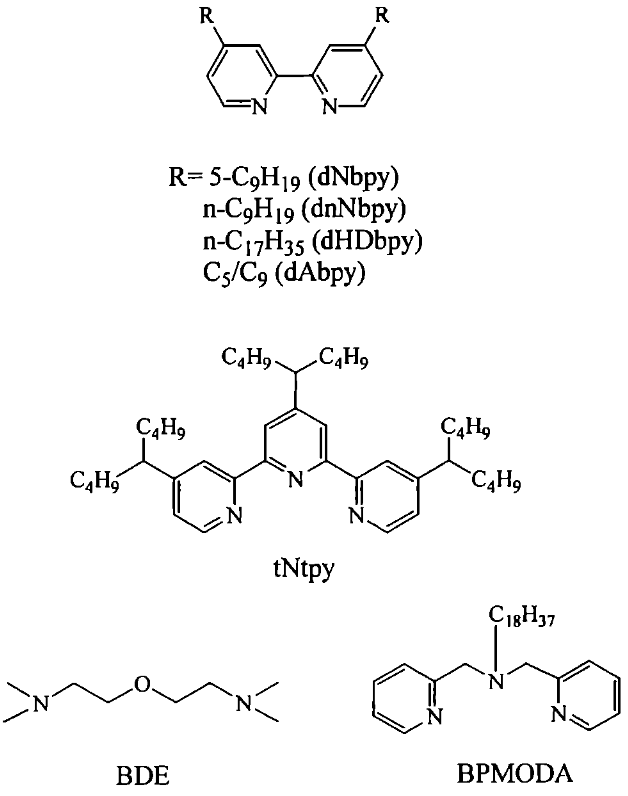


Fig. 7. Ligands successful for copper-based ATRP in aqueous dispersed media [38, 39]

(*iii*). The stabilities of the end group on growing chains and the catalytic system in the presence of water are also important. Since ATRP generally utilizes an alkyl halide as an initiator/dormant chain end, the hydrolysis of this group under the polymerization conditions should be minimized, if not totally avoided. From this point of view, acrylates and methacrylates are slightly better than styrene derivatives. Concerning the stability of the catalytic system, water is not a big threat to copper complexes owing to its much lower constant of coordination to copper as compared with the nitrogen ligands commonly used in copper-based ATRP [41]. Nevertheless, the partitioning study of CuBr/dNbpy and $CuBr_2$/dNbpy suggested partial dissociation of the copper complexes to occur in the presence of water [42].

Upon appropriate choice of the reaction recipe and the experimental conditions, a number of monomers, including acrylates, methacrylates, and styrenes, have been polymerized in a controlled way to yield well-defined homopolymers, and statistical and block copolymers with almost predictable molecular weights and narrow molecular weight distributions ($M_w/M_n < 1.5$) [37, 43]. An example is shown in Fig. 8. Analogous to those carried out in the organic system (*cf.* Part I), the atom transfer equilibrium can be approached in both

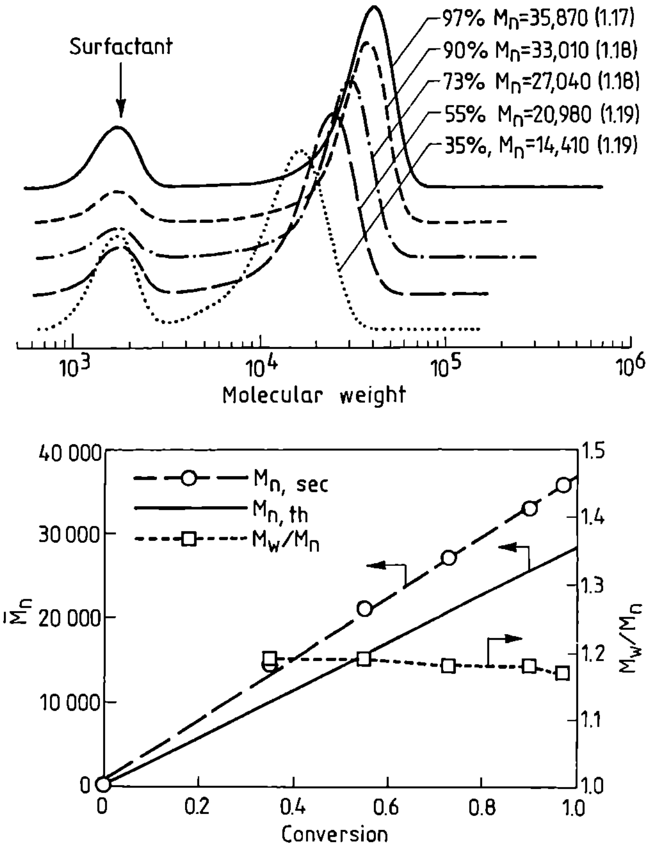


Fig. 8. SEC chromatograms and molecular weight evolution of the polymerization of n-butyl methacrylate (BMA) in aqueous dispersed media using dAbpy as the ligand. BMA/water = 1.5/10 (v/v), surfactant: Brij 98 (2 wt % vs. water); initiator: ethyl 2-bromoisobutyrate (EbiB); $[EbiB]_0$:$[CuBr]_0$:$[ligand]_0$ = 1:1:2; with 11% of $CuBr_2$ (vs. Cu total) added; 70°C

directions (eq. 7) in the aqueous dispersed media, namely, *via* direct and reverse ATRP.

The heterogeneous nature of the system makes the processes involved in the aqueous dispersed ATRP much more complex than those in the homogeneous systems. The kinetics and the colloidal properties have shown a strong dependence on the nature of the initiator and the experimental procedure. The direct ATRP, a process starting from an alkyl halide and a Cu(I) complex, usually yields particles with an average size larger than micron, suggesting a suspension mechanism. The reverse ATRP, which is started with a conventional water-soluble thermal initiator and a Cu(II) complex, produces particles similar in range as obtained in classical emulsion and miniemulsion polymerizations (< 500 nm). Despite this similarity, the kinetics of the reverse ATRP is fundamentally different from that of a classical emulsion or miniemulsion polymerization, and is controlled mainly by the atom transfer equilibrium [42, 44]. Miniemulsion process has also been successfully applied to ATRP. Highly stable latexes have been obtained regardless of the direct or reverse ATRP employed.

CONCLUSION

Although in its infancy, CLP in aqueous media is growing rapidly. With precise manipulation of the polymerization readily achievable in the aqueous dispersed media, it is anticipated that various polymers with tailor-made features should be available in the near future. This would tremendously enrich the materials synthesized in an environmentally favorable process, and extend the possibility of creating novel latex properties within a range far greater than previously envisaged.

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