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Modern trends in controlled synthesis of functional polymers: fundamental aspects and practical applications

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Major trends in controlled radical polymerization (CRP) or reversible-deactivation radical polymerization (RDRP), the most efficient method of synthesis of well-defined homo- and copolymers with specified parameters and properties, are critically analyzed. Recent advances associated with the three classical versions of CRP: nitroxide mediated polymerization, reversible addition-fragmentation chain transfer polymerization and atom transfer radical polymerization, are considered. Particular attention is paid to the prospects for the application of photoinitiation and photocatalysis in CRP. This approach, which has been intensively explored recently, brings synthetic methods of polymer chemistry closer to the light-induced processes of macromolecular synthesis occurring in living organisms. Examples are given of practical application of CRP techniques to obtain industrially valuable, high-tech polymeric products.
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1. Introduction

Currently, radical polymerization serves a basis for industrial production of polymers and materials based on them.[1,2] The proportion of polymers synthesized under the radical initiation conditions exceeds 50% of their global production. A great advantage of this method of synthesis is relatively low production cost of output products. Indeed, these polymerization processes are simple, low sensitive to impurities, proceed at rather high rates and afford a wide range of polymeric materials of different structure and chemical composition. However, classical radical polymerization has certain severe drawbacks originating from high reactivity of chain propagation radicals, especially, in regard to recombination and disproportionation processes. As a consequence, polymers synthesized under the radical initiation conditions are characterized by

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wide molecular-weight distribution while the properties of materials based on them often do not meet technological requirements. Besides, high polymerization rates and short lifetimes of growing chains significantly restrict the potential of macromolecular design and synthesis, in particular, in the synthesis of block copolymers and various branched polymer structures.

One of the most efficient solutions aimed at increasing the possibilities to synthesize polymers with specified properties and characteristics under the radical initiation conditions is to use the actively developing concept of controlled ('living') radical polymerization (CRP).[3–5] It offers great prospects for macromolecular design and makes it possible to synthesize polymers with specified architecture and chain-end functionalities. This creates prerequisites for subsequent structure modification and allows one to synthesize bioconjugates and organic/inorganic composites.

The aim of this review is to critically analyze the CRP concept and main trends of its development including prospects for practical application of this approach to industrial production of high-tech polymeric materials.

2. Radical-initiated controlled synthesis of homo- and copolymers: main techniques

The concept of controlled radical ('living') polymerization takes its origin from the concept of 'living' anionic polymerization proposed more than five decades ago[6] and is based on some original approaches that allow a growing polymer chain to survive for a time long enough to undergo certain synthetic transformations.

Numerous original studies and reviews have been published since the discovery of the CRP concept.[7–24] According to the Web of Science database,[25] more than 19 000 articles published since 1991 are available at the moment, thus being indicative of keen interest of researchers working in R&D departments of leading chemical companies and fundamental research institutions. Intensive research in this field is due to not only the development of ideas about the main regularities and methods for controlling radical polymerization of a wide range of monomers, but also the design of novel highly efficient regulators that enable different-scale (including industrial) synthesis of polymeric materials with specified properties.

2.1. Reversible deactivation of chain propagation radicals in polymerization processes: the timeline

The timeline of studies on CRP can be conditionally described as follows:

— discovery of reversible reactions between chain propagation radicals and various mediators;

— development of theoretical model for CRP using mediators based on compounds from different classes;

— practical application of reversible deactivation for 'living' polymerization of styrene and its analogues;

— development of CRP techniques and extension to controlled polymerization of a wide range of unsaturated compounds including acrylic and methacrylic monomers; and

— application of CRP techniques to macromolecular design including the synthesis of (co)polymers with specified architecture, topology and properties, as well as to industrial polymer synthesis.

The development of the CRP concept was preceded by intensive studies on ionic and coordination polymerization and on the use of inhibitors in radical processes and stimulated by advances in other fields of chemistry (Fig. 1).

The first attempts to perform controlled radical polymerization of vinyl monomers were made using sulfur-containing derivatives, in particular, thiuram disulfides.[26] However, these studies were unnoticed by the research community and in fact remained forgotten until the early 1980s when Otsu and Yoshida[27,28] proposed to use sulfur compounds for targeted control of polymerization kinetics and molecular-weight characteristics of polymers. They also coined the term 'iniferter' composed of fragments of the names for three elementary steps of radical polymerization, *viz.*, **ini**tiation, trans**fer** and **ter**mination. At present, iniferters include a wide range of organic compounds, *e.g.*, mono- and disulfides including cyclic ones, xanthogen disulfides, thiuram disulfides, thiocarbamates, (phenylazo)triphenylmethane, hexaphenylethane, diselenides, tetraphenylethane derivatives and other compounds.[29]

In historical perspective, foreign researchers working in the field of radical polymerization controlled by stable radicals usually give priority to publications by Rizzardo, Solomon and Moad,[30,31] who proposed to use sterically hindered nitroxide radicals, in particular, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), to control the polymerization kinetics and the molecular-weight characteristics of homo- and copolymers. These studies are often considered as the first attempts to use nitroxides in controlled synthesis of macromolecules. Not to take anything away from those authors, we find it necessary to say that very similar studies were carried out in the USSR well before. In particular, in the mid-1960s Buchachenko and co-workers[32] investigated the possibility of using nitroxide mono- and biradicals to inhibit radical

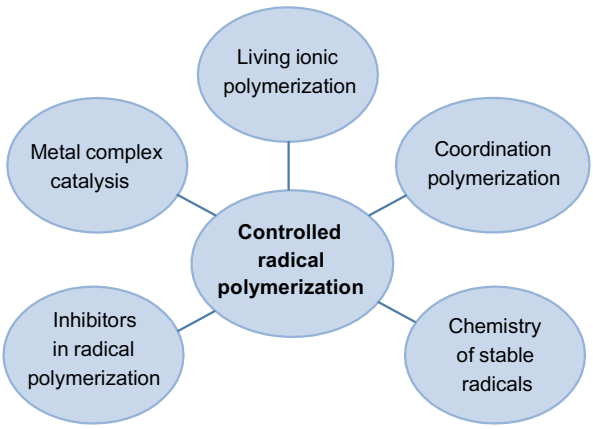


Figure 1. Main areas of chemical science underlying the development of the CRP concept.

polymerization processes. A few years later, researchers from the Ufa school of polymer chemistry thoroughly studied the inhibiting action of nitroxide spin adducts of different structure on the synthesis of polystyrene and poly(meth)acrylates under the radical initiation conditions.[33–35] They revealed the formation of alkoxyamines (AAs) in the polymerization system and established that AAs were rather stable at 60–80 °C and thus did not participate in subsequent reactions.

Georges *et al.*[36] reported an experimental study on the synthesis of polystyrene with low dispersity and for the first time made a substantiated assumption of the 'living' nature of styrene polymerization in the presence of nitroxide radicals at high temperatures. In fact, that work carried out as a logical continuation of the early research activity, appeared to be a cornerstone for one of the key avenues of research into controlled radical polymerization, related to reversible deactivation of growing macroradicals.

Theoretical models for controlled synthesis of macromolecules were developed more recently. First of all, mention should be made of B.R.Smirnov,[37] who was the first to formulate the concept of reversible-deactivation radical polymerization (RDRP) in the presence of both AAs[38,39] and metal complexes.[40,41] In 2001, Fischer[42] reported a fundamental theoretical review on CRP, a kind of a cornerstone for the concept of reversible deactivation in the presence of stable radicals. Subsequent rapid progress in this field was accompanied by accumulation of experimental data on 'pseudoliving' polymerization of a wide range of monomers in the presence of various iniferters and stable radicals, mainly nitroxides.[43]

In the mid-1990s the research groups headed by Matyjaszewski,[44] Sawomoto[45] and Percec[46] (unfortunately, he as a classic of CRP is mentioned much less frequently than the first two scientists) independently proposed to use systems based on organohalides and transition metal (in particular, copper, ruthenium and nickel) complexes to control polymerization processes. These studies led to emergence of a new direction of controlled synthesis of macromolecules, *viz.*, atom transfer radical polymerization (ATRP). Chemically, the main condition for realization of ATRP is the possibility for reversible redox reactions using transition-metal complexes to proceed in the reaction system.

2.2. Controlled radical polymerization: main methods, their classification and features

All methods of controlled synthesis of macromolecules known to date are based on the common principle of dynamic equilibrium between active ('living') and inactive ('dormant') states of the polymer chain. In this connection, the essence and main idea of CRP is to replace irreversible bimolecular chain termination through recombination or disproportionation of radicals including polymer growing macroradicals by reversible chain termination. In fact, in all these processes reversible thermal, photochemical and(or) chemical activation of 'dormant' polymer chains is used to regenerate the chain propagation radicals capable of interacting with the monomer and thus to continue the polymerization process and chain propagation.

Many CRP processes (except degenerative chain transfer) are based on the Fischer–Ingold effect (persistent radical effect),[42,43] *viz.*, predominance of highly selective cross-coupling reactions of active chain propagation radicals with stable radicals (or other mediators of polymerization) over bimolecular termination of growing chains even provided that the equivalent amounts of active and stable radicals are produced at the same rate from one source or two different sources. Predominance of cross-coupling products is due to the fact that active radicals produced upon breakdown of the 'dormant' chain can be irreversibly lost by the bimolecular chain termination mechanism, whereas stoichiometric amount of stable radicals generated during the same breakdown event are not lost and are accumulated in the system, which allows the polymerization process to proceed in controlled regime. However, the loss of radicals in homolytic processes through disproportionation or recombination cannot be totally excluded. To minimize the effect of the undesired bimolecular chain termination reaction resulting in a 'dead' polymer, the concentration of growing macroradicals in all controlled processes should be rather low compared to the concentration of stable radicals acting as mediators.

Successful control over the polymerization process requires that the deactivation rate of chain propagation radicals be more than tenfold higher than the rate of bimolecular termination of macroradicals. This numerical value of the ratio of the two parameters is responsible for specific features of both the polymerization kinetics and the molecular-weight characteristics of polymers being synthesized.

By and large, the features of RDRP are as follows.

1. A polymerization process affording well-defined polymers usually requires a high initiation rate (or the initiation time should be short enough compared to the duration of the overall process) to provide nearly simultaneous initiation of all polymer chains.

2. The concentration of active species in the system should be constant. This leads to linear dependence of the logarithm of the ratio of the initial monomer concentration to the current monomer concentration on time, if the chain propagation reaction is described by first-order kinetics with respect to the monomer concentration

$$\ln\left(\frac{[M]_0}{[M]}\right) = k_p[P^\bullet]\tau \qquad (1)$$

Here $[M]_0$ is the initial monomer concentration, $[M]$ is the monomer concentration at instant τ, k_p is the rate constant for chain propagation, and $[P^\bullet]$ is the concentration of growing radicals. In the case of monomolecular chain termination or poisoning of the catalytic system in the course of polymerization the concentration $[P^\bullet]$ and the polymerization rate gradually decrease. If initiation is slow or radicals are additionally generated in side reactions, the concentration $[P^\bullet]$ gradually increases and the process accelerates with time. The chain transfer step should not affect the reaction kinetics.[47]

3. Linear dependence of the molecular weight of the polymer on conversion is a key feature of CRP. Theoretical values of the molecular weight and degree of polymerization under ideal CRP conditions can be calculated from the equations

$$M_{\mathrm{n}} = \frac{[M]_0}{[I]_0} M_{\mathrm{mon}} S \quad (2)$$

$$P_n = \frac{[M]_0}{[I]_0} S \quad (3)$$

where M_{n} is the number-average molecular weight, $[M]_0$ is the initial monomer concentration, $[I]_0$ is the initial initiator concentration, M_{mon} is the molecular weight of monomer unit, S is the monomer conversion and P_n is the monomer polymerization.

The fact that the experimental degree of polymerization is lower than the theoretical one can be due to chain transfer reactions. The reverse situation is indicative of both inefficient initiation and a large contribution of bimolecular chain termination leading to a decrease in the concentration of active species and to an increase in the expected number-average molecular weight.

4. The dispersity of a polymer

$$Đ = M_{\mathrm{w}}/M_{\mathrm{n}} \quad (3a)$$

(M_{w} is the weight-average molecular weight) should decrease with increasing monomer conversion.

Usually, for a classical (uncontrolled) radical polymerization one has $M_{\mathrm{w}}/M_{\mathrm{n}} > 2$. This is due to the fact that the chain propagation time is much shorter than the overall duration of the polymerization process. In this connection, polymer chains formed at different monomer conversions actually grow under different conditions, in particular, at different medium viscosities and monomer concentrations, which influences the polymer chain length. In addition, high concentration of radical sites causes acceleration of the chain termination reaction proceeding as second-order reaction with respect to the monomer concentration; as a consequence, the molecular-weight distribution is broadened.

In an ideal CRP (no bimolecular chain termination) all polymer chains emerge nearly simultaneously and grow under identical conditions throughout the polymerization process. This favours efficient control over the molecular weight and a narrow molecular-weight distribution. However, the dispersity can increase if the chain termination reactions contribute largely.

The polymerization process is re-initiated upon adding a fresh portion of the monomer (so-called postpolymerization). The structure of the polymer being prepared can be controlled by carrying out chemical reactions involving chain-end groups, including block copolymerization. Such reactions do not proceed in the case of slow initiation and inefficient reversible exchange between the macroradical and the reactive additive. Besides, their efficiency decreases if contribution of side processes is large.

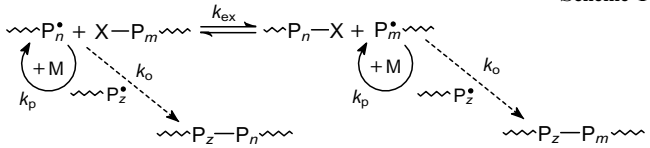
2.3. Reversible chain transfer and reversible deactivation as key factors of 'living' polymerization

In radical polymerization, growth of a material chain can be stopped through transfer and termination (including inhibition). The CRP concept implies that these elementary steps are reversible and determine the equilibrium between active and 'dormant' states of chain propagation radicals. Correspondingly, depending on the transition mechanism of active radicals to 'dormant' ones and subsequent reversible activation of 'dormant' species, the CPR techniques can be divided into two groups, namely, methods based on reversible chain transfer and reversible termination processes.

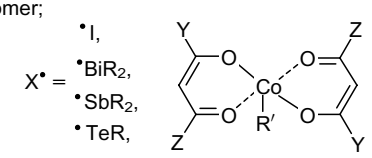
The first group includes the polymerization processes involving exchange between active and 'dormant' chains as a result of degenerative chain transfer (DT).[48 – 58]

The simplest example of this mechanism is provided by the polymerization mediated by iodine compounds (Scheme 1, $X^{\bullet} = I^{\bullet}$). In this case one deals with transfer of iodine atom ($X^{\bullet}$)[48] from various alkyl and aryl iodides or iodine-containing carboxylic acid esters and nitriles. Degenerative chain transfer can also be mediated using alkyl tellurides, dialkyl ditellurides, alkyl- and dialkylbismuthines, alkyl- and dialkylstibines,[51 – 54] as well as organocobalt compounds.[49, 50] It proceeds as described above except that the transferred species is bulkier.

Scheme 1

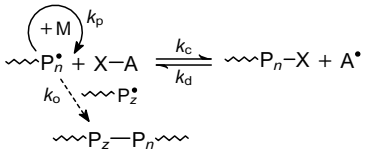


$P_n^{\bullet}$, $P_m^{\bullet}$, $P_z^{\bullet}$ are polymer radicals;
X is group being transferred; k_{ex}, k_p, k_o are rate constants for chain transfer, chain propagation and chain termination, respectively;
M is monomer;



When tin, germanium or phosphorus iodides are used, the polymerization process is termed 'reversible chain transfer catalyzed polymerization' (RTCP).[55, 56] It differs from the technique described above in that chain transfer involves intermediate formation of species bearing an unpaired electron (see $A^{\bullet}$ in Scheme 2).

Scheme 2

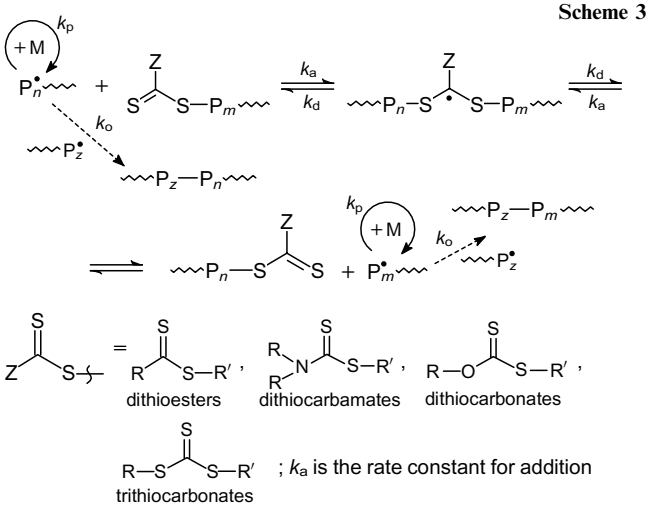


X—A is reversible chain transfer agent (X—A = I—SnI_3, I—GeI_3, I—PI_2); k_c, k_d are rate constants for recombination and dissociation, respectively

One more mechanism of degenerative chain transfer in the course of a polymerization process is reversible addition-fragmentation chain transfer (RAFT), that is, the addition of a growing radical to the chain transfer agent to give an intermediate followed by fragmentation of the intermediate.[29] The commonly used RAFT agents include sulfur-containing compounds, in particular, thioesters, dithiocarbamates, xanthogenates and trithiocarbamates.[27, 29, 57]

Degenerative chain transfer can proceed either with (Scheme 3) or without the formation of an intermediate corresponding to a minimum on the reaction coordinate (see Scheme 1). Therefore, the energy profiles of RAFT processes differ from those of the DT process proceeding in the presence of iodine, tellurium, bismuth and antimony compounds (Fig. 2). RAFT polymerization is accompanied by the formation of rather stable intermediates. On the one hand, a stable intermediate is formed more readily, which favours better control over the process. On the other hand, the lifetime of the intermediate should be short

Scheme 3



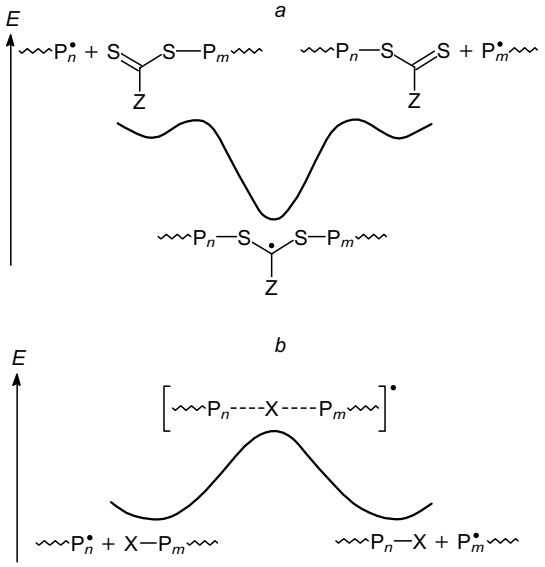


Figure 2. Hypothetical reaction coordinates of the DT polymerization with (*a*) and without the formation (*b*) of an intermediate.[54]

to minimize undesired chain termination reactions. It should be noted that all elementary steps of the RAFT polymerization are reversible and the intermediate can decompose with elimination of any growing radical.

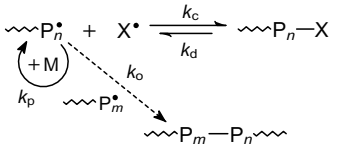
In contrast to RAFT polymerization, a process based on reversible chain transfer in the presence of, *e.g.*, tellurium compounds as DT agents will proceed *via* a transition state containing a hypervalent tellurium atom in the oxidation state +3. In this case, the energy of the intermediate is higher than the energies of the initial states. Therefore, degenerative chain transfer should proceed concertedly, so the formation of a stable intermediate and its participation in side processes are unlikely.

Processes based on DT mechanism have certain undoubtful advantages, which provide an explanation for considerable interest in RAFT polymerization including practical applications of this process. In particular, it can be performed in a wide temperature range and in various solvents. The range of commercially available RAFT agents covers almost all classes of monomers suitable for radical polymerization. Paradoxically, this is also a kind of a drawback of the technique since there is a particular range of monomers for each RAFT agent; as a consequence, the synthesis of block copolymers or multifunctional polymeric materials requires a complicated and multistage procedure. One more severe drawback of RAFT polymerization is the need to use relatively large amounts of RAFT agent (one RAFT agent molecule per polymer chain), which is particularly disadvantageous for the synthesis of low-molecular-weight polymers.

It should be noted that polymers described in most publications are characterized by low degree of polymerization (500 – 5000 on the average) except a few cases where this parameter was high, namely, in the range of $10^4 - 10^5$ (see, *e.g.*, Ref. 58). Besides, RAFT agents have high colours and unpleasant smell. Many of them are unstable on long-term storage, while sulfur-containing fragments, as constituents of polymers, can gradually decompose with the formation of low-molecular-weight sulfur compounds (H_2S, SO_2, *etc.*); therefore, additional purification of the polymers is required. These drawbacks often cause significant deterioration of the properties of polymers synthesized under the RAFT conditions, thus making them of limited use.

The second group of processes follows the mechanism of reversible deactivation[7, 9, 12, 13, 17] based on the reversible chain termination reaction (Scheme 4). This is so-called stable free-radical polymerization (SFRP).[4, 14, 16] First of all, mention should be made of polymerization using stable organic and metal-centred radicals ($X^{\bullet}$) that can react with the chain propagation radicals ($\sim P_n^{\bullet}$) with the formation of a labile bond ($\sim P_n$—X).

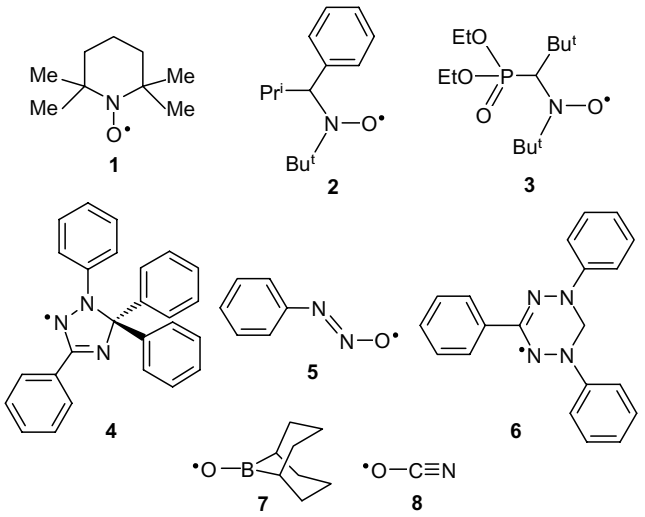
Scheme 4



These processes can be performed using stable radicals of different structure and their sources (see Scheme 4). In particular, they include SFRP using iniferters[27, 28, 59 – 63] (see above). A major drawback of CRP using iniferters (most often, these are mono- and disulfides, thiocarbamates, diselenides, or tetraphenylethane and hexaphenylethane derivatives) is that the dispersity of polymerization products at high conversions is rather high.

Examples of application of stable radicals for controlling the polymerization kinetics can be found in original publications and reviews.[4, 9, 12 – 17] At present, stable radicals from different classes have been studied as mediators of polymerization, *viz.*, nitroxide (**1** – **3**), tetrazolinyl (**4**), arylazooxyl (**5**), verdazyl (**6**), boroxyl (**7**), cyanoxyl (**8**), *etc*. The most widely used are nitroxide radicals, first of all, commercially available TEMPO (**1**), 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO, **2**), *N*-*tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)]oxyl (SG1, **3**) and their analogues. Polymerization using these radicals is termed nitroxide-mediated radical polymerization (NMP).[13, 64 – 68]

Structures 1 – 8

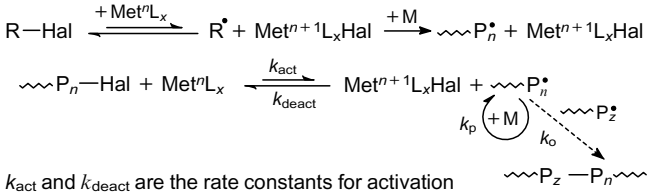


The SFRP processes are mediated by not only stable organic radicals, but also transition-metal complexes capable of forming labile σ-bonds with alkyl radicals; this is so-called organometallic mediated radical polymerization (OMRP).[20, 69 – 77]

Efficient control over the polymerization process is possible only if organic and metal-centred radicals used as polymerization agents are stable. According to this imperative, it is assumed that stable radicals are not involved in the initiation, chain transfer and some other reactions that can lead to an increase in dispersity of resultant homo- and copolymers.

Atom transfer radical polymerization also proceeds by the reversible chain termination mechanism based on reversible (redox) atom transfer between the chain propagation radical and the metal complex catalyst (see Scheme 5). Most often, ATRP involves transfer of halogen atoms; other atoms and groups are more rarely used as ATRP agents.

Scheme 5



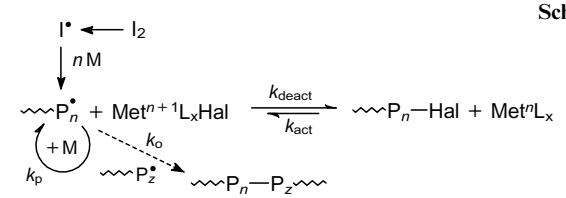
k_{act} and k_{deact} are the rate constants for activation and deactivation, respectively;
P$_n$—Hal is polymer chain in dormant state;
Met^{n+1}L$_x$Hal is metal complex in the highest oxidation state;
Met^{n}L$_x$ is metal complex in the lowest oxidation state

At present, various catalytic systems and binary compositions for performing ATRP are available. Among them, copper,[21, 22, 44, 46, 78 – 80] ruthenium[19, 45, 81 – 83] and iron compounds[84 – 88] are most widely used. Other catalysts of ATRP include nickel,[89 – 92] manganese and some other metal complexes.[93 – 95]

Classical ATRP is initiated using alkyl halides and metal complexes containing metal atoms in the lowest oxidation state (see Scheme 5). Major drawbacks of ATRP processes often include heterogeneous character of the system and high concentrations of metal complex catalysts (from 1000 to 10 000 ppm; this was typical of the early stage of development of the technique). The need to use relatively large amounts of catalysts was due to the fact that compounds containing metal atoms in the lowest oxidation state are prone to oxidation by the residual oxygen. Irreversible loss of radicals causes accumulation of the oxidized form of the catalyst which is removed from the reaction (see below). As a consequence, the concentration of the active form of the catalyst decreases and the polymerization process decelerates. In some cases the use of large amounts of metal complex catalysts can favour the synthesis of coloured polymers. This deteriorates their physicochemical properties, reduces degradability and narrows the field of potential applications since the presence of even trace amount of metal in the polymer can be critical for materials for biomedical applications, electronics and some other areas of human activity and high-tech industries.

Yet another ATRP technique involves the use of transition metal compounds containing metal atoms in the highest oxidation state[96 – 99] since they are more stable to atmospheric oxygen. In this case, the polymerization process is initiated using a conventional radical initiator (I_2) introduced into the system and the metal complex reversibly terminates growing

Scheme 6



I_2 is initiator; I$^•$ is initiating radical

chains as shown in Scheme 6. This version of ATRP is termed reverse ATRP.

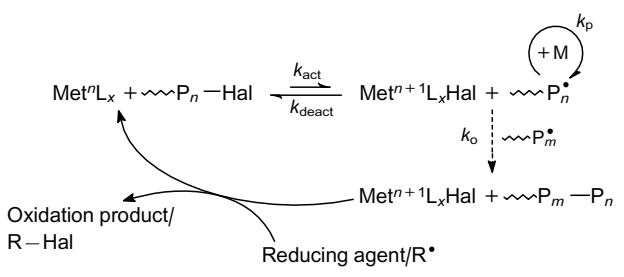
3. Atom transfer radical polymerization: prospects and methods to improve efficiency

Most studies on controlled synthesis of macromolecules published in the last decade were devoted to ATRP.[25] Undoubtedly, this is due to considerable advantages of ATRP over other methods of controlled synthesis of macromolecules, *viz.*, a wide range of suitable monomers, catalysts and initiators as well as almost boundless opportunities for macromolecular design and synthesis of nanosized macromolecular structures.[21, 100–102]

A drawback of pioneering ATRP techniques was high concentration of metal complexes, which caused steeling of polymers and thus made them of limited use in high-tech industries. To eliminate this drawback, a number of original approaches generally termed 'green technologies' were proposed. They are based on the use of low concentrations of metal complexes provided continuous *in situ* reduction (regeneration) of their catalytically inactive forms containing metal atom in the high oxidation state ($Met^{n+1}L_xHal$) to the catalytically active form containing metal atom in the low oxidation state (Met^nL_x). As a result, the concentration of the catalyst active species increases, which accelerates the process on the one hand and allows one to use much smaller amounts of metal complexes on the other hand. In particular, green technologies enable efficient CRP using rather low concentrations of metal-containing catalysts (< 10 ppm).

All methods for regeneration of ATRP catalysts can be conditionally divided into chemical and physical ones. Chemical methods to improve the efficiency of ATRP are based on the introduction of activators into the polymerization system (Scheme 7). Usually, the role of activators is played by compounds that can efficiently reduce the metal atom in the complex from the highest to the lowest oxidation state, thus regenerating the catalyst. This can be done using conventional radical initiators introduced into the polymerization system for additional generation of active radicals.[103–109] This method is known as initiators for continuous activator regeneration (ICAR) ATRP. An interesting example of this mechanism is presented by the synthesis of polystyrene and its analogues. In particular, a feature of styrene polymerization, namely, efficient thermal initiation (so-called self-initiation) of the polymerization process, can induce *in situ* (from-the-monomer) production of relatively high concentration of active radicals which can react with the metal complex. This removes the necessity to introduce additional radical initiator into the polymerization system to regenerate the catalyst.

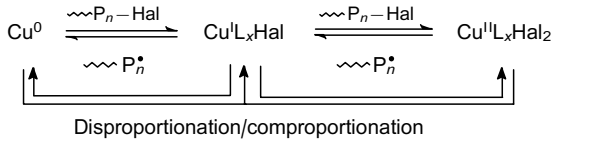
Scheme 7



Chemical methods for improving the efficiency of ATRP also include the use of activators that reduce the metal complex catalyst using one-electron transfer.[110–121] An analysis of published data shows that currently this CRP technique is one of the most promising methods, including applied aspects, since it utilizes ultralow concentrations of metal complex catalyst for the synthesis of polymers with specified molecular-weight characteristics.

Metal complexes are most often reduced using electron-donor nitrogen- and oxygen-containing organic compounds[113–115] and inorganic reagents, *e.g.*, divalent tin derivatives[112, 121, 122] and other compounds.[122–125] In particular, the use of zero-valent metals as reducing agents is an efficient and original method for ARTP activation.[126] Reduction with zero-valent copper has been best studied[110, 127–131] since reversible switching between different oxidation states of this metal is not difficult to achieve (Scheme 8).

Scheme 8



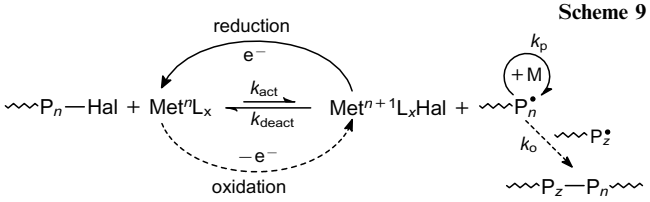
This mechanism offers prospects for performing ATRP using zero-valent metal (*e.g.*, metallic copper or iron) complexes with various organic ligands (L). An important feature of such a polymerization process is that the transition-metal complex acting as catalyst is formed *in situ*. This synthesis of polymers using this version of ATRP was described by two similar alternative mechanisms termed 'supplemental activator and reducing agent' (SARA)[129–133] and 'single electron transfer living radical polymerization' (SET LRP).[133–137] In fact, they differ only in the ratio of the contribution of the disproportionation/comproportionation processes to the contribution of activation of the polymerization process using the reaction between 'dormant' chains and the zero-valent metal. It was reported[138] that the former mechanism better describes the polymerization kinetics, which makes SARA ATRP more feasible.

Methods for physical activation of ATRP catalysts using external factors, *e.g.*, electric current[139–144] or sonication,[145–147] have been developed recently.

Since certain ATRP activation techniques are based on electron transfer, it is logical to assume that electric current can be used as a tool for regenerating the metal-containing catalyst by switching between the high and low oxidation states of the metal atom (Scheme 9).

This method called eATRP was used to perform CRP in the presence of copper,[143, 144] ruthenium and some other metal compounds.[141] The process is performed under electrochemical regeneration of the catalyst and can be terminated with ease by applying the oxidation potential which causes the metal to go to

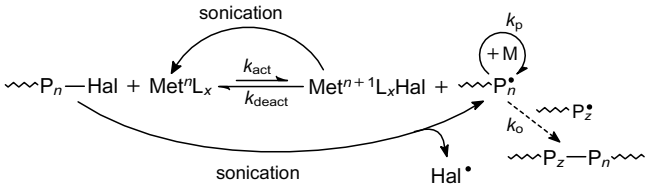
Scheme 9



the highest oxidation state. A severe drawback of the process consists in the need to use an electrochemical cell and a supporting electrolyte that should be removed from the system and then regenerated. This makes the technique of limited use for preparative-scale research and the more so for industrial polymer synthesis.

Not only electric current, but also sonication was proposed [145–147] to improve the ATRP efficiency. In particular, Matyjaszewski and co-workers [147] developed an efficient method for polymerization of 2-hydroxyethyl acrylate and some other monomers in the presence of copper(II) bromide complexes with nitrogen-containing ligands. The process proceeds in aqueous media under sonication (40 kHz, 110 W) at room temperature and is characterized by high degree of control over the molecular weight. It is believed [145, 147] that sonication induces piezocatalytic reduction of the divalent copper complex to a monovalent copper complex whose reaction with alkyl halide or with the polymer bearing a halogen-containing end group re-initiates the polymerization and further chain propagation (Scheme 10). In addition, sonication produces active radicals owing to homolytic dissociation of the terminal carbon–halogen bond.

Scheme 10



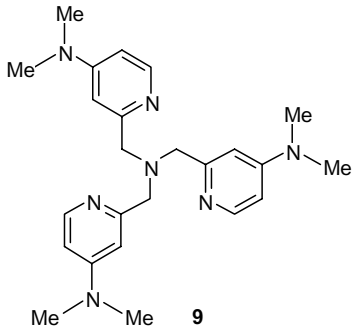
Similar results were obtained in a study of the polymerization of n-butyl acrylate (BA) under sonication in the presence of iron complexes and alkyl halides.[148]

All these methods for activation of ATRP catalysts allow the polymerization process to proceed at rather high rates at low catalyst concentrations, being, however, unsuitable for semi-scale and industrial polymer synthesis. This is first of all due to high sensitivity of components of the polymerization systems, in particular, chain propagation radicals and many metal complexes containing metal atom in the lowest oxidation state to atmospheric oxygen. In the case of laboratory-scale experiments, this drawback can be eliminated by conducting ATRP in anaerobic conditions (in inert atmosphere or in evacuated tube); however, this is difficult to achieve for large-scale syntheses, especially, for polymerization processes in aqueous media. To solve this problem, an original 'biological' ATRP technique was proposed, which uses enzymes as oxygen deactivators. In particular, Matyjaszewski and co-workers [149] proposed to use glucose oxidase as oxygen deactivator that can react with atmospheric oxygen in the presence of glucose to give D-glucono-1,5-lactone and hydrogen peroxide. However, hydrogen peroxide has a negative impact on the polymerization since it can additionally initiate a chain propagation reaction similar to the Fenton reaction [150] in the presence of the metal-containing catalyst. It was proposed to compensate the effect of hydrogen peroxide using sodium pyruvate, which reacts with hydrogen peroxide to give carbon dioxide, water and acetate anion (by analogy with the Krebs' tricarboxylic acid cycle).[151] This approach made it possible to perform ATRP in aerobic conditions in aqueous media for the first time.[149]

The methods using the reducing agents introduced into the polymerization system or generated *in situ* under the action of external factors made it possible to achieve considerable progress in ATRP. However, do not forget that the key component of the system is the metal complex catalyst and that the degree of control over the polymerization process depends on the catalyst structure and on the ability of the metal to rapidly switch between different oxidation states.[152, 153] Intensive studies on relationships between the structure and properties of metal complex catalysts allowed one to develop catalysts with much higher activity compared to those used earlier. At present, the most efficient copper-containing catalysts include copper complexes with tris[(2-pyridyl)methyl]-amine derivatives, *e.g.*, compound **9**.[154]

Among the compounds studied to date, complex CuBr–**9** is characterized by the lowest Cu^I/Cu^{II} redox potential, which enables efficient control of ATRP using ultrasmall amounts of the catalyst.

Structure 9



9

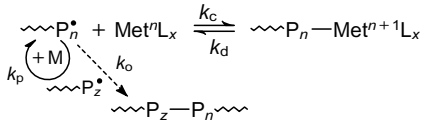
4. Reversible-deactivation radical polymerization using metal-centred and nitroxide radicals

Chronologically, reversible-deactivation polymerization is the first and thus most thoroughly studied CRP technique (see above). Numerous original publications and reviews (including recently published ones) devoted to CRP are available,[7–9, 12–17, 64–71, 155] most of them being related to the application of metal-centred and nitroxide radicals to control the polymerization processes.

4.1. Reversible-deactivation radical polymerization using metal complexes

The use of metal-containing compounds in RDRP is based on fast and reversible homolytic dissociation of labile metal – carbon bond (Scheme 11).

Scheme 11



In this case, transition-metal complexes play the role of reversible spin traps. The process can be initiated using both traditional free-radical initiators and the metal complexes containing a labile metal – carbon bond. These processes are rather slow. Note that for classical radical polymerization the concentration of chain propagation radicals is in the range of $10^{-7}-10^{-8}$ mol L^{-1}, being much lower for CRP, since the equilibrium dissociation constant for reversible deactivation

$$K = \frac{k_d}{k_c} \quad (4)$$

is usually rather low, *viz.*, $10^{-8}-10^{-12}$ mol L^{-1}. If the constant K falls in this range, one deals with optimum CRP conditions. Indeed, if the equilibrium dissociation constant is high, the process is accompanied by an increase in the concentration of chain propagation radicals and, therefore, in the polymerization rate, which makes side reactions more probable (they lead to the loss of macroradicals and to increase in dispersity). If the constant K is too low, the 'dormant' adduct is characterized by high bond dissociation energy and the polymerization process thus becomes near-impossible. As to the optimum CRP conditions, the dissociation energies of the carbon – metal bond and the carbon – oxygen bond in AAs should fall in the range of 12 – 20 kcal mol^{-1}, thus being thermodynamically labile bonds.

A drawback of the OMRP technique is the possibility for certain side reactions (*e.g.*, DT) to proceed concurrently. In the case of DT active radicals are released from 'dormant' state through associative exchange with other similar radicals (see Schemes 1 – 3). The polymerization proceeds in controlled regime if the associative exchange rate

$$v_{ex} = k_{ex}[P^{\bullet}][XP] \quad (5)$$

(k_{ex} is the rate constant for exchange, [XP] is the concentration of 'dormant' chains) is much higher than the chain propagation rate

$$v_p = k_p[P^{\bullet}][M], \quad (6)$$

i.e., $k_{ex}[XP] \gg k_p[M]$ (see Scheme 1). Since for DT dissociation of the metal – carbon bond is accompanied by the formation of an identical bond, its strength (*i.e.*, bond dissociation energy) is not the key parameter. In this case, the primary criterion is rapid degenerative exchange.

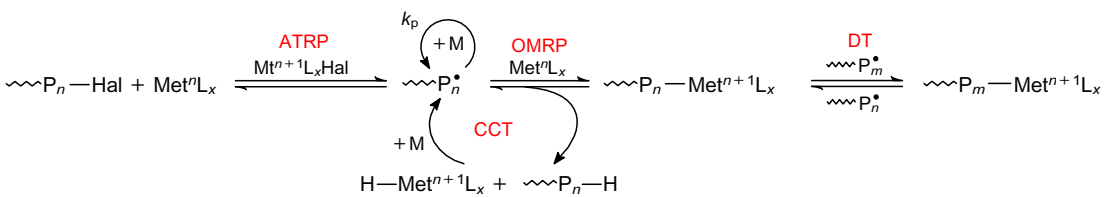
Catalytic chain transfer (CCT) to monomer is one more important side reaction that should be taken into account when performing OMRP. Monomers containing α-methyl groups with labile hydrogen atoms are highly prone to CCT. In particular, CCT is most characteristic of certain cobalt complexes;[156 – 158] some of them are characterized by chain transfer constants in the range of 10^2-10^4.

Eventually, the third process that can proceed along with reversible deactivation during OMRP is ATRP (see above). It can be realized when OMRP is catalyzed by metal complexes containing halogen atoms. In turn, the possibility of reversible deactivation of OMRP should be always taken into account when considering ATRP. Scheme 12 illustrates interrelations between the mechanisms discussed above.

When polymerization is mediated by transition-metal complexes, the key role in realization of a particular mechanism is played by the ligand environment of the metal atom. The nature of the monomer also significantly influences the probability for the polymerization process to proceed by one mechanism or another. In particular, the polymerization of methyl methacrylate (MMA)[40, 156 – 158] and other methacrylates in the presence of cobalt porphyrin and cobaloxime complexes proceeds by the CCT mechanism.[154, 157, 159] However, poly(butyl acrylate) (PBA) is synthesized in the presence of cobalt porphyrin complex by the reversible deactivation mechanism.[41] The polymerization of acrylic acid,[160] styrene,[161] vinyl acetate[162 – 165] and acrylonitrile[166] proceeds as OMRP catalyzed by cobalt complexes. It should be noted that the results of these studies can be described both within the framework of the theory of reversible deactivation of metal-centred radicals and using the DT scheme.[56, 163 – 165] In particular, kinetic studies showed[55] that continuous introduction of radicals into a reversible deactivation process leads to transformation of this mechanism to DT. Emphasize that the concentration of the cobalt(II) complex can decrease under the DT conditions, thus excluding hydrogen transfer to the cobalt complex (in other words, the contribution of catalytic chain transfer is minimized).

The OMRP process, which in fact proceeds by the reversible deactivation mechanism, is mediated by not only cobalt complexes, but also other metal compounds where the metal (*e.g.* titanium, vanadium,

Scheme 12



chromium, molybdenum, iron, *etc.*) atom can reversibly change its oxidation state.[167 – 173]

It should be noted that most metal complexes used as mediators of OMRP are efficient in the synthesis of polymers based on not only methacrylic monomers, but also ethylene, vinyl acetate and their analogues that usually cannot be polymerized using ATRP. In particular, OMRP was successfully used for 'living' polymerization of ethylene,[174] vinyl fluoride and certain other fluorine-containing monomers.[175 – 177]

A significant drawback of OMRP is that one has to use higher concentrations of metal complexes as compared to ATRP. For instance, an efficient OMRP requires a stoichiometric ratio of the catalyst and initiator. This raises the product cost due to extra expenses for subsequent purification of polymers.

4.2. Reversible-deactivation radical polymerization using nitroxide radicals and alkoxyamines

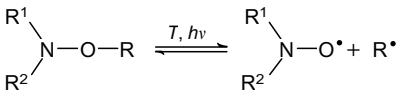
There are two main strategies of carrying out CRP under the reversible deactivation conditions using nitroxide radicals. One of them involves the introduction of nitroxide species into the polymerization system. Nitroxide radicals are used in thermally initiated polymerization and in combination with traditional radical initiators (benzoyl peroxide, azobisisobutyronitrile, *etc.*).[178 – 183] Usually, polymerization in the presence of a nitroxide – initiator system is performed at 120 – 130 °C. The most efficient processes include the syntheses of polystyrene and its analogues (4-bromostyrene,[178] 3-chloromethylstyrene, 4-chloromethylstyrene,[180] *etc.*). Usually, they are mediated by TEMPO (**1**)[180, 181] and its substituted analogues, *e.g.*, 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl,[178] 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl[179] and other nitroxide radicals.[4, 14] These species are attractive from the standpoint of availability since they are widely used as reagents in organic chemistry, biology and medicine.[183 – 185] Specific features of CRP in the presence of nitroxides have been studied in considerable detail and there is a huge body of literature devoted to their analysis, including reviews and numerous original articles (see, *e.g.*, Refs 13 – 17, 66 – 68, 180 – 183).

The second strategy of performing CRP in the presence of nitroxides is to use compounds capable of generating stable nitroxide radicals *in situ*. This first of all concerns nitrones and nitroso compounds, amines and AAs, as well as hydroxylamines and oxytriazenes that can serve as sources of stable nitrogen-containing radicals in addition to organic and inorganic nitro derivatives.

Decomposition of AAs in the polymerization system is one of the best known methods for *in situ* generation of nitroxides.[4, 7, 12 – 17, 179] The carbon – oxygen bond in the AA molecule can dissociate on heating or irradiation to give an active radical and a nitroxide spin adduct (Scheme 13).

This RDRP technique has considerable advantages over the use of bimolecular compositions based on nitroxide radicals and traditional radical initiators. In particular, the case in point is unambiguously determined nature and strictly specified concentrations of the initiator and controller of polymerization. This makes it possible not only to clearly describe the polymerization kinetics, but also to correctly predict the molecular-weight characteristics of resulting polymers and offers great prospects for the synthesis of macromolecules with specified architecture.

Scheme 13



Processes using TEMPO-based AAs have certain drawbacks, *e.g.*, the need to use rather high temperatures (⩾120 °C) for efficient polymerization to proceed and a low rate of the process. For instance, styrene polymerization under these conditions should take more than 48 h to achieve high monomer conversions.

The CRP rate of styrene and certain other monomers in the presence of AA can be increased as follows:[4, 14, 68]

— by increasing the concentration of active initiating sites through additional introduction of high-temperature peroxide initiators (*e.g.*, *tert*-butyl hydroperoxide, cumene peroxide, *etc.*) into the system;

— by introducing activating additives, *e.g.*, carbohydrates, aldehydes, *etc.*;

— by photochemical activation of AAs;

— using new mediators based on sterically hindered AAs of different structure, characterized by higher efficiency compared to TEMPO and its analogues; and

— by chemical activation of the C – ON bond in AAs containing various functional groups; this can be done using protonation and deprotonation, activation through coordination to Lewis acids, oxidation of functional groups of the AA molecules, complexation with metal-containing enzymes, 1,3-dipolar cycloaddition, *etc.*

Undoubtedly, the most elegant and promising method to improve the efficiency of controlled synthesis of macromolecules using AAs is targeted structure modification of the nitroxide fragments in the AA molecules. Indeed, a nitroxide, as a constituent of the AA molecule, is involved in the reversible chain termination and chain re-initiation reactions that repeatedly occur in the system. In this connection, it is the structure of the nitroxide that has the key impact on both the reversible chain termination and the entire polymerization process.

An original activation technique of functionalized AAs is to chemically modify them in the course of polymerization. It was thoroughly analyzed in a recent review[68] of original publications on chemical activation of alkoxyamine homolysis.

As mentioned above, pioneering studies on NMP were devoted to styrene polymerization in the presence of TEMPO[179, 186 – 190] and its analogues.[178, 179, 191] In particular, it was found that the introduction of polymer[192] or dendrimer fragments[193] in position 4 of the TEMPO molecule led to a decrease in the temperature of polystyrene synthesis from 140 to 120 °C.

According to published data,[194 – 197] sterically hindered groups in positions 2 and 6 of piperidine-type nitroxide radicals allow one to significantly decrease the temperatures of styrene polymerization under the

reversible deactivation conditions in the presence of sterically hindered/crowded TEMPO analogues and corresponding AAs. In particular, the main regularities of CRP of styrene under these conditions are observed even at 70 °C and the polystyrene samples are characterized by sufficiently low dispersity. Interestingly, raising the temperature causes the equilibrium to shift towards the AA decomposition (see Scheme 13); correspondingly, the contribution of reversible deactivation decreases. For instance, styrene polymerization at 120 °C affords a polymer with a rather wide molecular-weight distribution ($M_w/M_n > 1.7$ at 75% conversion). Based on the results of studies on the polymerization of styrene and its analogues in the presence of nitroxides with spiro structure,[194–197] it was shown that the efficiency of these nitroxides is immediately related to the steric shielding of the nitroxide fragment by the substituents introduced into the α-position.

It is interesting to perform low-temperature polymerization of styrene in the presence of organosilicon AAs.[198,199] It was established that controlled synthesis of polystyrene in the presence of silyloxyalkyl-substituted nitroxides and AAs based on such nitroxides proceeds at 70 – 105 °C.

An efficient route to well-defined polymers synthesized under the reversible deactivation conditions involves the use of nitroxide radicals (and AAs based on them) that are structurally different from TEMPO. One of the first examples is the application of sterically hindered dialkyl nitroxides, in particular, di-*tert*-butyl nitroxide in the synthesis of polymers under the radical initiation conditions. It was shown that di-*tert*-butyl nitroxide and AAs based on this compound are efficient mediators of radical polymerization of certain vinyl monomers proceeding under relatively mild conditions (90 – 100 °C).[200] Considering this type of mediators, the TIPNO (**2**) and SG1 (**3**) radicals seem to be most promising; specific features of polymerization of a wide range of monomers in the presence of **2** and **3** were described in detail in a series of publications[201–211] (see also Table 1). It cannot be ruled out that higher efficiency of these mediators compared to TEMPO is related to the presence of hydrogen atom at an α-carbon atom since TEMPO contains no such hydrogen atoms.

Chemists from Canada proposed[212] to use sterically hindered 1,1-diadamantyl nitroxide as mediator of styrene polymerization. The corresponding AA can decompose with the formation of a stable radical at about 100 °C and thus mediate the polymerization process (see Table 1). However, the polymerization proceeds very slowly, as in the case of TEMPO-mediated process. It can be significantly accelerated by introducing activators including benzoic and camphorsulfonic acids into the polymerization system.

Among other low-temperature mediators of polymerization of vinyl monomers under the reversible deactivation conditions, dinitroxide radicals and corresponding bis(alkoxy)amines, *e.g.*, 2,5,5,8,8,11-hexamethyl-4,9-bis(1-phenylethoxy)-3,10-diphenyl-4,9-diazadodecane[213] appeared to be efficient. This type of compounds allows one to perform controlled synthesis of not only polystyrene, but also polymers based on (meth)acrylic monomers including *tert*-BA and *N*,*N*-dimethylacrylamide under relatively mild conditions (70 – 110 °C, see Table 1). This is due to the fact that the rate constants for homolytic bond dissociation in bis(alkoxy)amines in this temperature range are nearly twice as high as those of analogous mono-AAs.

It was proposed to use sterically hindered piperazine nitroxides and AAs based on them for polymerization of BA and styrene at 50 – 60 °C.[214] Morpholine-based nitroxides and AAs containing bulky groups were successfully tested[215] in the polymerization of BA and styrene at relatively low temperatures (see Table 1).

Chemical modification of nitroxides is an efficient method to accelerate NMP.[68] Using this approach, it was shown[216] that coordnation-initiated AAs containing pyridine group coordinated to $Zn(hfac)_2$ cause a 30-fold increase in the constant k_d. These complexes demonstrate high efficiency in the polymerization of styrene and BA at 90 °C.

An analysis of published data shows that the thermal conditions of the polymerization of not only styrene, but also various styrene derivatives including those containing hydroxyl, alkyl and other substituents in the benzene ring can be optimized by varying the structure of the nitroxide fragment and the alkyl radical in the AA molecules.[178,179,182] The structure of these substituents immediately influences the kinetic parameters of polymerization. For instance, the introduction of electron-withdrawing substituents (Cl, CH_2Cl, CF_3, *etc.*) causes the polymerization rate to increase almost tenfold.[178,179] On the contrary, the introduction of electron-donor groups significantly decreases the polymerization rate.[181]

As mentioned above, in the initial stage of development of the CRP concept, alkoxyamines were mainly used in the synthesis of polystyrene and its analogues. Extension of the range of nitroxide radicals used in CRP processes made it possible to apply them in the polymerization of acrylic monomers including acrylic acid and its esters,[188,208] in particular, BA,[217,218] as well as 1,3-dienes,[202] 4-vinylpyridine, *N*,*N*-dimethylacrylamide[201,208] and acrylonitrile[201] (see Table 1).

For long, carrying out a CRP of MMA by introducing stable nitroxide radicals was thought impossible based on the fact that AAs containing the methacrylate chain propagation radical can undergo intramolecular disproportionation reactions with the formation of a polymer with terminal π-bond and corresponding hydroxylamine. One more negative circumstance is the reaction of nitroxides produced upon decomposition of AAs with growing polymer radicals, which is accompanied by hydrogen transfer[225,226] and formation of hydroxylamine.

Researchers from Italy and France developed novel AAs based on the stable nitroxide, 2,2-diphenyl-3-phenylimino-2,3-dihydroindol-1-yloxyl (DPAIO),[219] which appeared to be efficient mediators of controlled polymerization of MMA (see Table 1). The process in the presence of these AAs proceeds in controlled regime until a deep monomer conversion (> 80%) and yields polymers with relatively narrow molecular-weight distributions ($M_w/M_n \approx 1.3 – 1.4$). The samples synthesized in the presence of DPAIO-based AAs can initiate block copolymerization of MMA with BA at

Table 1. Efficiency of nitroxide radicals and alkoxyamines in polymerization.

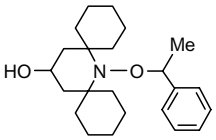
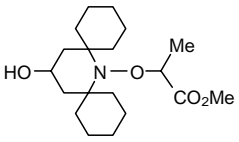
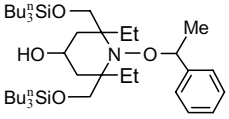
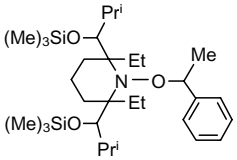
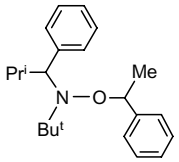
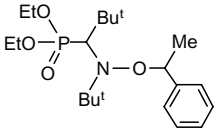
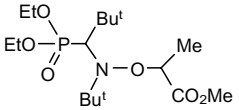
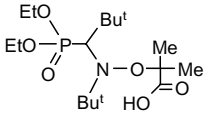
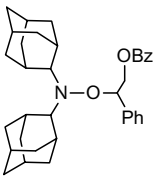
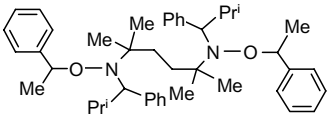
Nitroxide or alkoxyamine [a]	Monomer	T, °C	t, h	Conversion (%)	$M_n \times 10^{-3}$	$Đ$	Ref.
	Styrene	80	400	~70	–	1.22	194
	Styrene	70	800	~70	60	1.25	197
	Styrene	105	15	85	10	1.12	198
	Butyl acrylate	70	96	34	6	2.12	199
	Styrene	70	6	59	10	1.39	199
	Butyl acrylate	70	3	82	13	1.38	199
	Styrene	123	18	~90	22	1.14	201
	Isoprene	120	36	~75	20	1.08	201
	Butyl acrylate	123	2	90	27	1.44	201
(TIPNO as nitroxide)							
	Styrene	90	28	55	10	1.17	207
	4-Vinylpyridine	110	1.3	54	61	1.15	208
	N,*N*-Dimethylacrylamide	110	33	64	16	1.54	208
(SG1 as nitroxide)							
	Styrene	90	49	65	13	1.55	207
	Styrene	120	4	75	14	1.31	207
	Butyl acrylate	90	87	64	10	1.26	207
	Acrylic acid	120	5	90	9	1.40	209
(MONAMS)							
	Styrene	120	4	90	25	1.12	207
	Butyl acrylate	120	1.5	92	20	1.30	207
	Methyl methacrylate	45	0.5	9	22	1.39	210
	Vinyl chloride	42	24	57	11	1.49	211
(BlocBuilder®)							
	Styrene	104	7	34	14	1.10	212
	Butyl acrylate	124	5	50	7	1.56	212
	Styrene	70	264	65	46	1.18	213
	Butyl acrylate	70	264	24	22	1.64	213
	N,*N*-Dimethylacrylamide	70	216	69	24	1.47	213

Table 1 (continued).

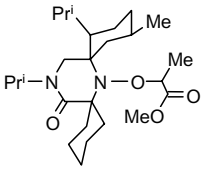
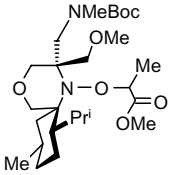
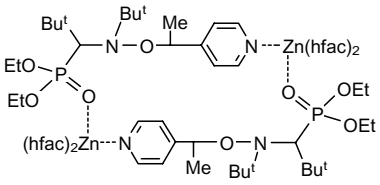
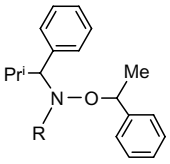
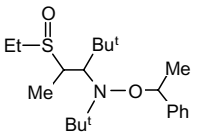
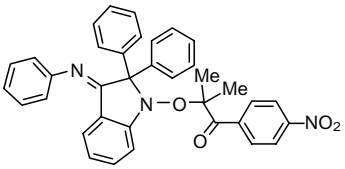
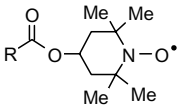
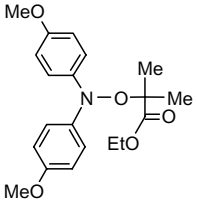
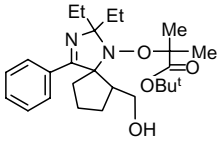
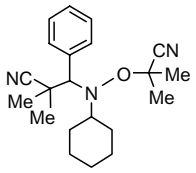
Nitroxide or alkoxyamine [a]	Monomer	T, °C	t, h	Conversion (%)	$M_n \times 10^{-3}$	$Đ$	Ref.
	Styrene	60	24	64	8	1.12	214
	Styrene	50	96	74	8	1.13	214
	Butyl acrylate	60	24	81	13	1.16	214
	Styrene	60	47	79	8	1.23	215
	Butyl acrylate	60	26	93	24	1.29	215
	Butyl acrylate	50	125	79	23	1.23	215
	Styrene	110	~8	70	48	1.30	216
	Styrene	90	~8	35	11	1.30	216
	Butyl acrylate	90	56	94	25	1.40	216
	Butyl acrylate (R^1)	125	6	41	8	1.20	217
	Butyl acrylate (R^2)	90	72	56	10	1.16	217
	Butyl acrylate (R^3)	125	6	49	14	1.18	217
R is acrylamide group (R^1), 1,1-diethylpropyl (R^2), 1,1,3,3-tetramethylbutyl (R^3)							
	Butyl acrylate	90	–	60	60	1.30	218
	Ethyl acrylate	90	–	–	–	1.50	218
	Methyl methacrylate	100	8	65	17	1.35	219
(nitroxide – DPAIO)							
	Methyl methacrylate (R^1)	25	40	77	33	2.19	220
	Methyl methacrylate (R^2)	25	40	50	21	1.37	220
R — 2-benzoylphenyl (R^1), 2–naphthyl (R^2)							
	Methyl methacrylate	110	~28	~65	~28	1.4	221
	Methyl methacrylate	90	~35	~40	~18	1.4	221

Table 1 (continued).

Nitroxide or alkoxyamine [a]	Monomer	T, °C	t, h	Conversion (%)	$M_n \times 10^{-3}$	$Đ$	Ref.
	Styrene	120	–	25	~9	1.27	222
	Methyl methacrylate	80	–	55	~20	~1.44	222
 (Dispolreg 007)	Methyl methacrylate	90	5	68	~8.5	1.49	223
	Styrene	126	7	97	33.9	1.30	224
	Styrene	136	4	>99	35	1.18	224

Note. Notations are as follows: Bz stands for benzyl, Boc stands for *tert*-butoxycarbonyl and $Zn(hfac)_2$ stands for zinc hexafluoroacetylacetonate.
[a] Listed are commercial names of the compounds mentioned in the text of the review.

120 °C. To improve the polymerization of MMA and styrene, indolinic nitroxides and corresponding DPAIO-based AAs were developed.[220] It was shown that polymerization of both styrene and MMA at relatively low temperatures can be controlled using the same mediator.

It was shown[223] that CRP of MMA in the presence of *N*-phenyl-substituted nitroxide [di(4-methoxyphenyl)nitroxide] and AA based on this compound proceeds un to 65% monomer conversion (see Table 1). Controlled character of polymerization was substantiated by the data on postpolymerization and block copolymerization. The proportion of 'living' chains was > 85% (EPR data). It was also established that unsubstituted phenyl nitroxide is inefficient for controlling the molecular-weight characteristics of poly(methyl methacrylate) (PMMA) due to undesired cross-coupling reaction between two nitroxides. The polymer thus synthesized has a broad bimodal molecular-weight distribution.

Polymerization of MMA and styrene was performed[222] using AAs based on imidazoline nitroxides with bulky spirocyclic moieties in positions 2 or 5 of the imidazole ring. It was found that the polymerization of MMA proceeds in controlled regime up to a monomer conversion of 55% and that the polymer thus prepared can then initiate the polymerization of styrene (see Table 1). The proportion of 'living' chains exceeded 90%.

One of the most efficient AAs capable of controlling the polymerization of MMA is 2,2-dimethyl-3-phenyl-3-[((2-cyanopropyl-2)oxy)(cyclohexyl)amino]-propanenitrile, or Dispolreg 007 (see Refs 223 – 226 and Table 1). It is characterized by very low rate constant for hydrogen transfer from the growing macroradical and by high rate constant for recombination, thus being appropriate for the polymerization of methacrylates[227] and styrene and for the synthesis of block copolymers based on these monomers.

One more significant problem in NMP is the synthesis of poly(vinyl chloride) (PVC). Recently, PVC was synthesized at low temperatures (30 and 42 °C) using 2-[*N*-*tert*-butyl-*N*-(diethyoxyphosphoryl)(2,2-dimethylpropyl)aminoxy]-2-methylpropionic acid (BlocBuilder®) as AA.[211] An NMR study revealed that the polymer contains a small amount of structural defects and that the proportion of chain-end functional groups in SG1 was about 91%. To prove the presence of 'living' chains, experiments on chain extension using vinyl chloride, MMA and a mixture of monomers (90% MMA and 10% styrene) were carried out. However, it was proposed that controlled polymerization proceeds by the mechanism of SG1-mediated dehydrochlorination rather than attainment of 'classical' equilibrium between activation and deactivation. This point of view on the polymerization mechanism was confirmed by the results of quantum chemical calculations that gave a high C – O bond dissociation energy in the PVC – SG1 alkoxyamine. The polymerization processes in the presence of nitroxides and AA include the synthesis of homopolymers, random copolymers and diblock copolymers,[228] as well as terpolymerization with the formation of well-defined copolymers with complex structure,[229 – 231] *e.g.*, macromolecular structures with antimicrobial activity[232] and bioconjugates.[233, 234]

Thus, AAs are efficient mediators of radical polymerization of a wide range of monomers. The structure of the nitroxide moiety in the AA molecules has a primary impact on the polymerization kinetics and on the molecular-weight characteristics of the polymers being synthesized. However, the vast majority of AAs can control the reversible-deactivation polymerization at rather high temperatures (above the temperature range typical of industrial synthesis of polymers). In this connection, a topical problem in synthetic polymer chemistry is to develop methods and approaches to targeted synthesis of polymers under milder conditions.

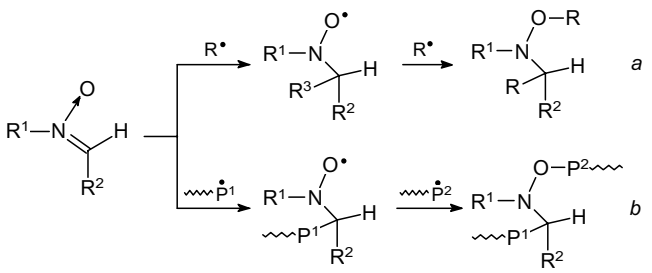
4.3. Controlled synthesis of polymers using spin traps as precursors of stable nitroxide radicals

Spin traps, most of them being nitrogen-containing compounds (nitrones, nitroso compounds, oxytriazenes, *etc.*), can react with short-lived radicals including polymer ones to give stable radicals, namely, nitroxide spin adducts.[227] That is why they are intensively studied in connection with controlled synthesis

of macromolecules.[13, 64, 235 – 246] Polymerization processes using spin traps can be conditionally divided into two groups:

— with the formation of low-molecular-weight AAs of particular structure (Scheme 14, route *a*); and

Scheme 14



— with the formation of macromolecular AAs (Scheme 14, route *b*).

An original concept of CRP mediated by *in situ* generated nitroxide radicals was proposed[238] and experimentally tested using *C*-phenyl-*N*-*tert*-butylnitrone (**10**), one of the best known spin traps widely used in free radical chemistry (Scheme 15).

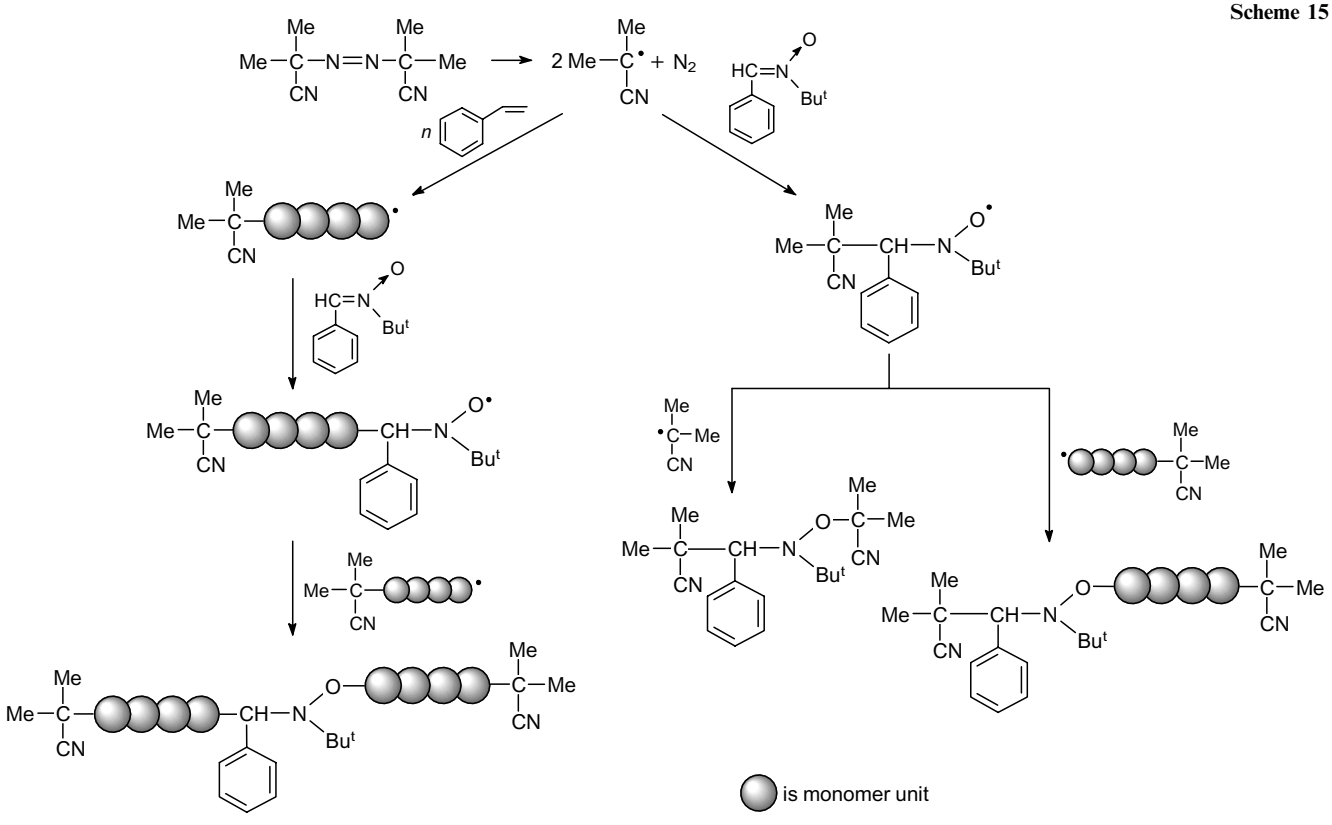
In 1999, researchers from Switzerland began to develop a concept of CRP in the presence of *in situ* produced nitroxides,[247] which was futher developed by other research groups.[240 – 245, 248 – 250] Interest in this CRP technique is due to the possibility to synthesize polymers based on monomers of different structure with specified molecular-weight characteristics, to modify the structure of the polymer molecule and to commercial availability and relatively low cost of CRP mediators.

This approach made it possible to perform not only homopolymerization of vinyl monomers including acrylic and methacrylic ones, but also the synthesis of corresponding random and block copolymers. More recently, Golubev, Zaremski and co-workers[240, 241] used this technique for high-temperature synthesis of macro-AAs. They evaluated the equilibrium constants for reversible dissociation of macromolecular AAs based on compound **10** ($\sim 4 \times 10^{-11}$ and $\sim 4 \times 10^{-10}$ mol L^{-1} at 90 and 120 °C, respectively) and found that these values are ten times higher those for 'pseudoliving' styrene polymerization in the presence of TEMPO.[43] Eventually, this is responsible for higher rate of the polymerization in the presence of macro-AAs based on them.

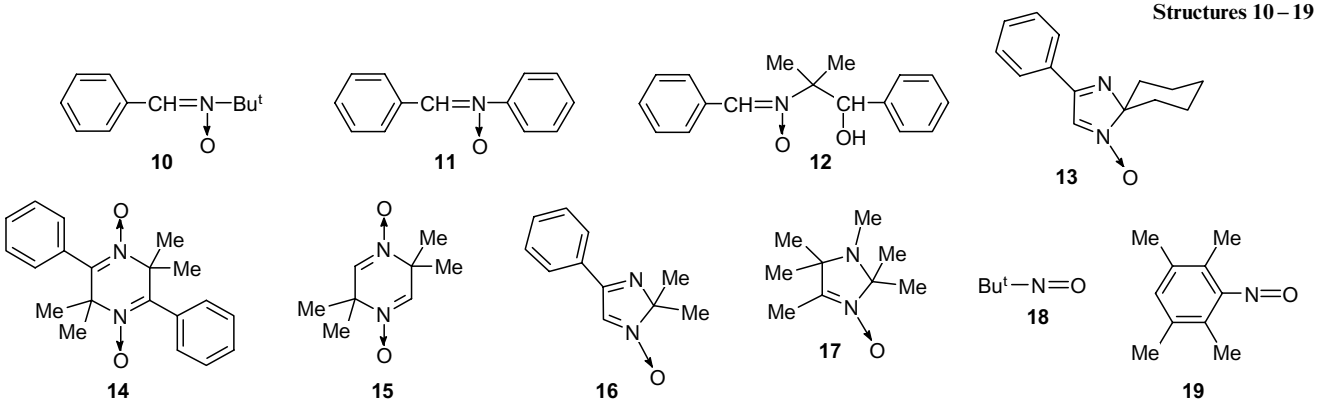
It should be noted that this method of low-temperature synthesis of macromolecular AAs was modified and called[251 – 253] 'enhanced spin capturing polymerization' (ESCP). Macromolecular AAs containing intra-chain nitroxide moiety were synthesized at low-temperatures (20 – 60 °C). Subsequent introduction of a new portion of the monomer made it possible to perform *in situ* NMP at higher temperature (110 °C) and to obtain postpolymers and the ABA block copolymers.[253] More recently, a tandem technique ESCP – click reaction and nitrones containing substituents with triple carbon – carbon bond were used to synthesize three-arm star polymers,[251] H-shape polymers[244] and dendrimers.[254]

The authors of most foreign studies on the use of spin traps as precursors of nitroxide radicals used the first group of polymerization processes (see

Scheme 15



Structures 10 – 19



Scheme 13, route *a*). Namely, low-molecular-weight AAs were formed *in situ* in a solvent at 60 – 90 °C and then used without isolation to perform homopolymerization and the synthesis of block copolymers at higher temperatures.[247 – 250, 255, 256] For instance, Detrembleur and co-workers[249] studied the polymerization of styrene in the presence of AAs based on nitrones of different structure (structures **10** – **17**) and established that the process is most efficient in the presence of compound **10**. Structural analogues of **10** can also be used as mediators of polymerization. However, replacement of phenyl group by an alkyl radical in the nitrone structure somewhat decreases the degree of control over the molecular-weight characteristics of polymer samples. Contrary to this, the introduction of electron-donating and electron-withdrawing substituents into the aromatic ring of the spin trap has almost no effect on the polymerization kinetics and on the molecular-weight distribution of polymers.[249] It should be noted that nitroso compounds, *e.g.*, **18** and **19**, are less efficient regulators of polymerization than nitrones. The process in the presence of these compounds proceeds slower and affords polymer samples with wider molecular-weight distribution.[13]

The results of studies on styrene polymerization in the presence of *in situ* formed macromolecular AAs unambiguously indicate that, in contrast to low-molecular-weight analogues, these compounds can be used for low-temperature NMP of styrene. The method for modification and thermolysis of macromolecular AAs using MALDI TOF mass spectrometry allowed one to determine their structure and, in particular, to locate the position of the nitroxide moiety. It was found that the *in situ* formed macromolecular AAs containing intra-chain nitroxide moiety differ in reactivity from nitroxide-terminated macromolecular AAs.

Thus, the *in situ* formed nitroxide radicals are efficient agents of controlled synthesis of macromolecules. The regularities of polymerization processes using these radicals are as follows:

— polymerization of vinyl and (meth)acrylic monomers proceeds without noticeable self-acceleration typical of uncontrolled radical polymerization;

— in spite of experimentally observed linear dependence of the molecular weight of the polymer on monomer conversion, the number-average molecular weight is not extrapolated to zero at zero monomer conversion; and

— polymers prepared in the presence of spin traps can act as macroinitiators, which allows one to perform postpolymerization and to synthesize block copolymers.

The results of studies on the polymerization of vinyl acetate in the presence of compound **10** appeared to be somewhat unexpected.[257, 258] It was established that in this case nitrone acts as inhibitor of polymerization and the polymerization process has an induction period. Although the initial rate of the polymerization process in the presence of nitrone is much lower than without nitrone, degeneration of the gel effect was not observed. The $\mathit{Đ}$ value significantly increases with increasing monomer conversion, which is atypical of controlled processes.

Summing up, the aforesaid suggests with certainty that sterically hindered nitroxide spin adducts containing macroradicals are promising regulators of molecular-weight characteristics of a wide range of monomers in the temperature range typical of industrial synthesis of polymers (50 – 100 °C). Their efficiency is determined by the thermodynamic factor associated with the degree of delocalization of the unpaired electron on the one hand and by the kinetic factor governed by the steric hindrances produced by blockage of the reaction centre (and, as a consequence, reduced reactivity of the radical) on the other hand. In addition, side reactions influencing the structure of the reaction centre of the nitroxide radical can also contribute largely.

5. Photoinitiated and photocatalyzed controlled synthesis of polymers

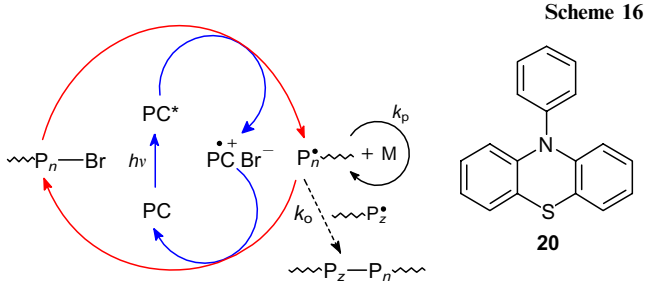
There are two main methods for inducing a classical radical polymerization, *viz.*, thermal and photochemical initiation.[1] The latter involves the use of light energy. All the controlled polymerization techniques mentioned above were initially developed for thermal initiation, which is most widely used in practice. Quite recently, the CRP methodology was successfully adapted to photoinitiated processes including ATRP.[259 – 264] It was found that polymerization can be catalyzed and initiated using not only transition metal complexes,[264] but also metal-free organic compounds. This relatively new CRP technique is termed 'metal-free atom transfer radical polymerization' (MF ATRP), 'organocatalyzed ATRP'[259] or 'photoinduced electron transfer (PET) ATRP'.[260 – 263] It contributes

largely to progress in the extremely important and popular green chemistry concept, thus attracting the attention of researchers.

By analogy with the ATRP considered above (see Scheme 5), MF ATRP is based on reversible transfer of halogen atom between the 'dormant' polymer chain and the catalyst (an organic compound). Usually, MF ATRP is catalyzed by polyaromatic and polynuclear heteroaromatic derivatives. A developed system of conjugated π-bonds allows them to absorb electromagnetic radiation and go to an excited state. The excited-state lifetime should be long enough for the catalyst molecule to participate in a redox reaction prior to ground-state transition. In turn, the oxidation or reduction of the photocatalyst (PC) should be reversible to close the catalytic cycle. Taking into account the activation mechanism of 'dormant' chains, MF ATRP processes can be divided into two groups:

— processes involving oxidative quenching cycle (Scheme 16)[265] where the catalyst is oxidized to corresponding radical cation upon transition to excited state; and

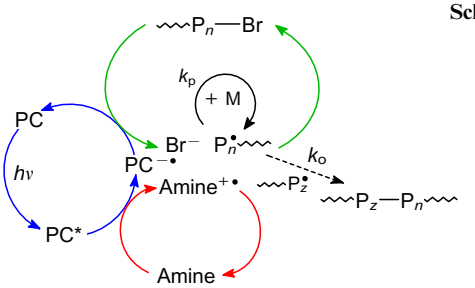
Scheme 16



20

— processes involving reductive quenching cycle (Scheme 17) where the catalyst in the excited state is reduced to the radical anion in the presence of a reducing agent.

Scheme 17



The tentative mechanism of the oxidative quenching cycle[265] involves photoexcitation of the PC to a singlet or triplet state as the first step, followed by transfer of an electron from the excited PC molecule (PC*) to the initiator (alkyl halide) or to a 'dormant' polymer chain and generation of an active radical and halide anion. The catalyst is oxidized to a radical cation with the formation of an ion pair with the halide anion. According to calculations and kinetic studies, reversible chain termination most probably occurs through a trimolecular reaction between the growing radical and the ion pair.

As mentioned above, MF ATRP is most often catalyzed by conjugated (especially, polynuclear) heterocyclic compounds that can efficiently absorb electromagnetic radiation with subsequent transition to highly reactive excited state. Among them, mention should be made of 10-phenylphenothiazine (**20**) that can catalyze CRP of methacrylic monomers under the action of near-UV radiation (λ = 380 nm).[261] The study on the catalytic activity of 10-phenylphenothiazine derivatives in MF ATRP revealed correlations between the structure of organic compounds, their physicochemical characteristics and the efficiency of control over the polymerization process.

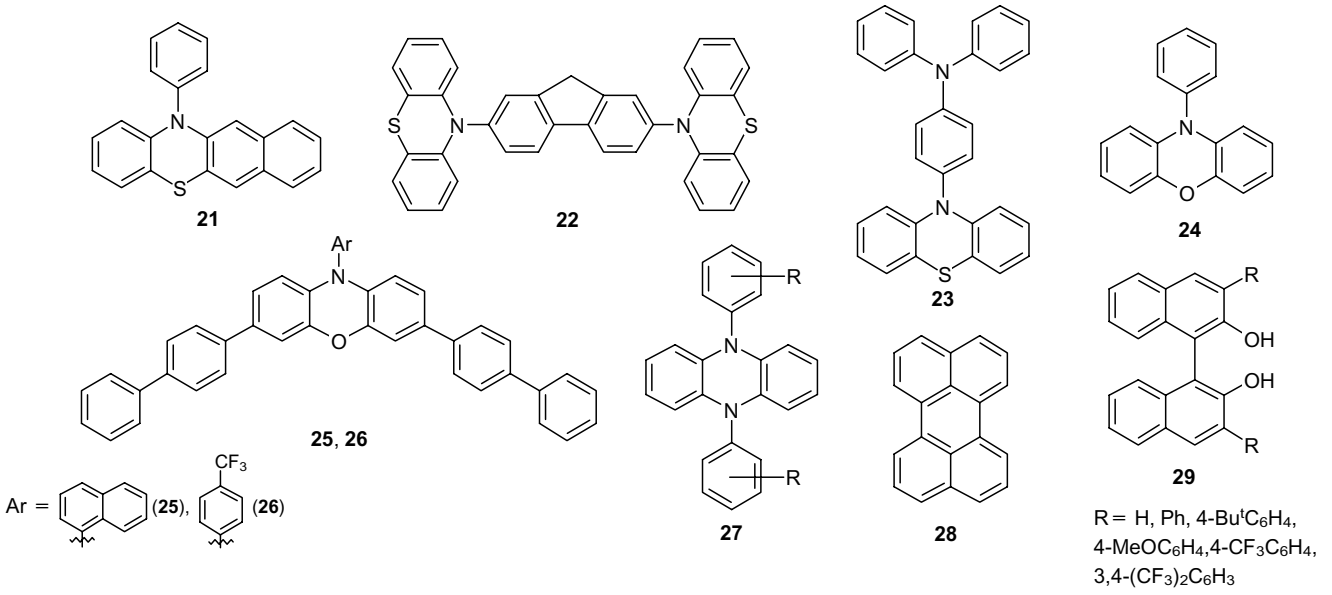
For instance, phenyl benzo[*b*]phenothiazine **21** has a better developed conjugation chain, is characterized by absorption at higher wavelengths and can be used as catalyst for visible light-driven polymerization of methacrylic monomers.[266] Compounds **22** (Ref. 267) and **23** (Ref. 268) were also successfully utilized in the CRP of methacrylic monomers. Polymerization in the presence of **22** and **23** can be performed to high conversions and is accompanied by linear increase in the molecular weight with monomer conversion and by the formation of polymers of low dispersity ($Đ \approx 1.3$).

10-Phenylphenoxazine (**24**) appeared to be less efficient catalyst for polymerization than 10-phenylphenothiazine. It provided a much poorer control over the polymerization process and the resulting polymer had a wider molecular-weight distribution.[269] The efficiency of phenoxazine derivatives in CRP catalysis was improved by extending the conjugation chain using a naphthyl moiety instead of phenyl one. For instance, compound **25** is one of the most efficient organic catalysts for CRP, which allows one to prepare well-defined polymers[269,270] with $Đ < 1.2$. A structurally similar derivative **26** was also successfully used to prepare a well-defined PMMA ($Đ = 1.27$) and its block copolymers with poly(ethylene glycol) using visible-light-mediated polymerization.[271]

N,*N*-Diaryldihydrophenazines **27** are one more class of heterocyclic compounds that can catalyze MF ATRP. Polymerization in the presence of these compounds proceeds in controlled regime in various solvents and affords polymers with low dispersity ($Đ \approx 1.1$).[272,273] The processes in question can be catalyzed by not only nitrogen-containing heterocycles, but also conjugated thiophene derivatives that are structurally similar to those used in organic light-emitting diodes.[274]

A detailed electronic spectroscopy and cyclic voltammetry study of PCs and quantum chemical modelling allowed one to set main criteria for potential PCs for CRP processes.[270,271,275] To achieve high monomer conversions, an organic catalyst should be characterized by high extinction coefficient at the wavelengths corresponding to exciting radiation and the PC* lifetime should be long.[265] In this respect organic compounds are way below transition-metal complexes. To prevent fast reverse ground-state transition, half-filled molecular orbitals in the excited triplet state should be spatially separated. These results can be obtained from quantum chemical calcu-

Structures 21 – 29



lations. In addition, the PC* should have a high reduction potential to favour efficient electron transfer to alkyl halide or 'dormant' chain. Of course, the oxidation of the catalyst should proceed reversibly. These criteria can be met by introducing electron-withdrawing substituents into the *N*-aryl moiety and by extending the conjugation chain in the donor fragment of the molecule.

Organic photocatalysts for MF ATRP should be have low ionization potentials (about -2 eV). 10-Phenylphenothiazine has an ionization potential of -2.1 eV, which is close to that of certain metal complexes used in photoinitiated atom transfer polymerization, *e.g.*, iridium compounds[276] used as catalysts for classical ATRP. Taking account of the value of this parameter, not only conjugated heterocyclic compounds, but also polynuclear aromatic hydrocarbons, in particular, perylene (**28**), anthracene and their derivatives can be of interest as CRP catalysts since the polymerization of MMA, styrene and BA in the presence of these compounds proceeds in controlled regime.[277, 278]

Derivatives of 1,1′-bisnaphthol (**29**) represent a new family of organic PCs for polymerization.[279] They can be used to perform MMA polymerization in dimethylacetamide under the action of violet light and MF ATRP under near-IR irradiation (λ = 870 nm). High-molecular-weight fused polycyclic aromatic compounds were also used as catalysts.[280]

The nature of the alkyl halide acting as initiator has a strong impact on the dispersity of the resulting polymers.[271] The most efficient initiators are diethyl 2-bromo-2-methylmalonate and α-bromophenylacetate (initiation efficiency is 92% and 74%, respectively), whereas ethyl 2-bromoisobutyrate and bromoacetonitrile often used in classical ATRP are characterized by lower initiation efficiency, so the corresponding processes yield polymers with a wider molecular-weight distribution.

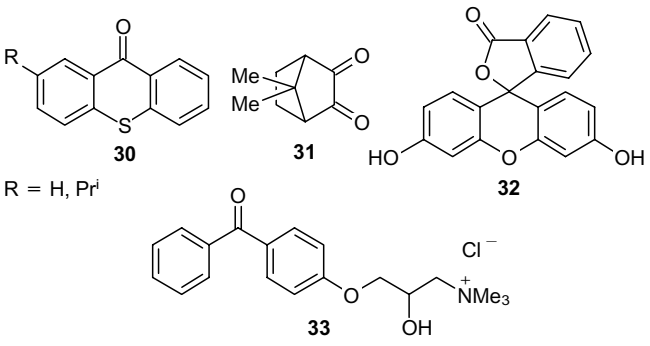
Controlled radical polymerization of many (meth)acrylic monomers including acrylonitrile, MMA, 2-(dimethylamino)methacrylate, *etc.* was performed using the MF ATRP technique. Similarly to classical atom transfer polymerization, in this case the molecular weight of the polymer linearly increases with monomer conversion. In addition, the process is characterized by linear time dependence of the logarithm of the ratio of the initial monomer concentration to the current monomer concentration, which is indicative of a constant concentration of growing polymer chains. A drawback of this CRP technique is a relatively high dispersity of the polymers synthesized.

The second mechanism of MF ATRP involves a reductive quenching cycle (see Scheme 17).[281 – 283] In this case, the role of PCs is played by conventional photoinitiators of radical polymerization (*e.g.*, benzophenone) and tertiary amine acting as reducing agent. After absorption of light the PC goes to an excited state (PC*) characterized by high oxidation potential and then PC* oxidizes the amine to a radical cation with simultaneous formation of the $PC^{-\bullet}$ radical anion (reductive quenching). In turn, the $PC^{-\bullet}$ radical anion reduces the alkyl halide or the 'dormant' polymer chain, thus initiating (or re-initiating) the polymerization process. The halide anion forms an ion pair with the amine radical cation. The interaction between the ion pair and the radical causes reversible chain termination. As an alternative, the amine radical cation can oxidize the bromide anion to bromine atom. In turn, the Br atom can either deactivate the growing macroradical or undergo dimerization to give a Br_2 molecule capable of deactivating carbon-centred radicals.

Tertiary amines suitable for being components of the catalytic system include donor polydentate ligands traditionally used in the classical systems for ATRP based on copper complexes, *e.g.*, pentamethyldiethylenetriamine[284] and tris(2-dimethylaminoethyl)amine (Me_6TREN).[285] It was also proposed to use simpler amines, *e.g.*, triethylamine.[286]

The processes in question were catalyzed by not only benzophenone, but also thioxanthone (**30**)[281] and benzaldehyde derivatives,[282] camphorquinone (**31**), flu-

Structures 30 – 33



orescein (**32**), fluorescein-based dyes (Eosin Y, erythrosin B)[286,287] and some other pigments.[288]

Metal-free ATRP can be performed both in bulk and in solution including aqueous media. A combination of Eosin Y with pentamethyldiethylenetriamine was used to perform polymerization of oligo(ethylene glycol acrylate) in aqueous medium affording polymers with rather narrow molecular-weight distribution ($Đ \approx 1.4$).[284] One more successful example of polymerization in aqueous medium is the synthesis of polyacrylamide in the presence of water-soluble benzophenone derivative **33** and Me_6TREN as reducing agent.[285]

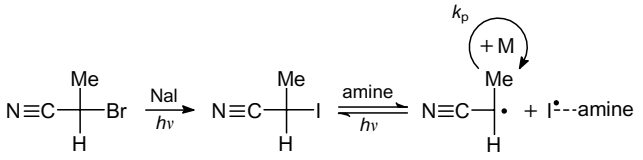
The synthesis of acrylonitrile-based polymers is a promising application field of photocontrolled polymerization techniques. In particular, the polymerization of acrylonitrile can be carried out using certain well-known dyes as organic catalysts, Eosin Y being the most efficient.[289] The process conducted in DMF under the action of visible light yielded polyacrylonitrile with a molecular weight of about 50 kDa and a dispersity of 1.7.

Photocontrolled polymerization is used for the synthesis of not only linear homopolymers, but also more complex architectures. For instance, block copolymers were synthesized[290] using a combination of MF ATRP and ring-opening polymerization (ROP) realized in orthogonal manner in the presence of perylene as catalyst. The synthesis of star polymers catalyzed by phenoxazine derivatives is yet another successful example of the macromolecular design using organic catalysts.[291] Photocontrolled radical polymerization in the presence of phenothiazine derivatives was also used to synthesize fluorine-containing polymers based on corresponding methacrylic monomers[292] and to modify solid surfaces by carrying out polymerization using a surface-grafted initiator.[293]

In spite of keen recent interest in MF ATRP processes, it should be mentioned that catalysts involved in control of MF ATRP with oxidative quenching cycle are difficult to synthesize and to isolate as individual compounds. Catalysts for MF ATRP processes with reductive quenching cycle (Type-2 catalysts) are often commercially available products and provide poorer control over the molecular-weight characteristics than metal-containing catalysts for ATRP. For instance, the dispersity of polymers thus prepared often is nearly two.

To eliminate these drawbacks, chemists optimize the available catalytic systems and offer unconventional solutions. For instance, recently,[294] it was proposed to use a ternary system based on alkyl bromide, sodium iodide and a tertiary amine as catalyst. The reaction of alkyl halide with sodium iodide causes *in situ* formation of alkyl iodide, which generates the initiating radicals under photoirradiation, and a complex of amine with iodine, a reversible chain termination agent (Scheme 18).

Scheme 18



This catalytic system was used to perform controlled polymerizations of various methacrylic monomers and, in particular, to synthesize block copolymers. The processes were characterized by linear increase in the molecular weight with increasing monomer conversion and by the formation of polymers with $Đ < 1.2$.

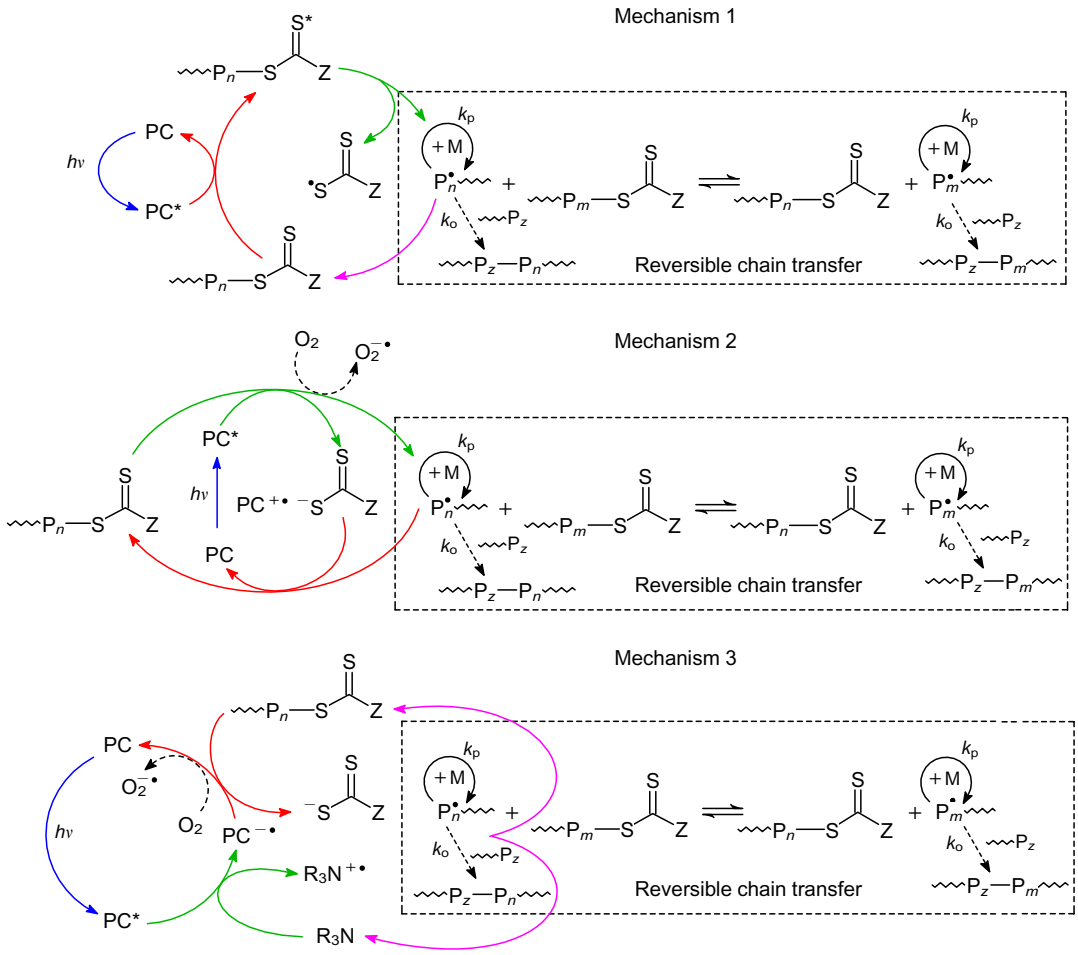
A feature of photochemical processes including those considered in this review is strong dependence of their efficiency on the reaction conditions, *viz.*, the power and shape of the light source, the wavelength of light, the shape of the reaction vessel, the mixing rate, *etc.*[295] In some cases this has a negative impact on the reproducibility of the synthesis of polymers, and complicates a comparative analysis of the results obtained by different authors. To make this dependence less pronounced, it was proposed to carry out the synthesis in photochemical flow reactors[296] suitable for more uniform irradiation of the entire volume of the reaction mixture to ensure a continuous character of the process.

Successful examples of performing a photocatalyzed RAFT polymerization were reported.[297] The process involves homolytic dissociation of the carbon – sulfur bond in corresponding adducts, accompanied by generation of free radical RAFT agents. This allows one to initiate the polymerization process without using radical initiators, as in the classical RAFT process, and thus enables better control over the molecular-weight distribution. A number of tentative mechanisms of the this process have been proposed, and all of them imply initial photoexcitation of the catalyst followed by energy transfer to the RAFT agent-capped 'dormant' chain and generation of active radical (Scheme 19).[298 – 300]

In the first mechanism the PC actually plays the role of a photosensitizer that absorbs electromagnetic radiation with subsequent energy transfer to the polymer chain. The excited macromolecule breaks at the bond with the RAFT agent to give a corresponding growing radical that can enter into the chain propagation and reversible chain transfer reactions, just like in the classical RAFT process.

The second mechanism[301,302] is by and large similar to the oxidative quenching cycle in MF ATRP (see above). The excited PC (PC*) reduces the RAFT agent at the end of 'dormant' macromolecule through one-electron transfer, thus producing a growing radi-

Scheme 19



cal and a thiocarbonate anion, and is then transformed to corresponding radical cation. The reverse reaction results in chain termination and regeneration of the catalyst.

If the system contains electron-donor compounds, the process can include the reductive quenching cycle.[302] In this case (see Scheme 19, mechanism 3) the PC* oxidizes the amine to give a radical anion, which reacts with the macromolecule to eliminate the growing radical and thiocarbonate anion. The reaction of the growing radical with the ion pair leads to chain termination and closure of the catalytic cycle.

A study[300] of polymerization in the presence of Eosin Y showed that the probability for the process to proceed by a particular mechanism depends on the irradiation wavelength. Irradiation with blue light (λ = 450 nm) allows the polymerization process to be initiated following all the three mechanisms considered. The energy of longer-wavelength green light (λ = 520 nm) is insufficient for homolysis of the carbon–sulfur bond according to mechanism 1 and the process can be initiated following two remaining mechanisms (see Scheme 19).

It should be noted that PC* can reduce not only 'dormant' chains, but also molecular oxygen. As a consequence, in some cases PET RAFT polymerization can be performed without degassing the polymerization mixture, which significantly simplifies the preparation of the composition.[301, 303]

The first catalysts for PET RAFT polymerization were the iridium complex *fac*-[Ir(ppy)$_3$] (ppy is 2-phenylpyridine)[298, 299, 301, 303, 304] and the ruthenium complex Ru(bipy)$_3^{2+}$ (bipy is 2,2′-bipyridine),[299, 305] both being known as PCs for other processes. They were used to perform polymerization of a wide range of well-known monomers including methacrylates, styrene, as well as vinyl acetate and *N*-vinylpyrrolidone, which are of low activity in CRP.[301, 303] Noteworthy is that the process can proceed even in the presence of small amounts of oxygen.

An important advantage of these catalytic systems is tolerance to functional groups. This allows one to simultaneously perform one-pot RAFT polymerization and ionic ROP, which offers prospects for the synthesis of novel materials with valuable properties. For instance, a catalytic system based on the iridium complex mentioned above was successfully used in the synthesis of poly[caprolactone-*b*-(methyl acrylate)] at room temperature.[306]

The amount of the iridium PC for RAFT polymerization consumed in the reaction is small (about 0.1% with respect to the RAFT agent); nevertheless, even so small content of heavy metals can be critical to certain applications, *e.g.*, microelectronics or medicine.[307] To solve this problem, it was proposed to replace the iridium catalyst by organic compounds. Among them, the best studied systems include fluo-

rescein derivatives, first of all, the dye Eosin Y, which is successfully used in MF ATRP processes.[302, 308 – 311]

Eosin Y and fluorescein (**32**) can catalyze PET RAFT polymerizations of various methacrylic monomers, including water-soluble ones, to give well-defined, short-chain-length polymers with specified molecular weights and narrow molecular-weight distributions.[302] The introduction of triethylamine into the system led to acceleration of the polymerization process and made it tolerant to atmospheric oxygen. In this case the amine acts as reducing agent that removes oxygen, which inhibits the process. Simple commercially available amines, namely, tributylamine, dimethylaminopyridine, pentamethyldiethylenetriamine and triethanolamine can be used as electron-donor additives.[309] The efficiency of the amine as catalyst correlates with the stability of the radical cation generated from the amine molecule. Compounds from other classes, *e.g.*, ascorbic acid can also be used as reducing agents for PET RAFT polymerization in air.[312]

Low sensitivity of the systems to oxygen allows them to be used in RAFT polymerization in flow photoreactors[310] or for 3D printing.[308] In the latter case one deals with photopolymerization of the composition containing cross-linking monomers, *e.g.*, ethylene glycol dimethacrylate.

Studies of relationships between the structure of compounds and their efficiency in PET RAFT polymerization resulted in formulation of the requirements for PCs;[302, 311] by and large, they are similar to the requirements for the catalysts for MF ATRP. First, for a PC to act as reducing agent, its reduction potential $E_{red}(PC^{+\bullet}/PC^*)$ should be lower than that of the RAFT agent. Next, the lifetime of PC* should be long enough to react with the 'dormant' chain prior to ground-state transition. This feature can be assessed using the quantum yield of fluorescence (it should be relatively low) and the rate of intersystem crossing (it should be high). The aforesaid, in particular, provides an explanation for the fact that polymerization in the presence of fluorescein proceeds much slower, although fluorescein is characterized by high quantum yield of fluorescence.

Based on these criteria, experimental data and results of quantum chemical modelling, a principle was established of structure optimization of fluorescein derivatives to prepare efficient catalysts for PET RAFT polymerization by varying the nature and arrangement of substituents.[311] New oxygen-tolerant fluorescein derivatives providing better performance were also proposed.

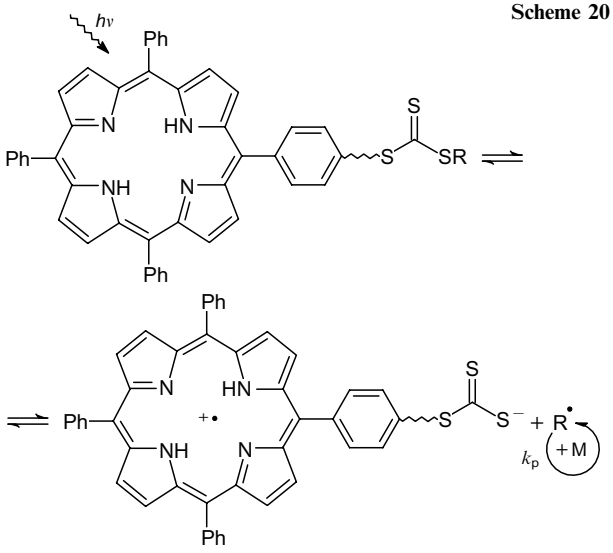
Porphyrin derivatives[313 – 317] including chlorophyll form a rather large group of catalysts for PET RAFT polymerization. The use of chlorophyll is of particular interest from the standpoint of green chemistry.[314, 316] Polymerization proceeds under irradiation at a long-wavelength ($\lambda = 635$ nm). The advantage of chlorophyll is its degradation in air upon completion of the polymerization process and subsequent decolouration; this holds for both pure chlorophyll and its extract from plant raw materials without fine purification.

Among synthetic analogues of chlorophyll that are used as PC for RAFT polymerization, mention should be made of tetraphenylporphyrin derivatives. Free tetraphenylporphyrin can act as PC for RAFT polymerization; however, its efficiency is low even if large amount is added.[258] At the same time, a tetraphenylporphyrin complex with zinc appeared to be more efficient catalyst for controlled polymerization of a wide range of monomers (acrylates, methacrylates, acrylamides, styrene).[317 – 319]

An original method for improving the catalytic activity of porphyrin derivatives involves preparation of RAFT agents based on them. Since the trithiocarbonate group responsible for control over the polymerization process and the porphyrin moiety acting as a 'molecular antenna' are covalently bound, being in the immediate vicinity of each other, the activation probability significantly increases.[313] Photoexcitation is followed by inner-sphere one-electron transfer from one part of the molecule to the other. A corresponding polymerization process is illustrated in Scheme 20.

Tetraphenylbacteriochlorin, a close analogue of tetraphenylporphyrin, appeared to be an efficient catalyst for polymerization proceeding under the action of far-red radiation ($700 < \lambda < 760$ nm; region between the visible and near-IR ranges).[315]

Scheme 20



Taking account of similarity between the mechanisms of PET RAFT polymerization and MF ATRP, one can assume that both processes can be catalyzed by the same compounds. An example is provided by *N*,*N*-diaryldihydropyrazines,[320] which can catalyze PET RAFT polymerization of various monomers including vinyl acetate having low activity in CRP. The ability of the same compound to catalyze both PET RAFT polymerization and MF ATRP allows one to synthesize block copolymers using bifunctional initiators. Other classes of compounds promising for photocatalysis of RAFT polymerization and ATRP include aromatic aldehydes[321 – 323] and thiophene derivatives.[324]

Perylene, a well-known catalyst for MF ATRP, was also studied as potential PC for PET RAFT polymerization.[325] It is assumed that the mechanism of polymerization in the presence of perylene includes an oxidative quenching cycle. The use of perylene

derivatives, *e.g.*, *N*,*N*-disubstituted water-soluble perylenediimine, instead of the parent compound, enables better control over the process and allows one to synthesize polymers based on hydrophilic monomers in aqueous media.[326] The polymerization mechanism is based on reductive quenching cycle with triethanolamine as reducing agent. According to calculations, complexation of the catalyst with cucurbit[7]uril allows the catalyst activity and the polymerization rate to increase owing to a decrease in the frontier orbital energies.

Graphitized carbon nitride, a non-traditional PC for PET RAFT polymerization,[327, 328] is of considerable interest owing to potential application in flow photoreactors. The material efficiently catalyzes visible light driven ($\lambda = 465$ nm) polymerization affording well-defined polymers with low dispersity.

In addition, PET RAFT polymerization can be catalyzed by various inorganic nanoparticles, *e.g.*, titania[329, 330] and zinc oxide.[331] Indeed, metal oxide PCs can reduce the RAFT agents (see Scheme 19), are cheap and readily available. However, polymers synthesized in the presence of metal oxides are characterized by rather wide molecular-weight distributions.

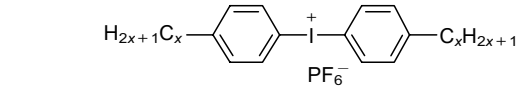
Quantum dots as catalysts for polymerization processes allow them to proceed at high rate and produce well-defined polymers with very low dispersity.[332, 333] Depending on the reaction conditions and on the choice of the RAFT agent, quantum dots can either be removed from the system[333] or left covalently bound with the polymer in the resulting organo-inorganic nanocomposite.[332] The use of sulfur- or phosphorus-doped carbon quantum dots possessing electron-donor properties also enables good control over the process.[334, 335] A nanocatalyst prepared by supporting carbon quantum dots on ferromagnetic Fe_2O_3 nanoparticles can be removed with ease from the polymerization medium and then re-used.

Chemists from South Korea and Spain proposed[336] a series of new polycyclic aromatic compounds as catalysts for PET RAFT polymerization. These compounds are highly stable in air and enable efficient control over the process even if their concentration in the system is 0.1% of the concentration of the RAFT agent.

The efficiency of controlled synthesis of macromolecules following the reversible deactivation mechanism can be improved using photoirradiation. In particular, back in 1997 Scaiano and co-workers[337] reported photopolymerization of styrene in the presence of AAs based on TEMPO and a photosensitizer xanthone. The authors believed that the synthesis of polymers was driven by intermolecular energy transfer from xanthone to AA.

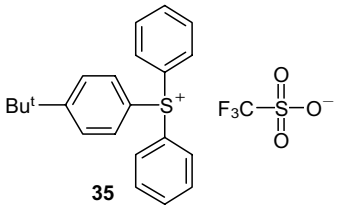
Taking polymerizations of a wide range of monomers in the presence of 4-methoxy-TEMPO and redox agents (iron complexes, iodonium and sulfonium salts **34** and **35**, respectively) as examples, Yoshida[338 – 344] for the first time demonstrated that nitroxide-mediated photopolymerization can be controlled (initiated, inhibited and re-initiated) by switching light on and off. However, the samples thus prepared were characterized by rather wide molecular-weight distributions despite the fact that polymerization proceeded with relatively high conversion even at room temperature.

Structures 34, 35



$x = 10 – 12$

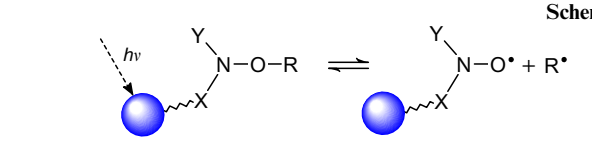
34



35

The results obtained by certain research groups suggested that efficient photoinitiated NMP requires that AAs be linked to an appropriate sensitizer (Scheme 21).

Scheme 21

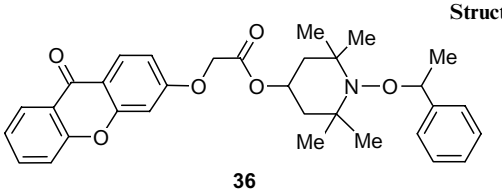


is sensitizer

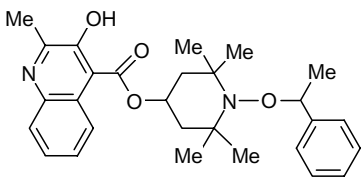
It is no coincidence that further studies[345 – 347] were aimed at developing a new class of AAs **36** – **38** containing sensitizing chromophores directly bound to the AA moiety to improve the efficiency of energy transfer in the systems. The new AAs were successfully used in CRP of styrene and BA; however, the polymer samples were characterized by rather high dispersity ($Đ > 2$).

Chinese chemists studied[348] photo-induced CRP of MMA at room temperature in the presence of photosensitive TEMPO-based nitroxides bearing various chromophoric groups (benzophenone, naphthalene and quinoline). The process was characterized by a linear increase in the molecular weight with monomer conversion and the polymer samples had low dispersity ($Đ = 1.3 – 1.4$). Controlled character of the polymerization was confirmed by successful postpolymerization of MMA.

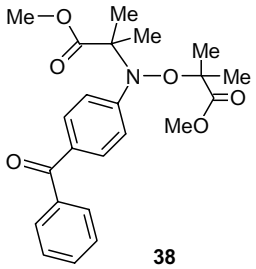
Structures 36 – 38



36



37



38

Concluding this Section, mention should be made that combining the advantages of CRP and photocatalysis offers new prospects for targeted synthesis of functional polymers of specified structure. Compared to other CRP techniques discussed above, this approach allows one to carry out polymerization in energetically favourable regimes without using metal-containing catalysts. This is of particular importance for reducing the cytotoxicity of polymers for biomedical applications including drug delivery systems as well as polymers for microelectronics and other high-tech industries where the presence of even trace amount of metals is critical. In fact, photocatalysis can bring synthetic methods of polymer chemistry closer to the light-induced processes of macromolecular synthesis occurring in living systems and organisms. Undoubtedly, this CRP technique is also promising in connection with 3D technologies for direct fabrication of polymeric items from monomeric raw materials. In this case, the development of novel efficient PCs including those tolerant to atmospheric oxygen as well as solving engineering problems associated with an increase in light penetration depth into opaque polymer media are of crucial importance.

6. Practical application of controlled radical polymerization techniques for industrial synthesis of functional polymers: examples

We believe that certain researchers initially treated the CRP concept as a near-future alternative to classical radical polymerization. However, a three decades experience demonstrated that the CRP techniques failed to overshadow the classical radical polymerization processes used in large-scale production of polymers and materials based on them. At the same time, the CRP concept allowed one to synthesize a variety of novel high-tech products and to significantly extend the application field of polymers. At present, polymers prepared by CRP are widely used as emulsifiers, dispersants and other surfactants, and thermoplastic polymers or chemically cured elastomers. They are also considered as potential agents for drug delivery systems. Methods of controlled synthesis of polymers are used for surface modification of solid materials and natural fibres to impart specific hydrophilic or hydrophobic properties to them, and for the synthesis of various bioconjugates for prostheses in regenerative medicine.[349]

The first patents in the field of CRP processes concerned the use of nitroxide radicals and AAs as regulators. For instance, in 1986 E.I.du Pont de Nemours and Co. (USA) patented[350] a polymerization process and polymers produced thereby in the presence of nitroxide radicals. The process produces not only relatively short-chain-length homopolymers with narrow molecular-weight distribution, but also block copolymers. More recently, this company patented[351] some other CRP techniques for the synthesis of block copolymers including RAFT polymerization.

Studies by Tordo and co-workers[203, 206, 207] supported by Arkema France S.A. (France) contributed largely to the development of reversible-deactivation polymerization techniques for the synthesis of commercially available products. First of all, mention should be made of the stable nitroxide SG1 (see above)[207] and the compounds based on SG1, *viz.*, BlocBuilder®, *N*-*tert*-butyl-*N*-1-diethylphosphono-2,2-(dimethylpropyl)-*O*-[1-(methoxycarbonyl)ethyl]hydroxylamine (MONAMS) and water-soluble bifunctional hexadiol-1,6-bis[(2-methyl-2-[*N*-(diethoxyphosphoryl)-2,2-(dimethylpropyl)aminoxy]propionate (DIAMS).[208 – 211, 352 – 358] Unlike the TEMPO derivatives, these AAs are prone to reversible dissociation to radicals at relatively low temperatures (70 – 75 °C), thus being more convenient for industrial synthesis of polymers. In addition, they provide efficient control of not only styrene polymerization, but also polymerization of acrylic monomers including BA.[357 – 369] Alkoxyamines produced by Arkema France S.A. allow one to perform not only homopolymerization, but also random copolymerization of different monomers[370 – 372] and block copolymerization including the synthesis of multiblocks, branched and star polymers.[360 – 364] These AAs are used for polymerization both in bulk and in solution including aqueous media, *e.g.*, in production of latexes containing nanosized inclusions.[365, 366]

At present, commercialized Arkema products synthesized using CRP techniques include:[349]

— BlocBuilder® initiator/controller for polymer producers;

— Flexibloc® macroinitiator (telechelic polymer with functional end groups, which can be re-activated under corresponding CRP conditions); and

— Nanostrength®, a PMMA-*b*-PBA-*b*-PMMA triblock copolymer.

Triblock copolymers Nanostrength® are composed of immiscible soft and hard blocks. Their microstructure is formed through self-organization of the blocks. Soft blocks (PBA) are responsible for high tackiness and low-temperature flexibility, while hard ones (PMMA) provide good adhesion and enhanced mechanical properties. Researchers at Arkema developed a family of Nanostrength® block copolymers that differ from one another in the weight fraction of the hard and soft blocks, molecular weight and functional groups (COOH, OH, epoxy group, *etc.*). From a practical standpoint it is important that these block copolymers served a basis for the development of hydrophilic block copolymers. These triblock copolymers exhibit high adhesive capacity, UV resistance and oxidative degradation stability. They are used to design glues and adhesives as well as coatings and composites that act as highly efficient modifiers of epoxy resins, cross-linking agents and compatibilizers for thermosetting and thermoplastic polymers. It is expected that the Nanostrength® acrylic block copolymers will find applications in cosmetic industry and surface coatings for, *e.g.*, electronics. In this connection, Arkema demonstrated commercial-scale feasibility of the synthesis of these block copolymers on a pilot facility in Mont (France).

A recent example of applications of the BlockBuilder® AA is the synthesis of water-soluble diblock copolymers of complex architecture, consisting of elastomeric and thermoplastic blocks.[373] The former represents a poly[BA-*b*-(methoxy)polyethylene glycol methacrylate] random copolymer, while the latter is a poly(BA-*b*-methacrylic acid-*b*-styrene) terpolymer.

Such copolymers are of undoubtful interest as dispersants for cosmetic and paint-and-varnish industries and as components of detergents and drilling fluids. One more patented application of water-soluble block copolymers is the use as support materials for 3D printing.[374, 375]

Chemists at Altuglas® International (a subsidiary or Arkema) developed a technology for manufacturing nanostructured PMMA-based glass, Altuglas® ShieldUp, using the BlocBuilder® initiator/controller.[349] The Altuglas® ShieldUp cast sheets have higher impact strength, transparency and chemical stability than those of PMMA synthesized using conventional radical polymerization and retain the key properties of PMMA, *viz*., low weight and design flexibility. This type of acrylic glass seems to be a candidate for automotive glazing, in particular, panoramic roof casting.[349]

Thermally stable nitroxide DPAIO (see Table 1) and AAs based on it were used to perform controlled synthesis of polystyrene and PBA at elevated temperatures (200 °C).[368] An original technique enabled polymerization with high conversion within a very short time (about 15 min!). The polymer chain linearly increased with increasing monomer conversion and the dispersity was 1.2 for polystyrene and 1.5 for PBA. Such a high-temperature CRP can be used to prepare polymeric materials with specific properties for applications in, *e.g*., coatings, ink and varnishes including printing industry.

Currently, the German company BASF SE is a leader in the application of CRP methods in industrial synthesis of polymers. The company produces a wide range of acrylic additives for paints and coatings based on organo- and water-soluble block copolymers. Studies on the use of CRP techniques including RAFT polymerization and atom transfer polymerization to produce dispersants began at BASF SE in the early 2000s.[368] From the BASF SE patents it follows that production of modern dispersants is a multistage process involving controlled synthesis of a polymer followed by its modification. In particular, a glycidyl methacrylate-based block copolymer synthesized in the first stage subsequently participates in polymer-analogous reactions where the copolymer structure is modified by introducing 'anchor' groups to stabilize pigments and to attain faster and more intense colours. The available side groups include succinimide derivatives[376] or benzoic acid derivatives.[377] Dispersants prepared using CRP techniques have low molecular weights (2500–8000 Da) and a dispersity in the range of 1.4–2.0. They allow one to stabilize dye particles less than 100 nm in size and thus to achieve deeper and more uniform colours using the same pigment. Copolymers developed at BASF SE are used in production of automotive coatings and wood paints. Commercialized BASF SE dispersants include two product lines, Efka® PX for organic paints and DISPEX® ULTRA PX for water-soluble enamels. From a practical standpoint it is important that the use of controlled synthesis of polymers does not raise the price of the commercialized end product.

In addition, BASF SE produces polymer-based active components for household chemistry and cosmetics using CRP techniques. In particular, multiblock copolymers prepared by RAFT polymerization and consisting of alternating neutral (acrylamide) and polycationic blocks are used in production of conditioning shampoos.[378] Modified block copolymers comprising BA, 2-dimethylaminoethyl methacrylate, styrene and poly(ethylene glycol) methacrylate blocks and synthesized using reversible-deactivation polymerization are utilized as components of highly efficient synthetic detergents produced by Henkel AG (Germany).[379]

One more player in the coating market, the company PPG Industries, Inc. (USA), actively uses atom transfer CRP techniques[380] to produce a line of ANDARO automotive coatings for leading global car manufacturers.

A method for preparation of pigment dispersants was patented[381] by the Lubrizol Corp. (USA). The first step of the technique involves DT CRP of copolymers consisting of methacrylic monomer blocks and poly(styrene-*b*-maleic anhydride) blocks. In the second step the product is modified by reacting with heterocyclic compounds containing primary and secondary amino groups. The reaction between the anhydride fragment of the polymer chain and the amino group causes the anhydride ring opening and the addition of the heterocyclic fragment. Dispersants thus synthesized are used in production of acrylic automotive coatings and also offer promise for microelectronics to manufacture liquid-crystal displays. Yet another important application field of the polymers thus synthesized is the production of Asteric viscosity modifiers for lubricating oils and hydraulic fluids.[349] For instance, block copolymers based on lauryl methacrylate and MMA synthesized by ATRP and by RAFT polymerization are used to prepare viscosity index improvers produced by Evonik Industries AG (Germany).[382]

In speaking of successful industrial application of block copolymers as dispersants and emulsion stabilizers, mention should be made of a poly(alkyl acrylate)-*b*-poly(acrylic acid) copolymer also known as Rhodibloc, which was developed at Rhodia, a Solvay Group company (Belgium).[383] These copolymers have been used for more than a decade as stabilizers of reverse emulsions in cosmetic industry, as drilling fluids and dispersant fuel additives.

Sika AG (Switzerland) is a global leader in production of a wide range of high-tech constructional materials, sealants and adhesives using controlled synthesis of polymers. Chemists at Sika proposed to use comb block copolymers of poly(ethylene glycol) methacrylate with cationic and anionic methacrylates[384] synthesized by RAFT polymerization as additives to improve the operating characteristics and stability of concrete fluids. Structurally similar copolymers based on poly(ethylene glycol) and ionizable monomers synthesized by RAFT polymerization[385, 386] or by reversible-deactivation polymerization in the presence of BlocBuilder[387] are used in production of dispersants for mineral binders.

One more example of practical application of RAFT polymerization is provided by protective coatings for aluminium door and window frames patented by Koninklijke DSM N.V. (Netherlands).[388] The coatings represent waterborne dispersions of copolymers

based on acrylic and methacrylic acids, diacetone acrylamide, BA and methacrylate prepared by controlled polymerization. Carboxylic groups improve the adhesion of the copolymers to the aluminium surface and thus the formation of protective films.

The 3M company (USA), a global leader in the field of adhesives and abrasives, developed, nearly nine decades ago, the transparent Scotch tape. At present, engineers at 3M actively use the CRP techniques to manufacture high-tech products. The company patented a number of mono- and bifunctional RAFT agents suitable for both traditional thermally induced and photo (UV)-induced controlled polymerizations. Block copolymers thus synthesized consist of 2-ethylhexyl acrylate, BA, isobornyl acrylate and some other monomer blocks and are used as binders for adhesive tapes.[389 – 393] The number-average molecular weight of such polymers varies in the range of 10 – 100 kDa, the dispersity being much lower than that of polymers synthesized using conventional polymerization.

Engineers at KANEKA Corp. (Japan) proposed atom transfer polymerization as a method for producing polymers used as sealant base.[394] They developed an efficient method for the synthesis of low-molecular-weight polymers or oligomers with reactive end groups that allow the oligomer to be cross-linked in the course of curing. Narrow molecular-weight distribution improves the rheological properties of the oligomers coated on the surface and allows one to form a uniform 3D network providing better operating properties. These sealants were commercialized as the XMAP™ product line. Since studies on the use of renewable sources of raw materials (including various manufacturing waste) to produce various marketable products are topical, mention should be made of a publication[395] concerning an original RAFT polymerization technique of triblock copolymers composed of BA and lignin-based monomers. The resulting polymers are of interest for production of adhesives with high glass transition temperatures, thermal stability and good adhesion to stainless steel.

The 3M company patented a composite material containing inorganic particles dispersed in a polymer matrix.[396] The material prepared by ATRP appeared to be promising for the preparation of light-scattering composites for light-emitting diodes. Covalent bonding between inorganic particles and the polymer matrix improves the stability of the material while variation of the nature of the monomer and the polymer chain length allows one to tune the optical properties of the finished material. A structurally similar composite material based on silica particles and synthesized using ATRP was developed at Rober Bosch GmbH (Germany) and positioned as anode active material for lithium batteries.[397] One more potential application of ATRP is the synthesis of polypropylene-*g*-PMMA as candidate membrane material for lithium batteries.[398]

An original application of ATRP for protecting the surface of copper wires on printed circuit board was proposed at Henkel AG.[399] It was established that precipitation polymerization of water-soluble hydroxyethyl methacrylate in aqueous medium causes the formation of insoluble polymer film creating a protective insulating coating on the printed circuit board tracks. This technology seems to be promising for application in the design of biomedical sensors.

Considering the application of polymers synthesized using CRP techniques in electronics, mention should be made of a series of inventions[400 – 405] made by LG Chem. (South Korea). They are concerned with adhesive compositions for production of liquid-crystalline displays for various devices. Block copolymers based on functional monomers are synthesized by RAFT polymerization,[400, 401] ATRP and by click chemistry methods.[402 – 405] Polymers thus prepared have molecular weights in the range of 10 – 60 kDa and a dispersity of at most 1.5.

Japanese companies widely use the CRP techniques to synthesize novel polymeric materials. In particular, Toagosei Co., Ltd. patented an adhesive composition representing poly(styrene-*co*-*N*-phenylmaleimide) prepared by RAFT polymerization. This elastomer exhibits rather high thermal stability.[406] As mentioned above, polymers synthesized by RAFT polymerization bear sulfur-containing groups that can decompose with time and release foul-smelling mercaptans. To eliminate this drawback, an efficient polymer modification technique *via* a reaction with amines was developed at Toagosei Co., Ltd.[407]

The Asahi Kasei Corp. (Japan) patented a method of synthesis of A – B – A triblock copolymers based on methacrylic monomers using reversible-deactivation polymerization.[408] The copolymers exhibit excellent optical properties, thermal stability and mechanical strength and can be used in manufacturing a wide range of products from household goods to solar cells. Thermally stable thermoplastic polymers for mechanical engineering are produced by the Mitsubishi Group (Japan) using cobalt-mediated radical polymerization with catalytic chain transfer.[409]

An original application of controlled polymerization is the synthesis of ionomeric thermoplastic elastomer for use in a golf ball cover layer with improved rebound resilience.[410] The prospects for application of controlled polymerization (including radical polymerization) techniques for the synthesis of various thermoplastic elastomers have been thoroughly considered in a recent review.[411]

Modern methods of controlled synthesis of polymers for manufacturing of high-tech products are also used in P.R.China. For instance, Wanhua Chemical Group Co., Ltd. patented a preparation method of block copolymers based on acrylic monomers using ATRP.[412] One more invention of Chinese researchers describes multiblock copolymers synthesized by RAFT polymerization and their application as viscosity index improvers for lubricant compositions.[413]

Acrylonitrile copolymers are of interest as precursors of high-strength carbon fibres.[414, 415] A narrow molecular-weight distribution provides better solubility of the polymers in spinning solutions and allows one to prepare a more uniform material on stretching, which is eventually responsible for higher breaking strength factor and elastic modulus of the carbon fibre. This type of copolymers can be prepared by ATRP[416 – 419] or by RAFT polymerization.[420, 421] Undoubtedly, the former technique is more promising since it one can use readily available reactants and the resulting polymers bear no sulfur-containing

groups that form sulfur oxides in the course of oxidative stabilization.

An indubitable advantage of ATRP, which is widely used in the synthesis of novel materials, is the possibility of surface modification of various substrates by grafting polymer chains. In this case an initiator molecule bearing a labile halogen atom capable of abstracting under the action of a catalyst is grafted onto the surface of the material being treated. In fact, one deals with application of modern methods of organic and organometallic synthesis in polymer chemistry.

For instance, this approach was used for surface modification of cotton fabrics with various (meth)acrylic monomers.[422] This made it possible to improve the mechanical properties the fabrics, to increase the degree of swelling or, *vice versa*, to impart hydrophobic properties to the fabrics, as well as to improve the ability of the fabrics to adsorb organic dyes, which is important for imparting colour fastness to the fabrics.

Modified silica particles, potential nanocontainers for drug delivery systems, were prepared by ATRP.[423] Coating nanoparticles with a polymer layer reduces protein adsorption on their surface, which enhances the therapeutic effect. Researchers from China established[424] that grafting poly[BA-*co*-2-(*N*-ethylperfluorooctanesulfamido)acrylate] polymer brushes to silica particles makes it possible to prepare superhydrophobic coatings.

Researchers from Japan used the CRP methodology to prepare water repellent coatings;[425] that work was supported by Daikin Industries, Ltd. (Japan). They synthesized comb polymers containing long-alkyl-chain monomer units (residues of $C_{14}-C_{18}$ fatty alcohols) in side chains using ruthenium complexes as catalysts. Owing to the presence of long alkyl chains the samples demonstrated high hydrophobiciy and formed coatings characterized by large water contact angles. Butyl acrylate star polymers synthesized using modified tannic acid as macroinitiator[426] are also of practical interest as hydrophobic coatings.

The synthesis of various 'smart' polymers capable of reversibly changing the structure under the action of external factors[427] is yet another important application field of CRP techniques. For instance, shape-memory cross-linked branched copolymers based on ethyl methacrylate were prepared.[428] One more example of such materials is provided by copolymers based on *N*-isopropylacrylamide and polyrotaxane-modified ε-caprolactone, promising as agents for targeted drug delivery systems.[429]

These examples of commercialized products demonstrate that the CRP techniques are with certainty among present-day methods of industrial chemical synthesis. Controlled syntheses of macromolecules under the radical initiation conditions are in fact the key stages of complex processes of fine organic synthesis to obtain compounds and materials with desired properties and operating characteristics.

7. Conclusion

Recently, the growth rate of global production of polymeric materials much exceeds that of global industrial production. In this connection, controlled synthesis of macromolecular compounds with preset properties and characteristics that can be specified during the synthesis steps is of paramount importance. Our analysis of published data (see above) demonstrates that at present targeted synthesis of novel polymers and macromolecular structures necessarily requires the use of CRP techniques, ATRP being the most efficient one. However, in some cases the presence of minor (even trace) amounts of metals in polymers for, *e.g.*, biomedical applications and microelectronics is critical. Therefore, recently, particular attention has been paid to the development of ATRP techniques using organic catalysts.

No less scientifically interesting and practically promising is the development of efficient methods for performing RDRP and RTCP under irradiation with near-UV and visible light emitted by, *e.g.*, such photochemically attractive light sources as commercially available light-emitting diodes. Using radiation with a particular wavelength, one can perform controlled synthesis of macromolecules at rather low temperatures (including ambient temperature), which has a positive impact on the dispersity and microstructure of polymer samples.

Two last-mentioned approaches can bring the CRP techniques much closer to the photoinitiated and photocatalyzed chemical processes occurring in living systems. In fact, the issue is the use of 'nature-like' technologies in the synthesis of functional polymers. High efficiency and selectivity of these processes can favour the expansion of the application field of CRP techniques to the synthesis of functional polymers with specified properties and characteristics. This branch of polymer chemistry, which naturally combines the advantages of free-radical polymerization (as the main method of industrial synthesis of polymers) and photocatalysis, seems to be of considerable promise for the development of theoretical foundations and practical applications of controlled synthesis of homo- and copolymers including oilgomers.

This subject area is not only basic research-, but also clearly practice-oriented in terms of the design of novel polymeric materials with improved properties. Among them, there are polymers and oligomers for biomedical applications including those used as capsules for targeted drug delivery, fabrication of new-generation implants and adhesives, synthesis of amphiphilic copolymers, design of polymeric printed-circuit resists and other functional polymers.

There is no doubt that since its discovery, methods of controlled synthesis of macromolecules failed not only to replace, but also overshadow the classical radical polymerization techniques used in production of basic polymers. However, it is clear that the development of the CRP concept furnished a variety of novel high-tech products and thus significantly extended the application field of high-molecular-weight compounds.

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The list of abbreviations and notations is as follows:

AA — alkoxyamine,
ATRP — atom transfer radical polymerization,
BA — butyl acrylate,
BlocBuilder® — 2-[*N*-*tert*-butyl-*N*-(diethoxyphosphoryl)(2,2-dimethylpropyl)aminoxy]-2-methylpropionic acid,
CCT — catalytic chain transfer,
CRP — controlled radical polymerization,
$Đ$ — dispersity,
DPAIO — 2,2-diphenyl-3-phenylimino-2,3-dihydroindol-1-yloxyl,
DT — degenerative chain transfer,
$[I]_0$ — initial concentration of initiator,
K — equilibrium dissociation constant,
k_a — rate constant for addition,
k_c, k_d — rate constants for recombination and dissociation, respectively,
k_{ex}, k_p, k_o — rate constants for chain transfer, chain propagation and chain termination, respectively,
M — monomer,
$[M]$ — monomer concentration,
Me_6TREN — tris(2-dimethylaminoethyl)amine,
Met^nL_x — metal complex catalyst,
MF ATRP — metal-free atom transfer radical polymerization,
MMA — methyl methacrylate,
M_n — number-average molecular weight,
M_w — weight-average molecular weight,
MW_{mon} — molecular weight of monomer,
NMP — nitroxide-mediated polymerization,
OMRP — organometallic-mediated radical polymerization,
$[P^\bullet]$ — radical concentration,
$\sim P_n^\bullet$, $\sim P_m^\bullet$, $\sim P_z^\bullet$ — polymer radicals,
PBA — poly(butyl acrylate),
PC — photocatalyst,
PMMA — poly(methyl methacrylate)
RAFT — reversible addition-fragmentation chain transfer,
RDRP — reversible-deactivation radical polymerization,
ROP — ring-opening polymerization,
RTCP — reversible chain transfer catalyzed polymerization,
S — monomer conversion,
SARA — supplemental activator and reducing agent,
SFRP — stable free radical polymerization,
SG1 — *N*-*tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)]oxyl,
TEMPO — 2,2,6,6-tetramethylpiperidine-1-oxyl,
TIPNO — 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide,
$X^\bullet$ — atomic group being transferred,
X – A — reversible chain transfer agent,
[XP] — concentration of 'dormant' chains in DT processes,
v_{ex} — exchange rate,
v_p — chain propagation rate,
τ — time.

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