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'Living'-chain radical polymerisation

G V Korolev, A P Marchenko

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Abstract. The review is devoted to various types of compounds used as agents for 'living' radical polymerisation, such as alkoxyamines formed upon addition of the chain carrier radicals, $R^{\bullet}$, to stable nitroxyl radicals, as well as products of the addition of the radicals to transition metal complexes with different ligands, *etc*. In all cases, the mechanism of the action of these agents consists in their reversible dissociation $A \rightleftarrows R^{\bullet} + X^{\bullet}$, where $X^{\bullet}$ is a stable free radical or a metal-containing complex which can accept radicals $R^{\bullet}$ ($R^{\bullet} + X^{\bullet} \rightarrow A$) and thus compete with the quadratic chain termination. Particular attention is paid to the studies which allowed a quantitative formulation of the mechanism of 'living' radical polymerisation in the form of a mathematical model suitable for predicting both the parameters of the polymerisation and the properties of the resulting polymer (molecular mass and polydispersity). The bibliography includes 359 references.

I. Introduction

'Living' radical polymerisation, or, more precisely, 'living'-chain radical polymerisation is a new line of investigation in the area of radical polymerisation, known from the early 1990s. The origination and development of this area of scientific exploration has become possible owing to the discovery in the last two decades of a new elementary act of polymerisation processes involving the chain carrier radicals $R^{\bullet}$, namely, the reversible addition of $R^{\bullet}$ to several metal complexes or to stable free radicals (in particular, to nitroxyl radicals).

Numerous studies on 'living' radical chains (LRC) reported over the last three years (100 articles and more *per annum*) confirm that this new field is of great scientific and technological importance and appears to have considerable promise. Most prominent in this research area are Matyjaszewski's group in the USA and Fukuda's group in Japan. In these research groups, studies on LRC are carried out by polymer chemists in co-operation with mathematicians and physicists, which indicates the high level of scientific co-ordination and financial backing.

This review is concerned with systematisation and critical review of a great body of data on LRC accumulated to date. The authors of the review have worked in the area of LRC since its inception. They appeared to be among the pioneers of the elementary processes which provide the basis for 'living'-chain radical polymerisation.

G V Korolev, A P Marchenko Institute for Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax (7-096) 576 40 09. Tel. (7-096) 517 10 89.
E-mail: korolev@icp.ac.ru (G V Korolev),
amarch@icp.ac.ru (A P Marchenko)

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II. 'Living'-chain anionic polymerisation

The concept of a 'living' polymer chain or simply a 'living' chain (LC) appeared in studies of anionic polymerisation and goes back to Szwarc.[1] He recognised that if a growing polymer anion (a chain carrier, R_A) cannot be quadratically terminated ($R_A + R_A \rightarrow$ 'dead' polymer), then, in the absence of reactive impurities (X) capable of breaking the polymer chain following a linear mechanism ($R_A + X \rightarrow$ 'dead' polymer), anionic polymerisation proceeds without chain breaking, as a 'living' process. In this case, the lifetime (τ) of growing polymer chains exceeds the time necessary for complete conversion (t). In other words, the polymer anions R_A remain 'living' not only during the polymerisation, but also following completion of the process, *i.e*., after complete consumption of the initial monomer. 'Livingness' of polymer chains is confirmed by the fact that the polymerisation process restarts upon addition of a fresh portion of the same monomer or any other monomer which can undergo anionic polymerisation at the same centres R_A.

A conventional anionic polymerisation proceeds in such a way that the initiation of R_A is a relatively fast reaction which takes a time interval τ_i much shorter than the time necessary for complete conversion (t). The condition $\tau_i \ll t$ implies that the initiation of all chains occurs nearly simultaneously and that they grow synchronously throughout the polymerisation, so that the number-average molecular mass (M_n) of the resulting polymer is proportional to time. The molecular mass distribution of the polymer chains narrows monotonically as M_n increases and reaches very low values (the polydispersity index, M_w/M_n, approaches a value of 1.0) already at not too high M_n values (several tens of monomer units). This remarkable property is inherent in the 'living' chains only ($\tau > t$ and $\tau_i \ll t$). In the case $\tau \ll t$ (short-lived chains), which corresponds to radical polymerisation, the lowest polydispersity of the polymer is either 1.5 or

2.0 depending on the type of chain termination reaction (disproportionation or recombination).

The use of these valuable properties of the products of 'living' polymerisation has led to design of a novel class of polymeric materials, *viz*., block copolymers of the $A_nB_mA_n$ type, where A is a polystyrene block, B is a polyisoprene or polybutadiene block, and m and n are the numbers of monomer units in the blocks. At particular m and n values and at the temperatures which are above the glass transition temperature of the elastic block B, but below the glass transition temperature of the block A, these types of copolymers behave as vulcanised rubbers possessing very good physicochemical properties. This is due to a specific structure of the block copolymers, *viz*., the presence of glassy domains comprising several blocks A arranged regularly in a continuous elastic B-block matrix. The domains playing the role of cross-link points of the polymer network are essentially the same size, which is provided by very low polydispersity of the blocks A. The sizes and regular spatial arrangements of the blocks, which govern the physicochemical properties of the material, depend on n and the m/n ratio. At temperatures above the glass transition temperature of the block A, the copolymer behaves as a nonvulcanised rubber. Depending on temperature, these polymers possess the properties of vulcanisate or devulcanisate. They have played an outstanding role both in the polymer technology and in ecology since in this case the recovery of wastes and exhausted products has become much easier.

At the same time, 'living' anionic polymerisation requires an extremely labour-consuming procedure for the removal of impurities X from an initial reaction system to prevent chain breaking. Additionally, the number of pairs of the monomers of the types A and B is rather limited. Thus, the idea of performing a 'living'-chain radical polymerisation appeared to be quite attractive.

III. 'Living'-chain radical polymerisation

The fundamental distinction between 'living'-chain radical and 'living'-chain ionic polymerisation is that quadratic chain termination is of great importance in the former case and plays a negligible role in the latter. In other words, 'living'-chain radical polymerisation includes deactivation of growing active centres by termination between them (R + R → 'dead' polymer).† Thus, implementation of 'living'-chain polymerisation requires basically different approaches, since in this case it is the main participant of the polymerisation process rather than a removable (*e.g*., by purification) impurity that plays the role of chain terminator, which results in a situation where $\tau \ll t$. Therefore, meeting the main condition for 'living' radical polymerisation, $\tau > t$, requires the development of a procedure for extending the lifetime of active centres (chain carriers) R. This also requires the retention of their high reactivities towards the monomer molecules (M) in order to provide the possibility for the polymer chain to grow following the 'R + M → chain' mechanism. This means that radicals R should be deactivated in order to preclude quadratic chain termination and, at the same time, should retain their activities in order to provide the polymer chain propagation (R + M). At first glance, this problem seems to be intractable.

The main advantage of 'living'-chain polymerisation consists in the possibility of obtaining a desired product with narrow polydispersity. At the same time, the second condition necessary for exploitation of this advantage, $\tau_i \ll t$, is also not met in the case of radical polymerisation. Here, initiation of new chains occurs throughout the polymerisation process rather than during a short initial period τ_i, thus disturbing the simultaneous chain propagation and unavoidably increasing the polydispersity of the resulting polymer even in those cases where the lifetime of radical R can be extended to time intervals $\tau > t$.

Eventually, 'living'-chain radical polymerisation seems to have no chance of success. However, a new elementary act of radical polymerisation has been discovered, namely, temporary entrapment of the chain carrier radical R by an acceptor A (R + A ⇄ RA) followed by release of R (the so-called reversible inhibition). This made it possible to solve both problems, *i.e*., to extend the time interval τ ($\tau > t$) and to achieve simultaneous propagation of all chains, thus meeting the condition $\tau_i \ll t$. Later, yet another solution to the problem was found, consisting of carrying out the reactions $R^1 + A \rightarrow R^1A$ and $R^1A + R^2 \rightarrow R^2A + R^1$, where R^1 and R^2 are the growing polymer chains of the same nature but different lengths, and/or the growing chains of different nature. Mention may be made that these two solutions differ only in the type of regeneration of the entrapped (accepted) chain carrier radicals. In the former case, the RA adduct dissociates into the initial components, whereas in the latter case the entrapped chain carrier radical R^1 is released from the R^1A adduct following the radical substitution reaction $R^1A + R^2 \rightarrow R^2A + R^1$.

Among the substances suggested for the use as acceptors A are stable free radicals R_s (nitroxyl radicals, triphenylmethyl, *etc*.) and metal complexes (porphyrin, phthalocyanine and cobaloxime cobalt complexes, copper and iron complexes with halide and organic ligands, *etc*.). Active chain carrier radicals R react with stable radicals R_s to give adducts in which the $R-R_s$ covalent bond is relatively weak and thus can dissociate at 373–423 K. For instance, if R is a growing polystyrene chain and R_s is a stable nitroxyl radical, the bond strength in the $R-R_s$ adduct is estimated at $E = 125.4$ kJ mol^{-1}, which provides a rather high rate constant for bond dissociation, $k_1 = 10^{-4}-10^{-5}$ s^{-1}, already at 373 K.

First, let us consider the above-mentioned elementary reactions as applied to the problem of 'living' chains taking the R + A ⇄ RA reaction as an example. Let us denote the rate constants for dissociation and reverse recombination as k_1 and k_2, respectively, the acceptor A as X (in order to specify it as a stable free radical) and the adduct as RX. If RX is used instead of conventional initiators (peroxides, azodinitriles, *etc*.) of radical polymerisation, the mechanism of the process can be described by the following scheme:

Scheme 1

$$RX \xrightarrow{k_1} R + X \quad \text{initiation}$$

$$R + M \xrightarrow{k_p} R' \quad \text{chain propagation}$$

$$\left.\begin{array}{l} R + X \xrightarrow{k_2} RX \\ R + R \xrightarrow{k_t} P \end{array}\right\} \text{chain termination} \left\{\begin{array}{l} \text{temporary} \\ \text{permanent} \end{array}\right.$$

At particular values of rate constants k_1, k_2, k_p and k_t, this four-stage mechanism provides a negligible contribution of chain termination reactions. Provided that $k_t[R] \ll k_2[X]$, the prevailing chain 'termination' by the R + X reaction simply makes the chain temporarily inactive (a 'dormant' chain, RX) until the next dissociation act of RX. In such a manner the condition $\tau > t$ is met. In the final stage of polymerisation (after complete consumption of the initial monomer), almost all chains, except for a small fraction of 'dead' (quadratically terminated) chains that form a conventional random (statistical) polymer P, appear to be 'dormant' in the form of RX. Obviously, the addition of a fresh portion of the initial or another monomer (if a block copolymer is synthesised) will re-activate the chain carriers R, which means that the situation will be quite adequate to a 'living' polymerisation.

To meet the second essential condition, *viz*., simultaneous chain initiation ($\tau_i \ll t$), it is sufficient that the half-life of the adduct RX, equal to $0.69/k_1$, be much (10 to 100 times) shorter than the time necessary for complete conversion, t. Provided that $0.69/k_1 \ll t$, each growing chain manages to be both in active and 'dormant' state tens or hundreds times. This synchronising mechanism of chain propagation provides a very low polydispersity of the polymer. It should be noted that corresponding fitting procedure for numerical values of rate constants uses the k_1 and k_p

† Hereafter, in some instances the radical sign will be omitted for simplicity.

constants as well as the temperature (taking into account the temperature dependence of k_1 and k_p) as independent variables.‡

Thus, the use of acceptors X that temporarily entrap the chain carrier radical R and then release the initial species X and R makes it possible to solve the problem of implementation of a 'living'-chain radical polymerisation. Unlike anionic polymerisation in which the chain carrier cannot undergo quadratic chain termination at all, it is appropriate to call the process discussed above a pseudo-'living' polymerisation (and, correspondingly, to consider pseudo-'living' chains), since the radical chains propagate only in the form of active chain carriers R following their 'recovery' from the 'dormant' state and thus can undergo quadratic termination.

It should be noted that the four-stage process discussed above is a non-steady-state process. Therefore, correct quantitative estimates of the parameters of the process can be obtained only after solving corresponding systems of differential equations rather than algebraic equations, as is the case of a steady-state process.

Finally, mention may be made that a 'living'-chain radical polymerisation process following this mechanism is stable towards such disturbing factors as additional initiation

$$I \xrightarrow{k_1'} R,$$

where I is an initiator supplied from an external source or the monomer itself (self-initiation involving the monomer molecules occurs, *e.g.*, in the styrene polymerisation at temperatures above 373 K). Provided that the $k_1'[I]$ value is at least 5 to 10 times smaller than the $k_1[RX]$ value, this disturbing factor can be ignored. This condition can be met, as will be shown in the next Sections of the review dedicated to consideration of particular experimental data.

The other type of 'living'-chain polymerisation using the following elementary stages,

$$R^1 + A \longrightarrow R^1A \quad \text{and} \quad R^1A + R^2 \longrightarrow R^2A + R^1$$

differs from that discussed above (using the $R + A \rightleftarrows RA$ reaction) only in that it requires the use of an initiator I (or the process should be performed under conditions of spontaneous initiation involving the monomer), since the R^1A adduct does not initiate polymerisation.§

IV. The progress in investigations on 'living'-chain polymerisation

The progress in studies on 'living'-chain radical polymerisation can be divided into three stages.

1. The discovery of temporary entrapment of chain carrier radicals R by compound A with the formation of labile adducts R—A from which R can be released by dissociation (or following a radical substitution reaction, as was shown later). This phenomenon was called reversible inhibition.

2. The use of reversible inhibition for designing a 'living'-chain radical polymerisation process (theoretical analysis, experimental studies).

3. Implementation of 'living' chain radical polymerisation following a procedure which includes an exhaustive system of proofs of successful polymerisation (registration of changes in the average molecular mass, molecular mass distribution and other characteristics during monomer conversion).

It is hard to mention a pioneering work for stages 1 and 2. More correct is to consider a number of pioneering studies carried out independently by investigators from different research groups. However, the third stage undoubtedly began with a pioneering study carried out by investigators from Canada.[2] Taking the radical polymerisation of styrene in the presence of a stable iminoxyl radical (X) as an example, they were the first to show that the chain carrier (the growing polystyrene chain) R is alternately present in the reaction system in the deactivated (in the form of adduct RX) and active (in the form of free radicals R + X) states. This was proved by corresponding kinetic studies and by measurements of molecular mass distribution and average molecular mass of the resulting polymer during the conversion. Unlike unsuccessful attempts of their predecessors, the success of investigators from this research group is due to an extremely fortunate (chance or predicted?) choice of styrene as the monomer, since the presence of a phenyl substituent in the α-position with respect to the R—X bond, which undergoes dissociation, makes this bond more labile, which allows its dissociation at a sufficiently high rate at temperatures below 423 K. This fact appeared to be essential since at $T > 423$ K the contribution of hydride transfer accompanying the dissociation increases and the dissociation mechanism changes from reversible

$$RX \rightleftarrows R + X$$

to irreversible

$$RX \longrightarrow R'(=) + XH,$$

where R′(=) denotes the 'dead' (terminated by intramolecular disproportionation) polystyrene chain with the end group containing a double bond and XH is the corresponding hydroxylamine.

This pioneering work [2] initiated the appearance of numerous publications and their number seems to have no limit as yet. At the same time, it should be remembered that the communication cited was preceded by a number of experimental and theoretical studies carried out at the first two stages. A scheme of the development of investigations in the area of 'living' polymerisation is presented below (Scheme 2).

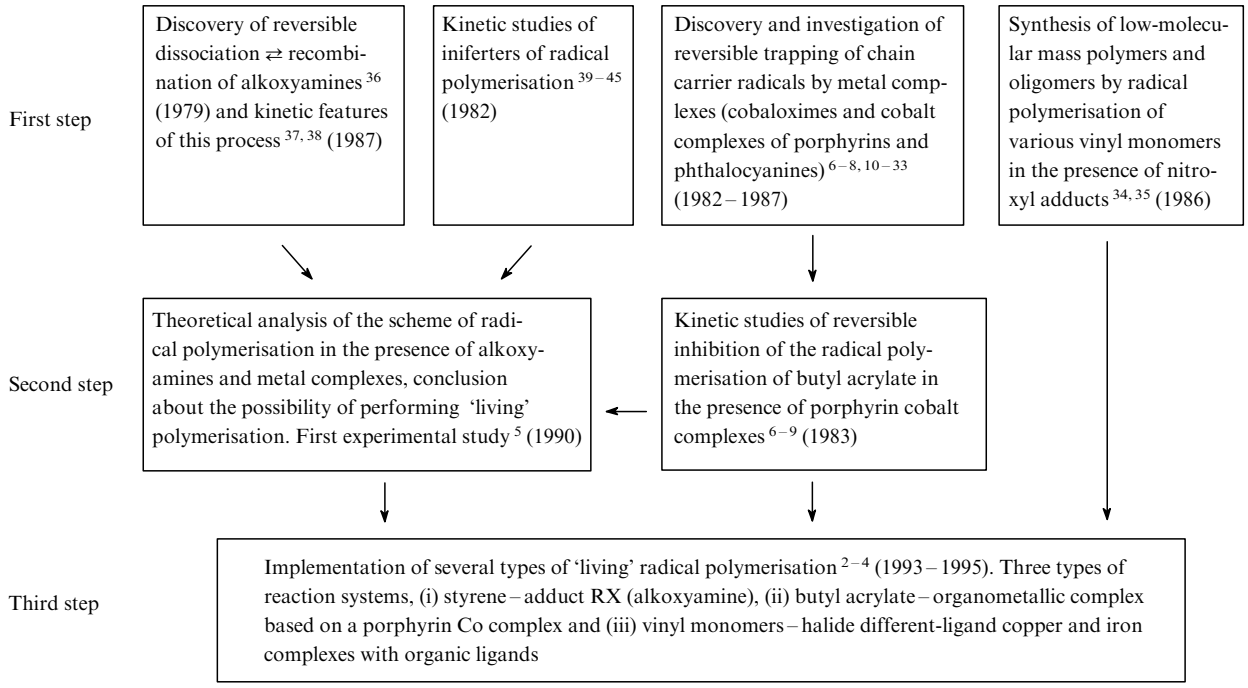
This scheme of pioneering studies may seem to be too cumbersome and overburden with details; however, it reflects the state-of-the-art in this area. First, at first glance different-type and non-related phenomena have been observed in studies of compounds of different chemical nature, such as alkoxyamines, macrocyclic cobalt compounds (later, copper and iron complexes), dithiocarbamates, *etc*. These studies were carried out concurrently and independently. Then, it was appreciated that, despite different chemical nature of compounds studied, all of them obey identical kinetic regularities as regards their ability to entrap temporarily (reversibly) active free radicals (including growing polymer chains) and release them after certain time intervals. Simultaneously, the investigators perceived the possibility of using this type of acceptors ('trappers') as agents for 'living' radical polymerisation. (This was best shown by Smirnov.[5]) Then, several types of 'living'-chain polymerisations were reported (each of these studies formed the basis for an independent investigation line). Further development of these investigation lines is based on these initial pioneering works.

In conclusion, it should be noted that we cannot say unambiguously who was the pioneer of 'living'-chain anionic polymerisation. Undoubtedly, Szwarc [1,46,47] has not only systematised and thoroughly analysed the key phenomena related to 'living' carbanions, thus having created a well-founded scientific discipline, but was also the first who discovered many of these phenomena. Nevertheless, his studies were preceded by investigations of other researchers. As early as 1936, Abkin and Medvedev [48] developed an original procedure for the determination of the lifetime (τ) of growing carbanion polymer chains and found that for anionic polymerisation of butadiene catalysed by sodium metal the τ value is so long that it exceeds the time necessary for complete conversion of the monomer. In other words, they discovered a 'living' chain carrier carbanion and established that the polymerisation proceeded without chain breaking (in a 'living' manner). However,

‡ The rate constants k_2 and k_t depend only slightly on both the nature of the reagents (R and X) and the temperature (their numerical values lie within the limits $10^7 \leqslant k_2 \leqslant 10^8$, $10^7 \leqslant k_t \leqslant 3 \times 10^7$ litre mol^{-1} s^{-1}).

§ The only exception are metal halide–alkyl halide systems in which free radicals can be generated (see Section VI).

Scheme 2



this study received little attention and in 1956 Szwarc *et al.*[46, 47] rediscovered 'living' polymerisation of vinyl monomers as though it were a new phenomenon.

V. Alkoxyamines as agents for 'living'-chain radical polymerisation

1. A brief history of investigations

As long ago as the 1970s, it was found [36, 37] that entrapment of active free (*e.g.*, polymethacrylate) radicals R by stable free (*e.g.*, iminoxyl) radicals X at moderate temperatures (below 323 K) results in the formation of stable adducts RX (alkoxyamines) which can release the initial radicals X and R upon raising the temperature to 373–423 K. More recently, this property of the adducts RX was used to perform one of the first 'living' radical polymerisations.[5] Other stable (*e.g.*, phenylmethyl) radicals were also tried as X;[49, 50] however, these attempts failed. In majority of studies, nitroxyl radicals were used, which react with hydrocarbon chain carrier radicals to give the corresponding alkoxyamines.

First of all, mention should be made of the pioneering works [5, 37, 38] (see Scheme 2), as well as of the studies in which alkoxyamines were used as initiators.[34, 51–55] It is these studies that best showed the salient features of 'living'-chain polymerisation, namely, a reduction of polydispersity and an increase in molecular mass during monomer conversion and the correspondence between the number of growing polymer chains (n_c) and that of alkoxyamine molecules introduced into the system (n_a). This correspondence means that at any degree of conversion (Γ), the following relationship is valid

$$\Gamma[M]_0 \frac{M_M}{M_n} = n_c = n_a ,$$

where $[M]_0$ is the concentration of A monomer in the initial system, M_M is the molecular mass of the monomer and M_n is the number-average molecular mass of the polymer at a given degree of conversion.

These publications [34, 51–54] were followed by a number of studies [2, 56–61] in which alkoxyamines were synthesised *in situ* from nitroxyl radicals introduced into the polymerisation system and radical initiators (peroxides, azodinitriles). The initiators were chosen so that their half-lifes would be a factor of several tens or even several hundreds shorter than the time necessary for complete conversion. Polymerisation of monomers in the presence of nitroxides (without added initiators) also belongs to processes in which alkoxyamines are synthesised *in situ*. The reaction is self-initiated by the monomer, as is the case of autopolymerisation of styrene.[61–65]

Studies dealing with the development of procedures for modification of alkoxyamines by catalytic amounts of strong organic acids or other compounds aimed at improving their efficiency occupy a special place.[61, 66–68] However, such a modification has little effect and its mechanism is still to be clarified.

The most serious drawback of alkoxyamines as agents for 'living' polymerisation is that they are effective only in the polymerisation of styrene and its derivatives.[69–72] For other monomers, alkoxyamines appear to be rather ineffective. They find a limited application to homopolymerisation of polar monomers (acrylates, methacrylates) [61, 73–78] and their copolymerisation with some other monomers.[79–83] The most plausible reason for reduction of the efficiency of alkoxyamines in the polymerisation of polar monomers is that the C–ON bond in their molecules is too strong. The temperature necessary fior dissociation of this bond at sufficient rate is too high, so that irreversible intramolecular disproportionation occurs instead of reversible dissociation into the initial radicals R and X. This irreversible reaction results in the formation of inert products, *viz.*, a hydroxylamine and an unsaturated compound R(=) with the terminal double bond. In styrene and its derivatives, as well as in the copolymers of styrene with polar monomers, the C–ON bond is weakened because of the effect of phenyl substituent.[84, 85] In the copolymerisation of styrene with polar monomers, the weakening effect of the styrene unit is achieved through the polar monomer unit [85] (the effect of the penultimate unit).

2. Synthesis of alkoxyamines

Several methods for the synthesis of adducts R_iM_nX, where R_i is the initiator radical (*e.g.*, Ph–CO–O$^{\bullet}$ formed upon decomposition of dibenzoyl peroxide, or BPO), M is the monomer (*e.g.*, styrene) and X is the nitroxyl radical (*e.g.*, 2,2,6,6-tetramethyl-1-piperidinyloxy, or TEMPO) have been reported.[34, 51–55] Depending on the composition, *i.e.*, the $[R_i]:[X]:[M]$ ratio in the reaction mixture, adducts with different content of M (from $n = 1$ to $n \simeq 10$) can be obtained. Obviously, these methods are effective only under the reported reaction conditions.[34, 51–55] Later, the

possibility of designing the syntheses of any adducts of the R_iM_nX type has been demonstrated.[86] A mathematical method was developed for calculation in the steady-state approximation of the yields of the adducts synthesised in the polymerisation processes described by the simplified Scheme 3 which includes the initiation, chain propagation and chain termination stages. This scheme assumes that only a linear chain termination occurs in the system (quadratic chain termination can be ignored because of a very high concentration of an agent X responsible for the linear chain termination).

Scheme 3

Initiation (zeroth stage)

$$I \xrightarrow{k_i} 2R_i^{\bullet}.$$

Chain propagation (first stage)

$$R_i^{\bullet} + M \xrightarrow{k_{pi}} R_iM^{\bullet},$$

$$R_iM^{\bullet} + M \xrightarrow{k_p} R_iMM^{\bullet},$$

.....

$$R_iM_{n-1}M^{\bullet} + M \xrightarrow{k_p} R_iM_nM^{\bullet}.$$

Chain termination (second stage)

$$R_i^{\bullet} + X^{\bullet} \xrightarrow{k_x} R_iX\ (A_0),$$

$$R_iM^{\bullet} + X^{\bullet} \xrightarrow{k_x} R_iMX\ (A_1),$$

$$R_iMM^{\bullet} + X^{\bullet} \xrightarrow{k_x} R_iM_2X\ (A_2),$$

.....

$$R_iM_{n-1}M^{\bullet} + X^{\bullet} \xrightarrow{k_x} R_iM_nX\ (A_n).$$

Here I is the initiator; $X^{\bullet}$ is the stable free radical; M is the monomer; R_i^*, $R_iM^{\bullet}$, ..., $R_iM_{n-1}M^{\bullet}$ are active free radicals and A_n are products of the corresponding reactions.

Analysis of Scheme 3 makes it possible to derive the following expressions for instantaneous rates of formation of any adduct, from A_0 to A_n, during the synthesis.

$$\frac{d[A_0]}{dt} = k_x[X][R_i] = \frac{W_i k_x[X]}{k_{pi}[M] + k_x[X]} = W_i \frac{1}{k_{pi}[M]/k_x[X] + 1}, \quad (1)$$

$$\frac{d[A_1]}{dt} = k_x[X][R^1] = \frac{W_i k_x[X] k_{pi}[M]}{(k_{pi}[M] + k_x[X])(k_p[M] + k_x[X])} = \quad (2)$$

$$= \frac{d[A_0]}{dt} \frac{1}{k_p/k_{pi} + k_x[X]/k_{pi}[M]},$$

$$\frac{d[A_2]}{dt} = k_x[X][R^2] = \frac{W_i k_x[X] k_{pi}[M] k_p[M]}{(k_{pi}[M] + k_x[X])(k_p[M] + k_x[X])^2} = \quad (3)$$

$$= \frac{d[A_1]}{dt} \frac{1}{k_x[X]/k_p[M] + 1},$$

.....

$$\frac{d[A_n]}{dt} = k_x[X][R^n] = \frac{W_i k_x[X] k_{pi}[M] (k_p[M])^{n-1}}{(k_{pi}[M] + k_x[X])(k_p[M] + k_x[X])^n} = \quad (4)$$

$$= \frac{d[A_1]}{dt} \left(\frac{1}{k_x[X]/k_p[M] + 1} \right)^{n-1},$$

where W_i is the rate of initiation and $R^1 = R_iM$, $R^2 = R_iM_2$, ..., $R^n = R_iM_n$.

For any stage of the synthesis, the yield (Y) of each adduct A_n at instant t is calculated by the formula

$$Y = \int_0^t \frac{d[A_n]}{dt}\, dt, \quad (5)$$

where the form of the function describing the dependence of $d[A_n]/dt$ on t is given by formulae (1)–(4) which take into account the dependences of the concentrations of all reagents on time.

The dependence of [I] on t is described by the familiar integral of the rate of a unimolecular reaction

$$[I]_t = [I]_0 \exp(-k_i t), \quad (6)$$

while the dependence of [X] on t is given by the equation

$$[X]_t = [X]_0 - 2f([I]_0 - [I]_t) = [X]_0 - 2f[I]_0[1 - \exp(-k_i t)], \quad (7)$$

where f is the fraction of free radicals that did not undergo intracage recombination (this quantity is also called the efficiency of initiation, $f \approx 0.5$). From Eqn (7) it follows that the concentration of stable radical X at instant t is equal to the difference between the initial concentration of this radical, $[X]_0$, and the concentration of free radicals generated by the time t as a result of the decomposition of the initiator I.

If the synthesis is carried out under standard conditions (the monomer is taken in a large excess, $[M]_0 \gg [I]_0 \simeq [X]_0$), the concentration [M] is constant at any instant. If the synthesis is performed either under specific conditions (without a large excess of M) or in such a way that the adducts R_iM_nX with large n values are obtained, the form of the function $[M]_t$ is determined by the integral of the stationary rate $d[M]/dt$. For long chains ($n > 10$), the following approximation is valid

$$-\frac{d[M]}{dt} \simeq \frac{k_p[M]}{k_x[X]} W_i, \quad (8)$$

whence, taking into account expressions (6) and (7), it follows that

$$[M] = [M]_0 \exp\left(-\frac{k_p k_i}{k_x} \psi \right), \quad (9)$$

where

$$\psi = \int_0^t \frac{[I]_t}{[X]_t} = \int_0^t \frac{[I]_0 \exp(-k_i t)}{[X]_0 - 2f[I]_0[1 - \exp(-k_i t)]}. \quad (10)$$

This calculation procedure makes it possible to predict the results of synthesis and to choose optimum conditions, since the values of all constants (k_i, k_{pi}, k_p and k_x) appearing in Eqns (1)–(10) can be rather accurately estimated from the reported data (see, *e.g.*, Ref. 87). The results of calculations for the styrene–TEMPO–BPO system, obtained for three temperatures, are listed in Table 1.

The reliability of the calculations has been confirmed experimentally. Both the type of the main adduct ($A_1 = R_iMX$) and its content ($[A_1]100/\sum_n [A_n] > 90\%$) in the overall product $\sum_n A_n$ nearly coincide with the corresponding calculated data. As can be seen from Table 1, the target product A_1 is the main product in the temperature range 348–368 K.

According to calculations, non-peroxide compounds (*e.g.*, azonitriles) are unsuitable for use as initiators since only peroxide radicals R_i with the free valence at the oxygen atom ensure a rather high value of the k_{pi}/k_p ratio (several orders of magnitude). If the values of k_{pi} and k_p are comparable, the adduct R_iX ($n = 0$) is formed as the main product instead of the target R_iM_nX adduct. However, R_iX cannot be used as the agent for 'living' polymerisation because its C–ON bond energy is too high.

The results of calculations for the styrene–TEMPO–dicyclohexyl peroxydicarbonate (DCPDC) system [86] (Table 2) imply that the main adduct is

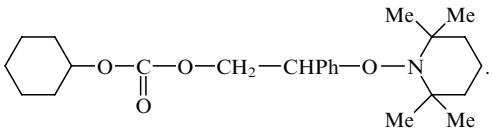


Table 1. Results of calculations of the yields of the adducts R_iM_nX in the course of 'living' polymerisation of styrene (M) in the presence of stable free radicals X (TEMPO) and initiator (BPO).

T/K	10^5k_i /s^{-1}	k_p (see [a])	$10^{-7}k_x$ (see [a])	$10^{-5}k_{pi}$ (see [a])	Yields of adducts $A_0\times10^6$, $A_1\times10^4$, and $A_2\times10^5$ (mol litre^{-1}) after every hour from the beginning of the process					
					1	2	3	4	5	6
348	2.6	262	1.8	10.2	3.5, 3.8, 1.0	6.2, 6.9, 2.0	8.3, 9.5, 2.8	9.9, 11.6, 3.5	11.2, 13.4, 4.2	12.2, 15.0, 4.7
358	8.3	352	2.1	12.5	5.2, 5.7, 1.8	8.6,9.9, 3.3	10.8, 13.1, 4.5	12.4, 15.4, 5.4	13.5, 17.1, 6.0	14.3, 18.4, 6.8
368	25.2	464	2.6	15.2	10.8, 13.1, 4.9	14.1, 18.3, 7.4	15.3, 20.4, 8.5	15.8, 21.3, 9.0	16.0, 21.7, 9.3	16.1, 21.8, 9.4

Note. Initial concentrations: [TEMPO] = 4.8×10^{-3} mol litre^{-1}, [BPO] = 2.3×10^{-3} mol litre^{-1}. [a] Dimensionality is litre mol^{-1} s^{-1}.

Table 2. Results of calculations of the yields of adducts in the course of 'living' polymerisation of styrene using DCPDC as the initiator.

T/K	10^5k_i /s^{-1}	k_p (see [a])	$10^{-7}k_x$ (see [a])	$10^{-5}k_{pi}$ (see [a])	Yields of adducts $A_0\times10^6$, $A_1\times10^4$, and $A_2\times10^5$ (mol litre^{-1}) after every hour from the beginning of the process					
					1	2	3	4	5	6
323	3.0	117	1.0	5.8	4.0, 4.3, 0.9	6.9, 7.8, 1.8	9.1, 10.6, 2.5	10.8, 12.9, 3.1	12.0, 14.7, 3.7	13.0, 16.2, 4.1
333	12.0	164	1.3	7.3	10.8, 12.8, 3.5	14.3, 18.2, 5.3	15.6, 20.5, 6.2	16.1, 21.5, 6.6	16.3, 21.9, 6.8	16.4, 22.1, 6.9
343	44.5	226	1.6	9.1	16.0, 21.2, 7.1	16.4, 22.0, 7.5	16.5, 22.1, 7.6	16.5, 22.1, 7.6	16.5, 22.1, 7.6	16.5, 22.1, 7.6

Note. Initial concentrations: [TEMPO] = 4.8×10^{-3} mol litre^{-1}, [BPO] = 2.3×10^{-3} mol litre^{-1}. [a] Dimensionality is litre mol^{-1} s^{-1}.

Dicyclohexyl peroxydicarbonate decomposes into radicals much faster than BPO (for DCPDC, the k_i value is 100 times greater than for BPO). This allows implementation of syntheses at lower temperatures, which is an additional 'insurance' against the risk of possible side reactions due to dissociation of R_iM_nX and ignored in Scheme 3.

According to calculations, there is little point in synthesising the adducts with long polystyrene chain ($n \simeq 10$) using a one-step process. In this case, a considerable amount of hard-to-remove contaminating adducts of nearly identical compositions can be formed, even if a very carefully 'adjusted' procedure with optimum 'recipe' is employed. Because of this, long-chain adducts R_iM_nX ($n = 10$) should be synthesised using a two-step procedure which includes (i) the synthesis of R_iMX ($n = 1$) and (ii) a controlled/'living' bulk polymerisation of M (in order to extend the M_n block until desired molecular mass value) at a higher temperature at which the rate of reversible dissociation of R_iMX is high enough. In such a manner, it is possible to extend the polymer chains by about 10 units over a period of 3–4 h at 393 K and to obtain the $R_iM_{10}X$ adducts with a polydispersity index of 1.15 and more (GPC data).

It thus follows that currently the synthesis of alkoxyamines is developed to the extent that it can be performed as a kinetically controlled process with accurate prediction of results.

3. Determination of the rate constant of reversible dissociation of alkoxyamines at the C–ON bond

Reversible dissociation of R_iM_nX (BX), which is the 'heart' of the mechanism of 'living'-chain radical polymerisation, is described by Scheme 4.

Scheme 4

$$BX \xrightarrow{k_1} B^{\bullet} + X^{\bullet},$$

$$B^{\bullet} + X^{\bullet} \xrightarrow{k_2} BX,$$

$$B^{\bullet} + B^{\bullet} \xrightarrow{k_t} P,$$

where P is the recombination (or disproportionation) product of radicals $B^{\bullet}$ and $k_2 \simeq k_t \simeq 10^7-10^8$ litre mol^{-1} s^{-1}.

Since dissociation of BX is a non-steady-state process, running concentrations of all compounds involved in the process can only be found after solving the system of differential equations (11)–(13).

$$\frac{d[B]}{dt} = k_1[BX] - k_t[B]([B] + [X]), \tag{11}$$

$$\frac{d[X]}{dt} = k_1[BX] - k_t[B][X], \tag{12}$$

$$\frac{d[BX]}{dt} = -k_1[BX] + k_t[B][X], \tag{13}$$

$$[BX] = [BX]_0 - [X], \tag{14}$$

$$[P] = [X] - [B]. \tag{15}$$

The following analytical solutions of the system of equations (11)–(15) were obtained for a time interval $(k_1k_t[BX]_0/3)^{-1/2} \ll t \ll (k_t[BX]_0/24k_1^2)$ which covers almost entirely the range of practically significant t values (from fractions of a second to tens of days) [88]:

$$[X] = [BX]_0\left(\frac{3k_1^2t}{k_t[BX]_0}\right)^{1/3}, \tag{16}$$

$$[B] = [BX]_0\left(\frac{k_1}{3k_t^2[BX]_0^2t}\right)^{1/3}. \tag{17}$$

From Eqn (16) it follows that if the k_t value is estimated to sufficient accuracy, the value of

$$k_1 = \frac{[X]^{3/2}k_t^{1/2}}{[BX]_0(3t)^{1/2}} \tag{18}$$

can be determined in the experiments on the decomposition of BX in inert media from the ESR measurements of the kinetics of accumulation of radicals $X^{\bullet}$. The most reliable k_t estimate is $k_t \simeq 10^7-10^8$ litre mol^{-1} s^{-1}. From Eqn (15) it follows that the data on the kinetics of accumulation of P can be used instead of the corresponding data for $X^{\bullet}$ if time t is rather long and $[X] \gg [B]$. This can be done if for any reason it is more convenient to perform experimental measurements of [P].

In most cases, ESR measurements of the kinetics of accumulation of radicals $X^{\bullet}$ in order to determine the k_1 value are carried out under conditions of reversible decomposition of alkoxyamines.[85,89–91]

Recently,[92] yet another procedure for the measurement of the k_1 values has been developed. It includes measurements of the

consumption of radical $B^{\bullet}$ in the reaction with benzoquinone (BQ), which is a highly efficient acceptor of radicals $B^{\bullet}$, instead of measuring the consumption of $B^{\bullet}$ in the reaction $B^{\bullet} + X^{\bullet}$. Each BQ molecule entraps two radicals $B^{\bullet}$ with the rate constant $k_x \approx 10^5$ litre mol^{-1} s^{-1} (for styryl radical at $T = 333-353$ K). If benzoquinone ($\sim 10^{-2}$ mol litre^{-1}) is introduced into the system, then, according to Scheme 4, the deactivation rate of radicals $B^{\bullet}$ by BQ will be $W_x = k_x[BQ][B] = 10^3[B]$ while the rate of the reverse transformation of $B^{\bullet}$ into BX will be $W_2 = k_2[X][B] = 10^2[B]$ (according to ESR data, $[X] \simeq 10^{-6}$ mol litre^{-1} at $k_2 \simeq 10^8$ litre mol^{-1} s^{-1}). Thus, the addition of BQ decreases the rate of the reverse reaction in Scheme 4 by at least an order of magnitude, which is tantamount to nearly complete suppression of this reaction.

Under these conditions, the rate of accumulation of $X^{\bullet}$ as obtained from ESR measurements will be virtually equal to the rate of dissociation of BX. This method for the determination of k_1 eliminates difficulties associated with side reactions ignored by Scheme 4, such as, *e.g.*, disproportionation of BX with the formation of XH and a polymer P(=) with a double bond in the end group. The side reactions transform a paramagnetic species $X^{\bullet}$ into an 'ESR stealth', thus disturbing the results of measurements. The new method [92] is also more advantageous than that reported by Fischer [88] because the k_1 constant is determined here without using the k_t value, which can only be determined with an accuracy of an order of magnitude. Therefore, the accuracy of the new method is higher by an order of magnitude.

An original method for measurement of the constant k_1 was suggested.[93] Here, the k_1 value is determined separately rather than in combination with the k_t value. This is achieved by performing the measurements in the bulk of the monomer. In this case, owing to the reaction with the monomer, the active dissociation product of the initial alkoxyamine (RM_nX), *viz.*, a hydrocarbon radical $RM_n^{\bullet}$, manages to extend its chain by several monomer units before the next act of conversion into alkoxyamine as a result of the reaction with iminoxyl.

$$RM_nX \underset{-X^{\bullet}}{\overset{k_1}{\longrightarrow}} RM_n^{\bullet} \xrightarrow{M} RM_{n+1}^{\bullet} \xrightarrow{M} \ldots \longrightarrow RM_{n+k}^{\bullet},$$

$$RM_{n+k}^{\bullet} + X^{\bullet} \xrightarrow{k_2} RM_{n+k}X.$$

This procedure makes it possible to distinguish between the initial alkoxyamine RM_nX and 'heavy' alkoxyamines $RM_{n+k}X$, $RM_{n+2k}X$, ..., $RM_{n+mk}X$ and allows determination of k_1 from the data on the decrease in the concentration of the initial RM_nX. The reversible character of the dissociation presents no problems to determination of the constant k_1, since only the first acts of dissociative decomposition of each initial molecule RM_nX are measured experimentally. The next decomposition acts that follow the reversible reduction involve compound $RM_{n+mk}X$ ($m = 1, 2, \ldots$) for which no measurements have been performed.

A procedure for separate determination of the concentration of the initial alkoxyamine RM_nX (M is styrene, $n = 1$) in the mixture with 'heavy' alkoxyamines $RM_{n+mk}X$ using gel-permeation chromatography has been developed.[93] For $n = 1$, the peak of the initial alkoxyamine on the chromatogram of the mixture can be resolved to an accuracy of 10%–20%, which is correspondingly the accuracy of the determination of k_1. The k_1 values thus obtained [$k_1 = 2.0 \times 10^{13}\exp(-124200/RT)$ s^{-1}] should be considered the most reliable. The limitation inherent in this method is due to the fact that it can only be applied to alkoxyamines containing one monomer unit per molecule. For $n > 1$, the resolution of the peak of the initial compound in a mixture of substances containing $n + mk$ monomer units decreases substantially. From this viewpoint, the use of the new method [92] discussed above (competitive entrapment of active hydrocarbon radicals by benzoquinone) seems to be more convenient for $n > 1$, since it has no limitations as regards the n values for the initial alkoxyamine.

The method for assessing the constant k_1 in combination with k_p and k_t, based on measurement of the k_1k_p/k_t ratio appears to be the most popular.[58, 89, 94–101] This requires plotting the kinetic curve $W_M(t) = -d[M]/dt = k_p[M][R]$ and the curve of accumulation of the iminoxyl radical $[X]_t$. If the equilibrium in a system

$$RX \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R^{\bullet} + X^{\bullet}$$

is established much faster than any perturbation (*e.g.*, the reaction $R^{\bullet} + R^{\bullet}$) is developed, the function $[X]_t$ can be calculated using the formula $[X]_t = k_1[RX]/k_2[R]$, where the concentrations of RX and $R^{\bullet}$ depend on t. The [RX] value is determined from the relationship $[RX] = [RX]_0 - [X]_t$, where $[RX]_0 \simeq 10^{-2}$ mol litre^{-1} and $[X]_t \simeq 10^{-6}-10^{-5}$ mol litre^{-1}. Hence to sufficient accuracy we get $[RX] \simeq [RX]_0$.

For a fixed $t = t_f$, the [R] value is determined from the kinetic curve $[R] = W_M(t_f)/k_p[M]$, where [M] is the running concentration at the same instant $t = t_f$. Then, by comparing the $W_M(t)$ and $[X]_t$ curves for the same t we can calculate the ratio

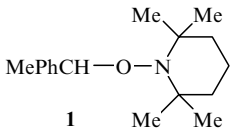
$$\frac{k_1k_p}{k_2} \simeq \frac{[X]_t W_M(t)}{[RX]_0[M]}.$$

Reliability of calculations can be checked for independence of the parameter k_1k_p/k_t on the conversion time t. The accuracy of the estimate of the constant k_1 by this method is also obviously dependent on the reliability of the values chosen for k_p and k_t. Usually, the values $k_p = 2 \times 10^3$ (for $T = 393$ K) [102] and $k_t = 10^7-10^8$ litre mol^{-1} s^{-1} are used. As a rule, calculations of 'living' polymerisation processes are carried out using the constant k_1 in the form of the ratio $K = k_1/k_2$ (the equilibrium constant), thus it is the equilibrium constant value that is the main goal of quantitative estimates reported in many studies.

Nevertheless, it should be noted that the scatter of k_1 values reported by different authors is extremely wide and, which is most important, the reasons for this phenomenon are unclear. For instance, the rate constant of dissociation of 1-phenyl-1-(2,2,6,6-tetramethylpiperidinyl-1-oxy)ethane (**1**) in deuterated styrene was reported to be $\sim 10^{-3}$ s^{-1} at 396 K.[103] On the other hand, the k_1 value obtained for the dissociation of the same compound at a higher temperature (413 K) was reported [104] to be equal to $\approx 8 \times 10^{-5}$ s^{-1} (dissociation in tetrachlorobenzene). Such a wide scatter in the k_1 values can hardly be explained by the solvent effect alone.

In conclusion, let us dwell on the side reaction of irreversible dissociation of alkoxyamines which occurs at high temperatures (above 408–433 K). Apparently, it is this reaction that makes alkoxyamines with increased (as compared to styrene-containing derivatives) strength of the C–ON bond 'inoperative'.

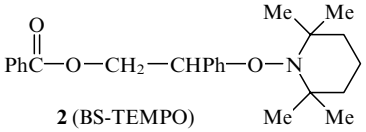
This side reaction was first studied taking a model alkoxyamine **1** as an example.[104]



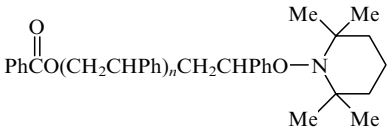
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It was concluded that dissociation of this alkoxyamine with the cleavage of the C–ON bond follows two pathways resulting in (i) an active hydrocarbon radical and the TEMPO stable radical and (ii) hydride transfer to give an unsaturated hydrocarbon and hydroxylamine.

The competition between the two types of cleavage of the C–ON bond was studied in detail by high-resolution NMR spectroscopy [105] taking alkoxyamines obtained upon radical decomposition of dibenzoyl peroxide in styrene as examples.



2 (BS-TEMPO)



3 (PS-TEMPO with $M_n = 1100$, $M_w/M_n = 1.03$)

Thermal decomposition of alkoxyamines **2** and **3** was performed in perdeuterated toluene in the temperature range 393 – 433 K. The products obtained during the conversion were analysed by ^{1}H NMR spectroscopy. This required preliminary assignment of the ^{1}H NMR spectra of mixtures using the ^{1}H NMR spectra of model compounds and specially developed auxiliary calibrations. The obtained rate constants (k_{dec}) of irreversible decomposition of alkoxyamines **2** and **3** were $4.7 \times 10^{14}\exp(-157\,000/RT)$ and $5.7 \times 10^{14}\exp(-153\,000/RT)$ s^{-1}, respectively.

Most probably, the irreversible decomposition reaction competes with reversible dissociation, *i.e.*, the former occurs concurrently rather than sequentially (as the second stage after the dissociation of alkoxyamines into an active hydrocarbon radical and TEMPO). One can calculate the ratio $k_{dec}/k_1 = P_{dec} = 29\exp(-29\,000/RT)$, which characterises the contribution of the side reaction of irreversible decomposition of alkoxyamines as a function of temperature, using the value $k_1 = 2.0 \times 10^{13}\exp(-124\,200/RT)$ s^{-1} (Ref. 93). At 433 K, we have $P_{dec} \simeq 10^{-2}$, which means that no more than 1% of the dissociating alkoxyamine molecules undergo irreversible decomposition. At first glance, this is a negligible value. However, taking into account the half-life of alkoxyamine (at this temperature $\tau_{1/2} = 0.69/k_1 \simeq 0.5$ min), we obtain that the alkoxyamine manages to enter into a reversible dissociation ⇄ recombination cycle hundreds of times over the time necessary for complete conversion (several hours). Therefore, at first glance small losses of the alkoxyamine due to the irreversible decomposition in each cycle are accumulated and become comparable with its initial concentration (complete deactivation). As temperature decreases (*e.g.*, down to 393 K), the P_{dec} value becomes nearly halved; however, the $\tau_{1/2}$ value increases dramatically (by about a factor of 40) with concomitant sharp decrease in the number of reversible cycles and losses due to deactivation of the alkoxyamine.

4. Kinetics of alkoxyamine-mediated polymerisation of styrene

The kinetics of styrene polymerisation in the presence of alkoxyamines was reported in most detail by Greszta and Matyjaszewski.[106] The main goal of this study was to reveal key features of the process, which make it possible to infer the details of the mechanism of 'living'-chain polymerisation. A short list of the most important characteristics of 'living'-chain styrene polymerisation is presented below.

— The rate of polymerisation is proportional to the concentration of the monomer (*i.e.*, the process is first-order with respect to the monomer) and independent of the concentration of alkoxyamine (a zero order process with respect to alkoxyamine) or of the concentration of a stable nitroxyl radical (as a rule, TEMPO), if the alkoxyamine is synthesised *in situ*.

— The molecular masses of polymers increase linearly with the degree of polymerisation (conversion). This is valid until at least $M_n \approx 20\,000 - 30\,000$.

— The polydispersity of the resulting polymer, which is characterised by the M_w/M_n ratio, decreases usually with conversion and then increases at later stages of the process. The M_w/M_n value varies depending on the reaction conditions, but, as a rule, remains less than 1.3.

— Throughout the polymerisation, the concentration of the stable nitroxyl radical, as determined by ESR spectroscopy, is 0.1% – 1.0% from the initial concentration of alkoxyamine (or its precursor, TEMPO) introduced into the reaction system.[107]

This makes it possible to draw some conclusions. The fact that the polymerisation rate, W, of the monomer is independent of the concentrations of alkoxyamine and the stable nitroxyl radical (TEMPO) and coincides with the rate of self-initiated polymerisation of the monomer shows that self-initiation is primarily responsible for maintaining the concentration of active centres [R], which, in turn, controls the polymerisation rate ($W \sim [R]$). Thus, the rate of self-initiation (W_i) (or, generally, any radical initiation) controls the polymerisation rate.

Despite the controlling effect of W_i with respect to W, alkoxyamine used as the agent for 'living' polymerisation controls almost completely the length of growing polymer chains so that they grow throughout the polymerisation process (at least, most of them do not undergo termination). This can only occur if $W_i \ll W_A$ (W_A is the dissociation rate of alkoxyamine, $W_A = k_1[A]$), *i.e.*, if each chain initiation act corresponds to many dissociation ⇄ recombination acts of alkoxyamine, so that each newly initiated chain manages to be involved repeatedly in this reversible cycle.

The narrowing of molecular mass distribution of the resulting 'living' polymer down to a M_w/M_n value of 1.3 (*cf.* $M_w/M_n = 1.5 - 2.0$ for conventional radical polymerisation) also suggests the 'living' character of polymer chains. On the other hand, the increase in the M_w/M_n ratio at later stages of polymerisation indicates some side reactions.

The fact that the relative concentration of a stable nitroxyl radical X$^\bullet$ is low ([X]/[A] = $10^{-2} - 10^{-3}$) and changes only slightly during the time necessary for nearly complete conversion of the monomer indicates that the equilibrium constant $K = k_1/k_2$ of the following process is very low.

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} R^\bullet + X^\bullet$$

This equilibrium is shifted rather slowly under the action of disturbing factors (first of all, quadratic chain termination, $R^\bullet + R^\bullet$) which are developed during the polymerisation; hence, it may be always thought that $k_1[A] \simeq k_2[R][X]$, where $[A] \simeq [A]_0$. If K can be measured independently, then, using this value, one can assess the concentration of active centres [R] over a period necessary for nearly complete conversion. For instance, the equilibrium constant of alkoxyamine-mediated 'living' polymerisation performed under standard conditions ($T = 393$ K) is 10^{-11} mol litre^{-1},[106] hence $[R] = k_1[A]/k_2[X] = 10^{-9} - 10^{-8}$ mol litre^{-1}. Usually, the concentration of alkoxyamine is 10^{-2} mol litre^{-1} and that of the nitroxyl radical is $10^{-5} - 10^{-4}$ mol litre^{-1}. Therefore, the polymerisation process proceeds almost entirely at [X] ≫ [R], which provides a complete control of the reversible dissociation ⇄ recombination cycle over the chain propagation, since quadratic chain termination makes a negligible contribution in this case. Actually, in the presence of dissociating alkoxyamine each growing chain undergoes either a linear termination following the mechanism

$$R^\bullet + X^\bullet \xrightarrow{k_2} A$$

(a fictitious, temporarily termination, since the adduct A can dissociate, thus retaining the 'livingness' of the chain) or a quadratic termination following the pathway

$$R^\bullet + R^\bullet \xrightarrow{k_t} \text{'dead' polymer.}$$

The contribution of the latter process determines the extent to which the alkoxyamine-mediated chain propagation can be not in control. Quantitatively, the contributions of linear and quadratic termination are characterised by the probabilities α_1 and α_2.

$$\alpha_1 = \frac{k_2[R][X]}{k_2[R][X] + k_t[R]^2},$$

$$\alpha_2 = \frac{k_t[R]^2}{k_2[R][X] + k_t[R]^2}.$$

Thus, taking into account that [X] ≫ [R] and $k_2 \simeq k_t$, we get $\alpha_1 \approx 1$ and $\alpha_2 \ll 1$.

5. Kinetics of alkoxyamine-mediated 'living' radical polymerisation

Initially, the kinetic analysis of a polymerisation process proceeding in the presence of alkoxyamines (as well as other reversible inhibitors, iniferters and other agents) was performed in the framework of rather rough approximations which oversimplified the situation under consideration. Most concisely, the mechanism of this polymerisation process is described by Scheme 1. This scheme should only be augmented with a new stage to describe the generation of active radicals upon decomposition of initiators I (organic peroxides, hydroperoxides, azonitriles, *etc.*) with the initiation rate $W_i = k_i[I]$ (Scheme 5).

Scheme 5

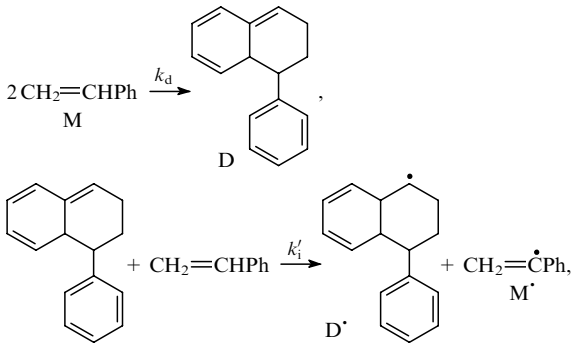
$$I \xrightarrow{k_i} R^{\bullet} \quad \text{initiation}$$

$$\left.\begin{array}{l} RX \xrightarrow{k_1} R^{\bullet} + X^{\bullet} \\ R^{\bullet} + X^{\bullet} \xrightarrow{k_2} RX \end{array}\right\} \text{reversible inhibition}$$

$$R^{\bullet} + M \xrightarrow{k_p} RM^{\bullet} \quad \text{chain propagation}$$

$$R^{\bullet} + R^{\bullet} \xrightarrow{k_t} P \quad \text{chain termination}$$

For a self-initiated polymerisation of the monomer, $W_i = k_{im}[M]^n$, where n can take any value depending on the specific generation mechanism of $R^{\bullet}$. For styrene, this mechanism involves the reactions [108, 109]



which proceed at 393 K with the rate constants $k_d = 3 \times 10^{-8}$ (see Refs 110 and 111) and $k_i' = 5 \times 10^{-8}$ litre mol^{-1} s^{-1} (see Refs 106 and 112). The n value lies between 2 and 3.

Reversible inhibition steps are the key stages of the reactions. Competitive entrapment of radical $R^{\bullet}$ by a stable free radical $X^{\bullet}$ prevents the growing chains $R^{\bullet}$ from being terminated quadratically. During the time interval between acts of chain initiation (or regeneration) the radicals $R^{\bullet}$ manage to react with the monomer, thus extending the polymer chain.

It is an easy matter to perform the kinetic analysis of such a polymerisation scheme (Scheme 5). In the steady-state approximation, the polymerisation rate W is calculated as follows

$$W = k_p[M]\left(\frac{W_i}{k_t}\right)^{1/2}. \tag{19}$$

This expression for W is the same as that used to describe a conventional radical polymerisation without reversible inhibition. This result is obvious. Indeed in the steady state the reversible inhibition reactions responsible for 'living' polymerisation make no contribution to the stationary concentration of growing polymer chains $[R]_s$ (and, correspondingly, to the W value), since all radicals $R^{\bullet}$ and $X^{\bullet}$ generated in the stage $RX \rightarrow R^{\bullet} + X^{\bullet}$ leave the reaction system by the stage $R^{\bullet} + X^{\bullet} \rightarrow RX$. Therefore, if the time necessary for establishment of a steady state in the polymerisation system (τ_s) is much shorter than that necessary for complete conversion (t), the alkoxyamine present in the system has no effect on the polymerisation kinetics from the moment $\tau_s \ll t$ onwards, *i.e.*, nearly from the beginning of the polymerisation process.

However, the chain propagation regime in the presence of alkoxyamine differs fundamentally from that in conventional radical polymerisation. Actually, in the latter case the average integrated chain length (ν) at instant t is given by the following expression

$$\nu = \frac{\int_0^t W\mathrm{d}t}{\int_0^t W_i\mathrm{d}t}, \tag{20}$$

where $\int_0^t W\mathrm{d}t$ is the total number of monomer units in the chains and $\int_0^t W_i\mathrm{d}t$ is the total number of the initiated chains. In a particular case, for $W \simeq \text{const}$ and $W_i \simeq \text{const}$, we get $\nu \simeq W/W_i \simeq \text{const}$. On the other hand, for 'living' polymerisation the average integrated chain length (ν_x) at instant t will be determined by the total number of 'dead' and 'living' chains accumulated by the instant t

$$\nu_x = \frac{\int_0^t W\mathrm{d}t}{\int_0^t W_i\,\mathrm{d}t + [RX]_t}, \tag{21}$$

where $[RX]_t$ is the stationary (quasi-stationary) concentration of alkoxyamine at instant t, which in turn is equal to the concentration of 'living' chains.

'Living'-chain polymerisation proceeds if $\int_0^t W_i\mathrm{d}t \ll [RX]_t$. In this case, the ν_x value is calculated by the formula

$$\nu_x \simeq \frac{\int_0^t W\mathrm{d}t}{[RX]_t} \simeq \frac{\Gamma}{[RX]_t}. \tag{22}$$

Here, $[RX]_t \simeq \text{const}$; if an iminoxyl is used as alkoxyamine, then $k_1/k_2 \ll 1$ and $[RX]_t \simeq [RX]_0$. Unlike conventional radical polymerisation in which the chain length remains virtually unchanged throughout the process [Eqn (20)], 'living' polymerisation in the presence of alkoxyamine is characterised by linear increase in ν_x with the degree of conversion Γ [Eqn (22)] provided that the overall concentration of chains generated by the initiator throughout the polymerisation process is much lower than the equilibrium (initial) concentration of the additive RX.

These are the results of the simplest and obvious analysis of the steady-state 'living'-chain polymerisation process described by Scheme 5. It should be noted that in the absence of additional initiation the system cannot reach the steady state and the analysis is complicated.

Theoretical studies on the mechanism of 'living' radical polymerisation can be divided into two groups.

1. Early studies [5, 113] aimed at revealing salient features of the mechanism responsible for the transformation of usual radical polymerisation into 'living' polymerisation.

2. More recent studies [88, 106, 114–118] on the kinetic analysis of the polymerisation mechanism and molecular mass distributions of polymeric products formed in the system carried out with the use of supercomputers and sophisticated mathematical procedures. Obviously, the mechanism presented in Scheme 5 is unsuitable for analysing the molecular mass distributions (MMD). To this end, Scheme 5 should be augmented with equations for chains of different length containing ν ($\nu = 1, 2, \ldots$) monomer units instead of the equations for a growing chain of an infinite length, while the chain propagation reaction should be written as a sequence of ν stages. Reversible inhibition and quadratic termination reactions should also be divided into a variety of identical

stages in which reagents R of different chain length are involved. The chain length effect of the reagent R on the rate constants can be ignored by assuming that they are the same for identical reactions. However, the number of differential equations to be integrated numerically increases by two orders of magnitude and more (instead of 5 equations shown in Scheme 5) even if the analysis is restricted to not very long chains. Calculations of MMD for the chains up to 500 monomer units long ($\nu = 500$) have been reported,[115] as well as some artificial simplifying procedures (introduction of special subsystems and 'closure reactions').[113]

Let us consider the results obtained in three theoretical studies[88,106,114] in which the results of calculations were compared in detail with the latest experimental results.

Computer simulation[106] of a process described by Scheme 5 for M = styrene and X = TEMPO was performed using the PREDICI programme package.[119–121] The numerical values of the rate constants and concentrations of reagents (for 393 K) are listed below.

Parameter	Numerical value	Ref.
Rate constants of reactions/litre mol^{-1} s^{-1}		
k_p	2000	102, 122
k_d	3×10^{-8}	110, 111
k_i'	5×10^{-8}	112
k_t	10^7	123, 124
Concentration/mol litre^{-1}		
[M]	10	106
[RX]	10^{-2}	106

Unlike the values of rate constants k_p, k_d, k_i' and k_t, the values of k_1, k_2 and some other rate constants were attenuated in the course of computer simulation because of a wide scatter of the data reported in different publications.

According to calculations,[106] Scheme 5 adequately describes all experimentally observed characteristic features of the process (see previous Section) assuming that $K = k_1/k_2 \leqslant 10^{-10}$ mol litre^{-1}. Based on detailed quantitative comparison of calculated and experimental dependences of the polydispersity index, M_w/M_n, on the degree of polymerisation, the values of the constants k_1 and k_2 were refined to be $K \simeq 10^{-11}$ mol litre^{-1}; $k_1 = 8\times10^{-4}$ s^{-1} and $k_2 = 8\times10^7$ litre mol^{-1} s^{-1}. This also made it possible to augment Scheme 5 with new stages necessary for improving the agreement between calculated and experimental data.

$$D + R \xrightarrow{k_{t_2D}} D^{\cdot} + P,$$

$$RX \xrightarrow{k_{dec}} P(=) + XH.$$

Here, P(=) is the polymer with a double bond in the end group, XH is hydroxylamine, $k_{t_2D} = 50$ litre mol^{-1} s^{-1} is the rate constant of chain transfer to dimer D formed in the self-polymerisation of the monomer (see above), k_{dec} is the rate constant of dissociation reaction accompanied by hydride transfer and $k_{dec} \simeq 10^{-5}$ s^{-1} (see Ref. 104).

These calculations have also confirmed that the reactions shown in Scheme 5 satisfy the principle of stationary concentrations. Using the above-mentioned values of rate constants, concentrations and temperature, the steady state is reached at a degree of polymerisation of less than 1%, *i.e.*, nearly from the beginning of the polymerisation process. The calculated stationary concentrations of growing chains [R] and stable iminoxyl radical [X] were found to be 10^{-8} and 10^{-5} mol litre^{-1}, respectively.

Similar results have also been obtained[114] for the same styrene–TEMPO reaction system using another type of computational procedure (the Monte Carlo stochastic algorithm[125–128]). This makes it possible to perform calculations without recourse to supercomputers. The results of calculations for $T = 393$ K were supplemented with those obtained for $T = 363$ K[114] which were then compared with the experimental results obtained at the same temperature.[78] The parameters listed below provided the best fit between the calculated and experimental data.

Parameter	Numerical value
Concentration/mol litre^{-1}	
[M]	8.75
[RX]	3.7×10^{-3}–4.4×10^{-2}
Rate constants of reactions	
k_1/s^{-1}	2.5×10^{-3}
k_2/litre mol^{-1} s^{-1}	2.5×10^8
k_p/litre mol^{-1} s^{-1}	950
k_t/litre mol^{-1} s^{-1}	10^7
k_d/litre mol^{-1} s^{-1}	1.5×10^{-9}
k_i'/litre mol^{-1} s^{-1}	4.5×10^{-9}
k_{dec}/s^{-1}	8×10^{-6}

The polydispersity indices, M_w/M_n, obtained analytically[90,129] and found from simulation have also been compared.[114]

The M_w/M_n ratio was calculated using the formula

$$\frac{M_w}{M_n} = \frac{1}{\gamma x} + \frac{1}{x}\left[2 + \frac{(\beta-1)(2-x)}{\alpha-\beta}\right] - \frac{2\alpha(1-\alpha)}{(\beta^2-\alpha^2)x^2}\left[1-(1-x)^{\frac{1+\beta}{\alpha}}\right], \quad (23)$$

where x is the degree of monomer conversion, $\gamma = [M]_0/[RX]$, $\alpha = [R]/[RX]$ and $\beta = k_2[X]/k_p[RX]$. It was found that the results of computer simulation fit well the theoretical curve.

Fischer[88] reported the most detailed computer simulation. He analysed two types of 'living'-chain polymerisation, without additional initiation (Scheme 1) and with varied intensity of initiation in order to establish the range of the effect of the initiation on polydispersity M_w/M_n (Scheme 5). Different versions of syntheses of the adducts RX were also considered, including the synthesis *in situ* and those with different dynamics of reversibility (this was achieved by varying the constants k_1 and k_2 over a wide range).

The first case (see Scheme 1) corresponds to a non-steady-state process. For very short times, $t \ll [k_1^2(k_t[RX]_0/k_1 - 1)]^{-1/2} \simeq (k_1 k_t [RX]_0)^{-1/2}$, the following relation is valid

$$[R] = [X] = k_1[RX]_0 t. \quad (24)$$

For the time interval $(k_1 k_t[RX]_0/3)^{-1/2} \ll t \ll k_t[RX]_0/24k_1^2$, which covers almost entirely the range of practically significant t values, one obtains

$$[R] = [RX]_0\left[\frac{k_1}{3(k_t[RX]_0)^2 t}\right]^{1/3},$$

$$[X] = [RX]_0\left(\frac{3k_1^2 t}{k_t[RX]_0}\right)^{1/3},$$

$$[RX] = [RX]_0 - [X] \simeq [RX]_0, \quad (25)$$

$$[P] = [X] - [R] \simeq [X],$$

$$[M] = [M]_0 \exp\left\{-\frac{3}{2}k_p[RX]_0\left[\frac{k_1 t^2}{3(k_t[RX]_0)^2}\right]^{1/3}\right\}.$$

For very long times, $t \gg 2k_t[RX]_0/k_1^2$, the concentrations vary as follows:

$$[R] = \frac{[RX]_0}{k_1 t},$$

$$[X] = [RX]_0\left(1 - \frac{k_t[RX]_0}{k_1^2 t}\right) \simeq [RX]_0, \quad (26)$$

$$[RX] = \frac{[RX]_0^2 k_t}{k_1^2 t},$$

$$[P] = [X] - [R] \simeq [X] \simeq [RX]_0.$$

Expressions (24)–(26) were derived assuming equal values of the constants k_2 and k_t in Scheme 1 ($k_2 \equiv k_t$). Successful applicability of relationships (25) throughout the polymerisation process (from $t_0 \simeq 10^2$ to $t_f \simeq 10^4$ s),¶ for a conventional $[RX]_0$ value of about 10^{-2} mol litre^{-1} requires that the condition $k_1 \ll 2$ s^{-1} (or 0.7 s^{-1}), depending on the choice of k_t value, 10^8 or 10^7 litre mol^{-1} s^{-1} be met. Since the k_1 values for alkoxyamines used in 'living' polymerisation do not exceed 10^{-2} s^{-1} at the operating temperatures, the conditions for the upper (t_f) and lower (t_0) bounds of the time interval are always met.

Using analytical expressions (24)–(26), one can assess the time taken to reach the maximum concentration of growing polymer chains $[R]_{max}$. We have $t_{max} = (2k_1k_t[RX]_0)^{-1/2} \simeq 0.02$ s for $k_1 = 10^{-2}$ s^{-1}, $k_t = 10^7$ litre mol^{-1} s^{-1} and $[RX]_0 = 10^{-2}$ mol litre^{-1}. Substituting this value into Eqn (24) gives $[R]_{max} \simeq 2 \times 10^{-6}$ mol litre^{-1}.

No practical implementation of the polymerisation mechanism described by Scheme 1 has been reported so far. This is due to self-initiation observed for those monomers which can undergo alkoxyamine-mediated 'living' polymerisation, such as styrene and several its derivatives, or mixtures of styrene with other monomers. Therefore it is reasonable to use the analytical solution of Eqns (24)–(26) for establishing the mechanism of the action of alkoxyamines (as well as any other agents which can reversibly accept growing polymer chains) as agents for 'living' polymerisation.

In particular, it seems to be very convenient to use expression (25) for the determination of the constant k_1 (in combination with k_t) of alkoxyamines from the data on the kinetics of the accumulation of X, which can be obtained from ESR measurements. Obviously, the corresponding experiments should be carried out using such solvents in which no self-initiation is developed in the temperature range chosen (the use of styrene and its derivatives is of course impermissible). For inert solvents, the absence of chain propagation step is of no significance since it is not considered in deriving Eqn (25).

For Scheme 1, analysis of MMD leads to the following interesting results. The contribution of quadratic chain termination ($R^\bullet + R^\bullet \rightarrow P$), which produces 'dead' chains and broadens the MMD, can be reduced to the extent that the value M_w/M_n will approach unity to the second decimal place. The conditions for minimisation are governed by the constant k_1. Assuming that the k_1 value for $[RX] = 10^{-2}$ mol litre^{-1} varies between 3×10^{-3} and 3×10^{-2} s^{-1} and taking $k_p = 2000$ litre mol^{-1} s^{-1}, $k_t = 2.5 \times 10^{-8}$ litre mol^{-1} s^{-1} and $[M] = 10$ mol litre^{-1}, we find that the ratio M_w/M_n lies in the range 1.01–1.03. As k_1 increases by one and two orders of magnitude, the polydispersity, M_w/M_n, increases to 1.107 (for $k_1 = 3 \times 10^{-1}$ s^{-1}) and 1.412 (for $k_1 = 3$ s^{-1}), respectively. However, it should be noted that no k_1 values meeting the condition $k_1 \geqslant 10^{-1}$ s^{-1} have been reported for alkoxyamines, so they seem to be unrealistic.

Varying the [RX] value at a given k_1 ($k_1 = 10^{-2}$ s^{-1}) has virtually no effect on the polydispersity, that is, the M_w/M_n ratio decreases by about 0.01 as [RX] increases by a factor of 30 (from 3×10^{-3} to 10^{-1} mol litre^{-1}).

All the above-mentioned values of the ratio M_w/M_n were obtained for 90% conversion (Γ). The dependence of the polydispersity index, M_w/M_n, on Γ is determined by the numerical values of k_1 and [RX]. For small k_1 and high [RX], the polydispersity is high in the early stages of polymerisation and then it decreases as Γ increases. For instance, calculations with $k_1 = 10^{-2}$ s^{-1} and $[RX] = 10^{-1}$ mol litre^{-1} show that the M_w/M_n ratio varies from 1.308 for $\Gamma = 5\%$ to 1.026 for $\Gamma = 50\%$ and reaches 1.017 for $\Gamma = 90\%$. On the contrary, for large k_1 the polydispersity increases as Γ increases. According to calculations with $k_1 = 3$ s^{-1} and $[RX] = 10^{-2}$ mol litre^{-1}, the M_w/M_n ratio is 1.079, 1.256 and 1.412 for $\Gamma = 5\%$, 50% and 90%, respectively.

The results of calculations make it possible to predict the efficiency of the use of adducts RX as agents for 'living' polymerisation. Actually, the early stages of the polymerisation process (at times t not too long compared with t_{max}) are characterised by comparable concentrations of growing polymer chains $R^\bullet$ and scavengers $X^\bullet$ (both of them are products of dissociation of the adducts RX) and by a large contribution of 'dead' polymer (the product of quadratic chain termination). Correspondingly, the polydispersity is also high ($M_w/M_n \rightarrow 1.5$–2.0). As [R] decreases and [X] increases, both the contribution of 'dead' polymer and the polydispersity decrease. The rate of the decrease is governed by the constant k_1 since both the decrease in [R] and the corresponding increase in [X] are due to the irreversible consumption of radicals $R^\bullet$ in the reaction of quadratic chain termination $R^\bullet + R^\bullet \rightarrow P$, which is responsible for the shift of the dissociation equilibrium toward the formation of X. Therefore, an increase in the number of dissociation $\rightleftarrows$ recombination cycles per unit time (*i.e.*, an increase in the k_1 constant) leads to accelerated accumulation of X (and to a decrease in [R]). In turn, a decrease in [R] and an increase in [X] lead to a decrease in the amount of 'dead' polymer produced in the reaction $R^\bullet + R^\bullet \rightarrow P$ and to an increase in the fraction of the polymer produced by 'living' polymerisation, $R^\bullet + X^\bullet \rightarrow PX$. Correspondingly, the polydispersity will decrease from values corresponding to large contributions of 'dead' polymer (1.5–2.0) to those typical of 'living'-chain polymerisation (~ 1.0).

However, in parallel with the positive effect (shortening of the time interval necessary for passage from the early stages of the process with large contribution of 'dead' polymer to the stage in which this contribution is small) there is also a negative effect of high k_1 values. For large constants k_1, the contribution of 'dead' polymer increases since the reaction of permanent chain termination, $R^\bullet + R^\bullet \rightarrow P$, is of higher order with respect to [R] than the reaction of temporary chain termination, $R^\bullet + X^\bullet \rightarrow PX$. In addition, for too high k_1 values, the polydispersity will increase with increase in the degree of polymerisation. Therefore it is necessary to find an optimum k_1 value. The limits for the optimum range of k_1 values can be evaluated using the results obtained by Fischer.[88]

The results of calculations for a polymerisation process described by Scheme 5 which includes an additional initiation stage have also been reported.[88] Both self-initiation (for styrene, this is a termolecular initiation with the rate constant $k_s = 2 \times 10^{-10}$) and initiation using a conventional radical initiator (a unimolecular initiation with the rate constant $k_i = 5 \times 10^{-3}$ s^{-1}, the initiator concentration $[I] = 4 \times 10^{-2}$ mol litre^{-1}) were considered. These results were obtained by computer simulation rather than using analytical methods.

The numerical estimate of the time t_s necessary for establishment of the steady state in the reaction system is one of the most important results reported by Fischer.[88] Unlike conventional radical polymerisation with $t_s < 1$ s, in the presence of RX the t_s value increases substantially and reaches 10^2 to 10^4 s depending on the ratio between the initiation rate of chain propagation reaction and the dissociation rate of RX. This numerical estimate shows that under certain conditions the steady-state approximation can actually be used to analyse Scheme 5.

Of great importance is also the establishment of the fact that the polymerisation rate and the polydispersity of the resulting polymer depend on the initiation rate in a different manner. As the initiation rate W_i increases, under certain conditions the polymerisation rate W increases faster than the polydispersity index M_w/M_n. Because of this, the polymerisation can be accelerated substantially with virtually no increase in the M_w/M_n ratio. Calculations for styrene ($T = 393$ K, $k_p = 2000$, $k_t = 2.5 \times 10^8$ litre mol^{-1} s^{-1}) with $[RX] = 10^{-2}$ mol litre^{-1} ($k_1 = 10^{-2}$ s^{-1}) show that without initiation ($W_i = 0$) the time necessary for 90% conversion is 165 h and the M_w/M_n ratio equals 1.017. For the initiation rate $W_i = 2 \times 10^{-4}$ mol litre^{-1} s^{-1},

¶ In this case, the upper (t_f) and lower (t_0) bounds for the time interval meet the conditions $t_f \ll k_t[RX]_0/24k_1^2$ and $t_0 \geqslant (k_1k_t[RX]_0/3)^{-1/2}$, respectively.

the average polymerisation rate is nearly doubled so that a 90% conversion is reached after 81 h, the polydispersity of the polymer being very low ($M_w/M_n = 1.04$).

Summing up the results of theoretical studies,[88, 106, 114] one can draw the following conclusions.

'Living' radical polymerisation in the presence of alkoxyamines (either supplied 'as is' from an external source or synthesised *in situ*) follows the mechanism shown in Scheme 1 with no additional initiation. The initiation is due to reversible dissociation ($RX \rightleftarrows R^{\bullet} + X^{\bullet}$) only. Here, we are concerned with the transformation of a usual radical polymerisation into 'living' polymerisation owing to conversion of a short-lived chain carrier R ($\tau < 1$ s $\ll t$, where t is the time necessary for complete conversion) into a long-lived one ($\tau > t \simeq 10^4$ s).

The process which includes only the stages shown in Scheme 1 is an 'ideal' process as regards the polydispersity of the resulting polymer. That is, at particular $K = k_1/k_2$ values characteristic of the known alkoxyamines and constants k_p and k_t typical of the known monomers there is a temperature range suitable for performing a polymerisation to yield a virtually 'monodisperse' product ($M_w/M_n = 1.0$). However, this mechanism is impracticable.

The real mechanism is described by Scheme 5. This is characterised by a higher polymerisation rate as compared to the rate of the process described by Scheme 1. If the rates of the initiation reactions, $I \rightarrow R^{\bullet}$ and $RX \rightarrow R^{\bullet} + X^{\bullet}$, lie within particular limits, the polymerisation process leads to nearly the same 'monodisperse' product ($M_w/M_n = 1.0$) as that obtained in the 'ideal' case (see Scheme 1).

Comparison of calculated and experimental results shows that the mechanism presented in Scheme 5 adequately describes all experimentally observed characteristic features of 'living'-chain radical polymerisaton (see previous Section), except for specific details of the evolution of the polydispersity (M_w/M_n) at deep stages of polymerisation. Rigorous quantitative description of these details was performed in the framework of a sophisticated mechanism augmented with side disproportionation reactions (see above).

Comparison of calculated and experimental results was also used for the evaluation of the numerical values of the reported (or measured independently) rate constants k_i, k_1, k_2, k_p, k_t, k_{t_2D} and k_{dec} for the styrene–TEMPO reaction system. If the difference between the known K values exceeded an order of magnitude, their values were corrected and the most plausible K were used.

Thus, the results of thorough quantitative studies[88, 106, 114] of the polymerisation processes proceeding in the presence of alkoxyamines or other compounds possessing similar properties can serve as a theoretical basis for designing various 'living' polymerisation processes because these have made it possible to find correlations between the reaction parameters (temperature and the concentrations of reagents) and the properties of agents for 'living' polymerisation (the values of the constants k_1 and k_2 at a given temperature). On the other hand, these results can be used for choosing optimum reaction conditions for conducting a polymerisation process in the styrene–TEMPO reaction system instead of performing labour-consuming experiments on 'adjusting' technological details of the process.

Very recently, ESR studies of the mechanism of 'living' polymerisation of styrene in the presence of alkoxyamines (a styrene–dibenzoyl peroxide–TEMPO system with alkoxyamine synthesised *in situ*) revealed[99, 100] the appearance of a doublet ESR spectrum of a system under study at medium degrees of conversion instead of the conventional singlet ESR spectrum of TEMPO. The additional component was attributed to an iminoxyl of unknown nature (we will denote it as X′). The same phenomenon was also observed[85, 130, 131] in studies of the polymerisation of styrene in the presence of alkoxyamine preliminarily synthesised from styrene and TEMPO.

The ESR spectrum of the 'additional' iminoxyl X′ is characterised by broader lines and a smaller hyperfine coupling constant $a_N = 13.6$ Œ, whereas for 'normal' TEMPO $a_N = 15.6$ Œ. This substantial change in the parameters of the ESR spectrum indicates essential changes in the nature of the substituents at the $^{\bullet}O-N$ group. Appreciable decrease in a_N accompanied by broadening of spectral lines could, *e.g.*, be observed if X′ contains the phenyl substituent [then the a_N value should lie between 12.1 and 13.5 Œ (see Ref. 132)]. This is also indicated by the fact that the 'additional' iminoxyl X′ is observed only if styrene is used as monomer. Neither the chemical mechanism of the formation of X′ nor the role it plays in the polymerisation process have been established so far. Probably, X′ is not involved in the reversible dissociation ⇄ recombination cycle and the accumulation of X′ merely increases[85] the overall concentration of iminoxyls. However, it is even more probable that X′ does participate in the reactions of the reversible cycle and forms an adduct RX′ which is characterised by higher equilibrium constant $K' = k'_1/k'_2$ than that of RX adduct.

Finally, experimental results obtained by Boutevin and Bertin[133] differ substantially from the calculated data obtained using the extended Scheme 5. The reasons for such discrepancies have also been discussed.[133]

6. Extension of the area of application of alkoxyamines. Copolymerisation of styrene and its derivatives with other monomers

Alkoxyamines appeared to be efficient agents for 'living' radical polymerisation only of such monomers as styrene and its derivatives (4-hydroxy-, 4-acetoxystyrenes,[69] 4-bromostyrene,[70] 3- and 4-chloromethylstyrene,[71] 4-ethyl-4′-vinylbiphenyl, 1,4-divinylbenzene,[74] *etc.*). Numerous attempts[61, 73–78] to perform 'living' polymerisations of other monomers (acrylates, methacrylates, vinyl acetate, *etc.*) in the presence of alkoxyamines either failed or were of little value, resulting in low yields and very low molecular masses of polymers. Synthesis of polyacrylates based on n-butyl acrylate and other monomers at 428 K in the presence of hydroxy-substituted TEMPO (4-HO-TEMPO) was the most successful, the polymers were obtained with $M_n = 10\,500 - 27\,000$ and $M_w/M_n \geqslant 1.53$.[73]

The most plausible reason for unsuccessful polymerisations is that, unlike styrene and its derivatives, the molecules of the above-mentioned monomers have no phenyl substituent which affects the strength of the C–ON bond in RX subject to reversible dissociation (see Section IV). The aromatic ring is known[84] to be responsible for the redistribution of the electron density in the vicinity of the nearest covalent bond in such a manner that this bond is weakened and the corresponding binding energy decreases by several tens of kJ. However, the C–ON bond in alkoxyamines RX based on (meth)acrylates and related monomers is too strong. Because of this, the attainment of a dissociation rate of this bond suitable for performing a 'living' polymerisation requires elevated temperatures. This may change the dissociation mechanism from a reversible process with the formation of $R^{\bullet}$ and $X^{\bullet}$ to irreversible transformation of RX into R(=) and hydroxylamine, XH. Possibly, this is the reason why polymerisations of acrylates at elevated temperature (428 K instead of 383–403 K for styrene) were, in general, unsuccessful.[75]

The ability of (meth)acrylates and related monomers to undergo 'living' polymerisation following the mechanism shown in Scheme 5, *i.e.*, by extending the polymer chains $R^{\bullet}$ at the instant of their release from adducts RX ($R^{\bullet} + M \rightarrow RM^{\bullet}$) is beyond question. This is supported by, *e.g.*, the possibility of producing block copolymers of styrene with (meth)acrylates by two-step polymerisation.[78] The first stage of the process is 'living' polymerisation of styrene in the presence of alkoxyamine until complete consumption of the monomer to give poly(styryloxyamine) RX (the polystyrene chains R capped with the end group X). The second stage is copolymerisation of poly(styryloxyamine) with a new monomer, *viz.*, (meth)acrylate. This stage is performed at the same or higher temperature. As a result, one obtains not only polystyrene, but also a rather large amount of poly[styrene-*b*-(meth)acrylate] block copolymer, which indicates that the second

stage of the synthesis proceeds at least in part as a 'living' polymerisation. The addition of a mixture of (meth)acrylate with styrene instead of neat (meth)acrylate in the second stage increases the yield of the block copolymer, which reaches $\sim 100\%$ at high styrene content in the mixture. In this case, the second block of the block copolymer is a poly[styrene-*co*-(meth)acrylate] random (statistical) copolymer.[60, 89–91, 95, 134–140]

The effect of styrene additives to (meth)acrylates introduced in order to improve the efficiency of alkoxyamines as agents for 'living' polymerisation has been studied in detail.[78, 79, 85] It was found that a nearly 'living' polymerisation can be implemented at a sufficiently high content of styrene in the mixture. In particular, it was shown[79] that the double bonds of methacrylates are involved in 'living' polymerisation controlled by alkoxyamines if the content of styrene was 50 mol. % and more. This result is nontrivial and not obvious. Actually, consideration of reversible dissociation $\rightleftarrows$ recombination, $RX \rightleftarrows R^{\bullet} + X^{\bullet}$, as a process which proceeds with involvement of only those polymer chains which bear the styrene unit as the end group at the instant of recombination, $R^{\bullet} + X^{\bullet}$, suggests very fast extinguishment of 'living' polymerisation. This is associated with the fact that both copolymerisation constants, r_1 and r_2, for the methacrylate–styrene system are less than unity ($r_1 \simeq 0.45$ and $r_2 \simeq 0.55$).[141] Close values of r_1 and r_2 result in distinct alternation of the styrene and methacrylate units, so they have nearly equal probabilities of being the end group at the instant of recombination. If the assumption that the aromatic substituent affects the strength of the C–ON bond in RX subject to dissociation (henceforth, R_M and R_S denote the chain with the methacrylate and styrene end group, respectively) is valid, nearly half of the polymer chains will return to the initial state RX in the form of inactive adducts R_MX after each dissociation $\rightleftarrows$ recombination cycle, thus resulting in fast extinguishment of 'living' polymerisation.

The time τ_d taken for complete deactivation ($R_SX \rightarrow R_MX$) of alkoxyamine R_SX introduced into the methacrylate–styrene mixture can be assessed from the repetition frequency of dissociation $\rightleftarrows$ recombination cycles determined by the value of the constant k_1. For $k_1 = 10^{-3}-10^{-2}$ s^{-1}, we get $\tau_d \leqslant t \simeq 10^4$ s, where t is the time necessary for complete conversion. Actually, during the time interval nearly equal to three half-lives of R_SX ($\tau = 3 \times 0.69/k_1 = 2 \times 10^2 - 2 \times 10^3$ s), almost all molecules of the initial adduct R_SX are, on the average, involved in the dissociation act and nearly half of them are deactivated in the form of R_MX. When this cycle is repeated many times, the concentration of R_SX will decrease by a factor of 2^n (n is the number of cycles) compared to the initial value, $[R_SX]_0$. For instance, for $n = 3$ the $[R_SX]$ value will decrease by a factor of 8, which is adequate for nearly complete deactivation of alkoxyamine as agent for 'living' polymerisation. Then, $\tau_d \simeq 3\tau = 6 \times 10^2 - 6 \times 10^3$ s, which means that deactivation occurs far before complete polymerisation.

This suggests that if complete conversion t takes $\simeq 10^4$ s, then copolymerisations of methacrylates with styrene in the presence of alkoxyamines at monomer ratios close to equimolar ones will proceed as 'living' polymerisations only in the initial stages of the processes. Then, the polymerisation process either undergoes transformation into conventional radical polymerisation (if the initiation rate, W_i, is sufficiently high) or is extinguished (if W_i is too low) because of the deactivation of the initial adduct R_SX. The absence of experimental data on such an evolution[79] was explained as follows.[80] It was assumed that not only the end group, but also the penultimate unit of the polymer chain affects the strength of the C–ON bond. If so, the aromatic ring substantially weakens this bond even if it is separated by the methacrylate unit and the adduct R_MX is not completely deactivated. Because of partial deactivation of R_MX, the rate constant for dissociation, k_d, remains rather high.

Copolymerisation of styrene with acrylates in the presence of TEMPO has been studied taking butyl acrylate as an example.[101] Here, both copolymerisation constants, r_1 and r_2, also are less than unity, but their values differ substantially ($r_1 = 0.15$ and $r_2 = 0.76$; M_1 is butyl acrylate and M_2 is styrene). This indicates that growing chains react mainly with the styrene rather than acrylate molecules. For acrylates, the deactivation frequency of the adducts R_SX in each dissociation $\rightleftarrows$ recombination cycle is lower than for methacrylates. Probably, that is why the results obtained for acrylates[82, 83, 101, 142] were encouraging. It was shown[101] that copolymerisation of styrene with butyl acrylate at 393 K with a styrene : butyl acrylate ratio of 77 : 23 (azeotrope) and $[TEMPO] = 6 \times 10^{-3}$ mol litre^{-1} exhibits distinct indications of a 'living' process. The M_n value increases as the degree of conversion increases. The best polydispersity index $M_w/M_n = 1.29$ (at $\Gamma = 65\%$ and $M_n = 59\,100$) differs appreciably from that typical of conventional radical polymerisation, while the process, according to ESR data, proceeds at a nearly stationary concentration of free iminoxyl, $[X] = (1.7-2.6) \times 10^{-5}$ mol litre^{-1} (at least in the range $20\% < \Gamma < 45\%$). Considering the concentration [X] and the polymerisation rate W in the 'steady-state' stage of polymerisation, one can evaluate the equilibrium constant, $K = k_1/k_2 = W[X]/k_p[M][X]_0$ ([M] is the overall running concentration of both monomers, $k_p = 2040$ litre mol^{-1} s^{-1}).[101] If $20\% < \Gamma < 45\%$, the $K \times 10^{11}$ value varies between 2.7(1.8) and 3.7(3.4) mol litre^{-1} (the data obtained in the experiments with the alkoxyamine synthesised *in situ* are given in parentheses). For the homopolymerisation of styrene under the same conditions, the K value reported by investigators from the same research group was found to be equal to $K = (1.50 \pm 0.3) \times 10^{-11}$ mol litre^{-1}.[99]

It is believed[101] that the observed decrease in K values during the copolymerisation is due to the deactivation of the adduct R_SX because of the substitution of the acrylate end group in R for the styrene end group. This assumption is confirmed by an increase in the polydispersity index at deep stages of the process ($M_w/M_n = 1.5\% - 1.7\%$ for 80% conversion). This also seems to be the reason why the M_n value increases nonlinearly with conversion and goes beyond the limits for $\Gamma > 70\%$. Unsuccessful attempts to perform homopolymerisation of acrylate under analogous conditions also indirectly confirm that R_SX is deactivated.

A procedure for improving the efficiency of 'living' polymerisation of dimethacrylate in the presence of alkoxyamines by performing its copolymerisation with styrene under conditions of three-dimensional radical polymerisation has been reported.[143] This includes the addition of a two- or threefold excess of styrene to the network-forming monomer (dimethacrylate) in order to perform a 'living' copolymerisation. It is essential that the number of cross-links per unit volume in the polymer network, ν, in the copolymer decreases only slightly compared to the homopolymers of dimethacrylate. The point is that, because of cyclisation in the macromolecules of homopolymers,[144–146] the effective ν value is much smaller than the 'nominal' one, so copolymerisation of dimethacrylate with monomers which cannot form polymer networks (*e.g.*, styrene) and contain only one double bond in the molecule increases the effective ν value.

To sum up, we can say that copolymerisation of (meth)acrylates and related monomers with styrene appears to be quite an efficient procedure for extending the area of application of alkoxyamines as agents for 'living' polymerisation.

7. Synthesis of block copolymers in the presence of alkoxyamines

A trivial method for the synthesis of block copolymers by 'living'-chain polymerisation includes two stages. The first stage is 'living'-chain polymerisation of the first monomer (M_1) to give a homopolymer with the desired molecular mass M_n and the lowest polydispersity (ideally, $M_w/M_n = 1.0$, block A). The second stage involves the extension of 'living' chains grown in the first stage with the other monomer (M_2) to give the second block (also with controlled M_n and M_w/M_n values, block B). Obviously, this approach can only be used if the 'living' end group of the chain A can initiate 'living' polymerisation of M_2. Taking into account the limitations on the activity of alkoxyamines as agents for 'living'

polymerisation (see above), this procedure allows only the synthesis of AB block copolymers based on styrene and its derivatives. Usually, polystyrene is used as the block A while a homopolymer of a substituted styrene is used as the block B, or *vice versa*.

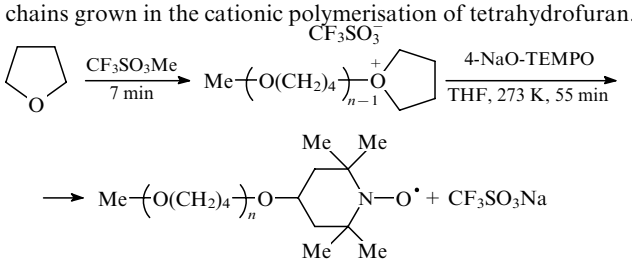
Synthesis of an AB block copolymer with 'living' poly(*p*-bromostyrene) as the block A and polystyrene as the block B has been described.[70] Block A was obtained by polymerisation of *p*-bromostyrene in the presence of 4-methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy and dibenzoyl peroxide. 'Living' poly(*p*-bromostyrene) thus obtained was used in the second stage to perform 'living' polymerisation of styrene (block B). The overall process resulted in the preparation of the AB block copolymer.

Yet another block copolymer was synthesised, with the homopolymer of 3- and 4-chloromethylstyrene (a mixture of isomers in a 2 : 1 ratio) as the block A and polystyrene as the block B.[71] Alkoxyamine was synthesised *in situ* from TEMPO and dibenzoyl peroxide in the bulk of 3(4)-chloromethylstyrene.

Blocks A and B can be synthesised not only from homopolymers, but also from copolymers with a rather high content of styrene or its derivatives (in order to ensure high efficiency of alkoxyamines as agents for 'living' polymerisation).[51, 55, 73, 76, 79, 140, 147–157] This allows substantial extension of the range of AB block copolymers.

This can be done[73] by performing, *e.g.*, polymerisation of alkyl acrylates (including butyl acrylate) at elevated temperatures (428 K) in the presence of an iminoxyl radical, such as 4-oxo-2,2,6,6-tetramethyl-1-piperidinyloxyl.† This procedure was used for the synthesis of not only the AB diblock copolymers (A is poly(alkyl acrylate) and B is polystyrene), but also the ABA and BAB triblock copolymers, as well as the AA′ diblock copolymers, where A and A′ are alkyl acrylates differing in the type of the alkyl substituent.

The use of different types of polymerisation for the synthesis of blocks A and B was proposed.[73, 158–160] In this case, stable iminoxyl radicals are modified by incorporation of additional functional groups with retention of the atomic group carrying the unpaired spin. 4-HO-TEMPO synthesised using the known procedure[161] is the most appropriate for such a modification. In this case, the hydroxy group is modified. For instance, a poly(tetrahydrofuran-*b*-styrene) block copolymer was synthesised[162] using a combination of cationic polymerisation to obtain poly(tetrahydrofuran) followed by 'living' radical polymerisation of styrene. First, 4-HO-TEMPO was treated with sodium hydride at room temperature to give 4-NaO-TEMPO which reacts with 'living' chains grown in the cationic polymerisation of tetrahydrofuran.

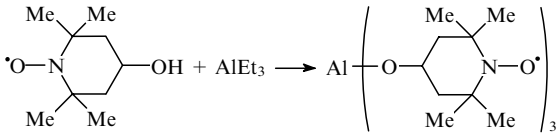


Being 'dead' in cationic polymerisation, poly(tetrahydrofuran) chains capped with the iminoxyl end group (block A) 'revive' in the bulk of styrene (or styrene derivatives and their mixtures with other monomers) and help the chain extension of the block B following the 'living' radical polymerisation mechanism. For instance, synthesis of the block B was performed in the presence of dibenzoyl peroxide (with alkoxyamine synthesised *in situ*) at 368 K over a period of 3.5 h and followed by heating at 398 K for 64 h.[162] The molecular masses, polydispersities as well as the lengths of blocks A and B expressed in the numbers of THF (block A) and styrene units (block B) for three specimens of the AB block copolymers were as follows:

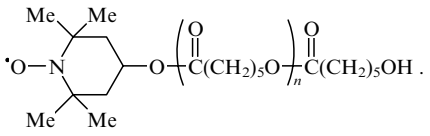
Parameter	Specimen 1	Specimen 2	Specimen 3
Block A			
M_n	1520	3300	10 600
M_w/M_n	1.38	1.43	1.26
n (THF)	14	24	77
Block B			
M_n	9690	12 600	38 800
M_w/M_n	1.22	1.25	1.40
n ($CH_2=CHPh$)	103	112	337

The use of anionic polymerisation in conjunction with 'living' radical polymerisation for the synthesis of a block copolymer based on ε-caprolactone and styrene has been reported.[163]

First, anionic polymerisation of ε-caprolactone was performed at room temperature in toluene solution for 3 h using tris(2,2,6,6-tetramethyl-1-piperidinyloxy-4-oxy)aluminium as catalyst.

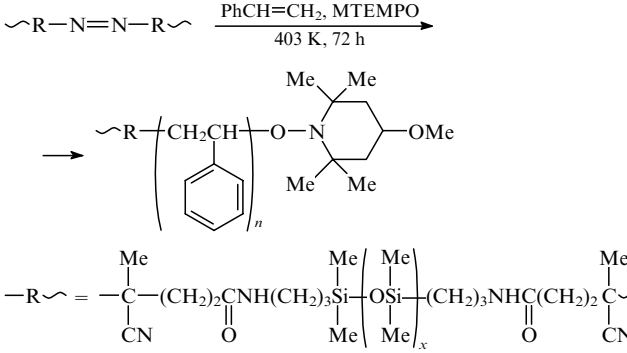


According to NMR data, this stage resulted in the formation of poly(ε-caprolactone) (block A) capped with the iminoxyl end group:



After isolation and purification, this block A was placed in the bulk of styrene, the iminoxyl group was *in situ* converted into the alkoxyamino group in the presence of dibenzoyl peroxide and a 'living' radical polymerisation of styrene (block B) was performed. The molecular masses and polydispersities varied respectively in the range $3200 \leqslant M_n \leqslant 6700$ and $1.28 \leqslant M_w/M_n \leqslant 1.33$ for blocks A and $20\,000 \leqslant M_n \leqslant 26\,200$ and $1.37 \leqslant M_w/M_n \leqslant 1.42$ for blocks B.

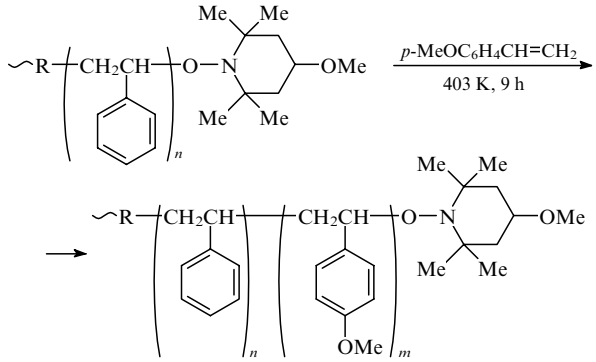
Yet another example of a combination of 'living' polymerisation performed in the presence of alkoxyamines with other types of polymerisation in order to prepare block copolymers has been reported.[160] Block A was prepared from poly(dimethylsiloxane) (M_n = 5000) telomerised with propylamine in the presence of 4,4′-azobis(4-cyanopentanoyl) dichloride. The macroinitiator (block A) thus formed was used for the initiation of 'living' polymerisation of styrene in the presence of 4-methoxy-2,2,4,4-tetramethyl-1-piperidinyloxy[164] (MTEMPO) to grow the polystyrene block B.



The degree of styrene conversion was varied between 70% and 85%. The 'living' AB block copolymer prepared in this manner

† Here,[73] the corresponding alkoxyamine was synthesised using azobis(isobutyronitrile) instead of dibenzoyl peroxide and polymerisation was performed at 378 K rather than at a conventional temperature of 363–368 K.

was used for chain extension of the next block B′ built of *p*-methoxystyrene units.



After 9 h, conversion of *p*-methoxystyrene reached 96%, which indicated that it is much more reactive than styrene during 'living' radical polymerisation.

According to NMR data, the ratio of dimethylsiloxane (block A), styrene (block B) and *p*-methoxystyrene (block B′) units in the ABB′ block copolymer was 1 : 6.67 : 44.5. The molecular masses and polydispersities of the macroinitiator, AB and ABB′ copolymers were as follows (GPC data):

Product	M_n	M_w/M_n
Block A (macroinitiator)	33 000	2.39
Copolymer AB	66 000	1.90
Copolymer ABB′	135 000	1.43

In addition to poly(dimethylsiloxane), poly(isobutylene),[165] poly(ethylene glycol),[166] polyethers,[167] polycarbonate[168] and polyamide[169] were also used as macroinitiators. There is a review dedicated to the synthesis of block copolymers by 'living' polymerisation using alkoxyamines.[170]

Summing up, studies on the use of alkoxyamines for the synthesis of unusual block and graft copolymers (including grafting onto fullerenes) should be mentioned[54, 70, 71, 151, 171–194] as well as those dedicated to the preparation of star-like and dendritic structures.[54, 151, 171, 175, 187, 190–192, 195, 196]

8. Prospects for the use of alkoxyamines and related compounds

Very recently (in the year 1999), it became possible to alleviate many problems in the use of alkoxyamines as agents for 'living' polymerisation. It was shown[52, 137, 185, 197–199] that the dissociation rate of the C—ON bond in alkoxyamines can be increased not only by introducing a phenyl substituent at the C atom of the monomer, but also by varying the nature of substituents at the nitrogen atom.

It was found that the use of di-*tert*-butylnitroxyl instead of traditionally used nitroxides, TEMPO or its derivatives, leads to weakening of the bond subject to dissociation in the alkoxyamine molecule to the extent that the rate constant for dissociation, k_1, appears to be high enough for performing a 'living' polymerisation of monomers devoid of aromatic rings at 393 K. For *tert*-butyl acrylate, the rate constant k_1 equals 10^{-3} s^{-1} at 393 K. Polymerisation of *tert*-butyl acrylate in the presence of di-*tert*-butylnitroxyl and dicumyl peroxide (with alkoxyamine synthesised *in situ*) was performed at 393 K. The 'living' type of the process was confirmed by both the increase in M_n with conversion and by the narrowing of MMD.

These examples indicate that the possibilities of the use of alkoxyamines in 'living' polymerisation can be extended.

Obviously, other adducts RX which can decompose during polymerisation into two free radicals, *viz*., an active radical R$^\bullet$, which can react with the monomer M ($R^\bullet + M \rightarrow RM^\bullet$), and a stable radical X$^\bullet$, which only can recombine with R$^\bullet$ ($R^\bullet + X^\bullet \rightarrow RX$), can also act like alkoxyamines. Some of these compounds (*e.g*., dithiocarbamates[40, 41, 200]) were used well before alkoxyamines. Currently, they are used much more rarely than alkoxyamines, most likely because of a larger number of side reactions which make 'living' polymerisation difficult. However, these and related compounds collectively called iniferters also have a number of advantages, the most important of which is photoactivity upon homolytic cleavage under the action of photoirradiation.

The search for new agents for 'living' radical polymerisation capable of undergoing a reversible photodissociation is one promising investigation line which seems to provide the possibility of substantial reduction of the operating temperature of the process (in the limit, down to room temperature). Low-temperature 'living' radical polymerisation of methyl methacrylate in the presence of RX containing piperidinothiocarbonylthio groups by photodissociation of the adduct RX instead of its thermal decomposition was attempted.[201]

At present, intensive search for compounds capable of undergoing reversible homolytic cleavage in polymerisation systems is being carried out. 'Living' copolymerisation of styrene with methyl acrylate at 393 K in the presence of di(isopropoxythiocarbonyl) disulfide as RX was reported in 1997.[202] The polydispersity of the copolymer obtained in this manner was lower than that of its analogue synthesised by conventional radical polymerisation. (A linear increase in M_n with conversion was also observed in this study.)

Very recently, halogen-containing organic compounds have been evaluated for use as agents for 'living' polymerisation. 'Living'-chain radical polymerisation of styrene at 353 K in the presence of ω-polystyryl iodide as a mediator and dibenzoyl peroxide as an initiator has been reported.[203] It was found that activation of the 'dormant' chains, RI, follows a radical substitution mechanism with the rate constant $k_{ex} = 3.1 \times 10^7 \exp(-27.8/RT)$ litre mol^{-1} s^{-1}

$$R^1I + (R^2)^\bullet \underset{k'_{ex}}{\overset{k_{ex}}{\rightleftarrows}} R^2I + (R^1)^\bullet$$

rather than a reversible dissociation mechanism, RI ⇄ R$^\bullet$ + I$^\bullet$. As can be seen, the activation energy of radical substitution reaction (27.8 kJ mol^{-1}) is much lower than that of thermal dissociation of alkoxyamines (124 kJ mol^{-1}).

Thus, the approach described above and based on the use of reversible homolytic cleavage of adducts RX remains rather promising. This is indicated by both an incessant stream of communications and the appearance of studies in which technological aspects are touched on.[81, 204–211] To mention just a few: studies dedicated to the search for procedures for performing not only bulk polymerisation, but also polymerisation in aqueous solutions, as well as emulsion and dispersion polymerisation.[81, 204–206, 210]

VI. Transition-metal halide complexes with organic ligands as agents for 'living'-chain radical polymerisation

Currently, an alternative approach to 'living' radical polymerisation is also being developed. This approach uses transition-metal compounds with mixed ligands including halogen atoms and organic ligands as agents for polymerisation. For brevity, we will call them transition-metal halides (TMH). The most commonly used compounds are transition-metal chlorides or bromides with the general formula $M^nY_nL_m$, where M is the transition metal, n is the valence of the transition metal, Y are the Cl$^-$ or Br$^-$ anions and L are organic ligands (as a rule, strong donors such as cyclic amines, linear polyamines, triphenylphosphine, *etc*.). The progress in this field is mainly associated with the studies by Matyjaszewski (USA).

Rapid development of the investigations on 'living' radical polymerisation controlled by the $M^nY_nL_m$ complexes is due to the fact that the new agents have three advantages over stable free radicals discussed in the previous Sections.

1. The most important is that, unlike TEMPO, the action of compounds $M^nY_nL_m$ is not confined to styrene and its derivatives, butyl acrylate, *etc.* as the monomers. On the contrary, these compounds can be used with almost all known monomers.

2. Compounds $M^nY_nL_m$ act at much lower temperatures (333–363 K)[212,213] than the TEMPO-type agents (393–428 K). It should be noted that the decrease in the operating temperatures makes it possible not only to solve the technologically important problem of reduction of power consumption, but also to reduce the risk of side reactions.

3. Using agents of the $M^nY_nL_m$ type, one can synthesise polymers with much narrower MMD and lower polydispersities ($M_w/M_n = 1.04-1.05$) than those of the polymers obtained with the TEMPO-type agents where $M_w/M_n \geqslant 1.15$ and often exceeds a value of 1.20.

Yet another (the most technologically important) advantage of compounds $M^nY_nL_m$ is that 'living' radical polymerisation can easily be carried out in friendly and environmentally safe aqueous solutions. Recently, the first studies on 'living' radical polymerisation in emulsions and dispersions in aqueous solutions have been reported.[214,215]

'Living' radical polymerisation controlled by agents of the $M^nY_nL_m$ type was called the Atom Transfer Radical Polymerisation (ATRP).

1. The mechanism of action

The mechanism of the action of $M^nY_nL_m$ compounds as agents for 'living' radical polymerisation is based on the known Kharasch reaction.[216] It was found that halides of transition metals in the lowest oxidation state n can react with alkyl halides RX to give alkyl radicals R$^\bullet$. This is accompanied by oxidation of the transition-metal atom. An essential feature of this reaction is its reversibility.

$$RX + M^nY_nL_m \rightleftharpoons R^\bullet + M^{n+1}Y_nL_mX.$$

Obviously, performing the reaction in the bulk of a monomer (we will denote it Mm) initiates polymerisation by the mechanism $R^\bullet + Mm \rightarrow (R^1)^\bullet$, where $(R^1)^\bullet$ is the primary growing polymer chain, followed by incremental propagation of the primary chain by the reaction

$$R^\bullet + x\mathrm{Mm} \longrightarrow \mathrm{RMm}_x^\bullet,$$

where x is the number of the monomer molecules which to add to R$^\bullet$ during the time interval between the instant of appearance of the active polymerisation centre (as a result of the reaction between alkyl halide and $M^nY_nL_m$) and the instant of deactivation of this centre as a result of the reverse reaction with $XM^{n+1}Y_nL_m$. Since activation occurs at regular time intervals, the deactivation is temporary, so that alkyl halide-induced polymerisation in the presence of $M^nY_nL_m$ is in essence implemented as a 'living'-chain process.

What actually happens is that the activation ⇄ deactivation cycle proceeds in a more complicated manner rather than follows a simplified scheme discussed above. The reverse reaction involves a stage of addition of the free radical R$^\bullet$ to $M^{n+1}Y_nL_mX$ with the formation of an intermediate $R-M^{n+1}Y_nL_mX$, which is a mediator of stepwise growth of the polymer chain. Chain propagation occurs as the monomer addition to the radical R$^\bullet$ formed upon reversible decomposition of the intermediate rather than monomer insertion into the $R-M^{n+1}$ bond. The intermediate undergoes deactivation by decomposing into the alkyl halide RX and the initial complex $M^nY_nL_m$.

To initiate a 'living' radical polymerisation, one has to start either a forward or a reverse reaction of the activation ⇄ deactivation cycle. When alkyl halides and $M^nY_nL_m$ are used as initiators, the forward reaction proceeds to give the active intermediate, $R-M^{n+1}Y_nL_mX$, which decomposes into the growing radical R$^\bullet$ and a complex $M^{n+1}Y_nL_mX$. If a halide of the transition metal in the highest oxidation state $[M^{(n+1)+}]$ is used, the active intermediate should be obtained in the reaction of the complex $M^{n+1}Y_nL_mX$ with the radicals formed in the decomposition of the initiator [*e.g.*, azobis(isobutyronitrile)]. In both cases, 'living' radical polymerisation proceeds in the presence of the monomer. The most commonly used initiators are alkyl halides RX and complexes $M^nY_nL_m$;[4,212–214,217–257] however, polymerisation can also be initiated by azobis(isobutyronitrile) in the presence of $M^{n+1}Y_nL_mX$ complexes.[224,227,237,258]

It should be noted that the process of 'living' radical polymerisation is often described using the concepts of a 'living' radical chain and a 'dormant' chain. If polymerisation is performed in the presence of stable nitroxyl radicals (TEMPO), a 'living' radical chain and a 'dormant' radical chain respectively mean a propagating radical R$^\bullet$ and an adduct (alkoxyamine TEMPO–R). For a polymerisation process proceeding in the presence of TMH, a 'living' radical chain also means a propagating radical R$^\bullet$ while a 'dormant' chain means an alkyl halide RX in the presence of $M^nY_nL_m$, where RX is either the initial alkyl halide or a polymeric product with the halogen atom in the end group. Polymer chains immobilised in the form of intermediates $R-M^{n+1}Y_nL_mX$ can be ignored since their concentrations are much lower than that of RX.

Thus, in both cases 'living' radical polymerisation is performed under conditions of dynamic equilibrium between the 'living' and 'dormant' radical chains.

The term 'living' chain, as applied to radical polymerisation, can also be used in another sense, much as in the case of, *e.g.*, anionic polymerisation. All chains which can grow are considered 'living'. These are all chains RX with the end group X which, under given conditions, can undergo homolytic cleavage to release an active free radical R$^\bullet$ (a growing polymer chain). In this case, it is believed that 'living' chains can be either 'dormant' in the form of RX or active in the form of R$^\bullet$.

An essential distinction between TEMPO- and TMH-based agents for 'living' radical polymerisation is that the latter are catalytic systems and, unlike the former, are not incorporated into the polymer chains after completion of the polymerisation process. TMH-based agents can be separated from the polymer and reused. However, this type of compound has a drawback consisting in the ability to initiate redox processes of polymer destruction.

The necessity of using well-defined terms can be illustrated taking calculations of the average lengths of polymer chains from the data on the degree of polymerisation, Γ, as an example. As is known, $\Gamma = \Delta[\mathrm{Mm}]/[\mathrm{Mm}]_0$, where $\Delta[\mathrm{Mm}]$ is the concentration of polymer and $[\mathrm{Mm}]_0$ is the initial monomer concentration. In this case, the chain length ν is defined by the ratio $\nu = \Gamma[\mathrm{Mm}]_0/[\mathrm{C}]$, where [C] is the concentration of chains. This implies that the [C] value refers to all polymer chains grown in a given polymerisation system during the time interval $\Delta\tau$ needed to reach the specified Γ value. In other words, [C] is the sum of the [RX] value averaged over $\Delta\tau$ with averaged [R$^\bullet$] value. If quadratic chain termination during time interval $\Delta\tau$ can be ignored, then, taking into account that [R$^\bullet$] is negligible as compared to [RX], it is admissible that $[\mathrm{C}] \simeq [\mathrm{RX}]_0 \simeq \mathrm{const}$. Following this reasoning, all chains with the end group X are considered 'living'. The majority of calculations of ν rest on this consideration.

2. 'Living' radical polymerisation controlled by transition-metal halides

The simplest scheme of a 'living' radical polymerisation controlled by TMH is presented below (Scheme 6).[259,260]

Scheme 6

$$P_kX + M^nY_nL_m \underset{k_d}{\overset{k_a}{\rightleftharpoons}} P_k^\bullet + X-M^{n+1}Y_nL_m$$

$$P_k^\bullet \xrightarrow{k_p,\ \mathrm{Mm}} P_{k+1}^\bullet$$

Here $P_k^\bullet$ is the growing polymer chain, X is a halogen, and k_a, k_d and k_p are the rate constants for chain activation, deactivation and propagation, respectively.

For $10^{-3}\ \mathrm{s} < t < 10^2\ \mathrm{h}$, theoretical analyses[88,261] of Scheme 6 have led to a number of analytical expressions which

describe the kinetics of (i) polymerisation, (ii) reduction of instantaneous concentration of growing chains and (iii) increase in the instantaneous concentration of growing chain acceptor (a complex of the transition metal in the highest oxidation state, $X-M^{n+1}Y_nL_m$) throughout the process. The corresponding formulae are as follows:

$$\ln\frac{[Mm]_0}{[Mm]} = \frac{3}{2}k_p\left([RX]_0[M^n]_0\right)^{1/3}\left(\frac{k_a t^2}{3k_d 2k_t}\right)^{1/3}, \quad (27)$$

$$[P_k^{\bullet}] = \left([RX]_0[M^n]_0\right)^{1/3}\left(\frac{k_a}{3k_d 2k_t t}\right)^{1/3}, \quad (28)$$

$$[M^{n+1}] = \left([RX]_0[M^n]_0\right)^{2/3}\left(\frac{3k_a^2 2k_t t}{k_d^2}\right)^{1/3}. \quad (29)$$

Comparison of the results obtained after solving the system of differential equations (27)–(29) with the experimental results [258] revealed considerable quantitative and qualitative (the shape of the kinetic curves) discrepancies between them.

To establish the reasons for such a sharp distinction between theory and experiment, computer simulation of a more detailed Scheme 7 was performed [259] for Mm = styrene and M = Cu using the PREDICI programme package [262] and the results of reported studies.[106, 262–266]

Scheme 7

$RX + M^nY_nL_m \rightleftarrows R^{\bullet} + XM^{n+1}Y_nL_m$,
$R^{\bullet} + Mm \longrightarrow P_1^{\bullet}$,
$3\,Mm \longrightarrow 2\,R^{\bullet}$.
} Initiation

$P_kX + M^nY_nL_m \rightleftarrows P_k^{\bullet} + XM^{n+1}Y_nL_m$,
$P_k^{\bullet} + Mm \longrightarrow P_{k+1}^{\bullet}$.
} Chain propagation

$P_k^{\bullet} + Mm \longrightarrow D_k + R^{\bullet}$ Chain transfer to monomer.

$2\,R^{\bullet} \longrightarrow D_2$,
$P_k^{\bullet} + P_m^{\bullet} \longrightarrow D_{k+m}$,
$P_k^{\bullet} + P_m^{\bullet} \longrightarrow D_k + D_m$,
$P_k^{\bullet} + R^{\bullet} \longrightarrow D_k$.
} Chain termination

The numerical values of rate constants k used in computer simulation of a styrene polymerisation at 383 K with $[Mm]_0^*$, $[RX]_0^*$, $[M^n]_0^*$ and $[M^{n+1}]_0$ equal to 8.7, 0.087, 0.087 and 0 mol litre^{-1}, respectively, are shown below:

k/litre mol^{-1} s^{-1}	Numerical value	Ref.
k_i	1.6×10^4	267, 268
k_p	1.6×10^3	102
$2k_{tc}(0)$	10^9	267
$2k_{td}(0)$*	10^8	267
$2k_{to}$	10^9	267
k_{tr}	0.22	269
k_d^*	1.1×10^7	270
k_a	0.45	270
k_{tp}	10^9	267, 271
k_{term}^*	4.8×10^{-11}	112

(the asterisked parameters were used as independent variables).

The discrepancies between the results of computer simulation and the known experimental data [258] appeared to be as substantial as in the case of comparing with the results of analytical solutions of Eqns (27)–(29). Variation of the initial k values over a wide range under assumption that they remain unchanged during the process does not make the situation better. It was found that calculated data can fit experimental results only assuming that the numerical values of particular rate constants vary during the process, *i.e.*, that they are dependent on the degree of conversion Γ (degree of polymerisation).

The appearance of the $k = f(\Gamma)$ dependence during polymerisation is largely caused by an increase in the viscosity of the reaction mixture. This prevents the reagent molecules A and B from approaching each other in the bimolecular reaction A + B to the extent that the reaction becomes diffusion-controlled.[267, 268, 272–290] In other words, after the viscosity of the reaction medium reaches a particular threshold (because of accumulation of the polymer), the rate of the bimolecular reaction A + B appears to be controlled by the diffusion characteristics of A and B rather than their reactivities. Quantitatively, a bimolecular reaction goes under diffusion control if the condition $k > k_D$ (k_D is the rate constant for pairwise collisions between molecules A and B) is met. Evaluation of k_D according to Smoluchowski [272, 277–283, 291]

$$k_D = 4\pi R(D_A + D_B)$$

(R is the distance between the centres of gravity of the colliding molecules and D_A and D_B are the diffusion coefficients of molecules A and B in the reaction medium) shows that for low-molecular mass compounds ($D \simeq 10^{-5}$ cm^2 s^{-1}) the k_D value is $\sim 4\times10^9$ litre mol^{-1} s^{-1} for $\Gamma \simeq 0$. This implies the absence of diffusion control over every elementary act (all k values are much less than 4×10^9). For dilute polymer solutions ($0 < \Gamma < 10\%$), the D value ($D \simeq 10^{-7}$ cm^2 s^{-1}) is about two orders of magnitude smaller than for low-molecular mass compounds. Here, the threshold k_D value decreases down to $\sim 4\times10^7$ litre mol^{-1} s^{-1}, which is comparable with the rate constant for quadratic chain termination. For $\Gamma > 10\%$, polymer solutions become so viscous that the diffusion coefficients do not exceed 10^{-9} cm^2 s^{-1} and $k_D \leqslant 4\times10^5$ litre mol^{-1} s^{-1} even for low-molecular mass compounds. Thus, not only quadratic termination reactions of growing chains, but also elementary bimolecular reactions between small molecules (provided that their rate constants meet the condition $k \geqslant 4\times10^5$ litre mol^{-1} s^{-1}) go under diffusion control at $\Gamma > 10\%$.

The $k = f(\Gamma)$ dependence for high rate constants for quadratic chain termination, due to diffusion control of the corresponding elementary reactions, was also suggested.[259] The corresponding formula is as follows [292, 293]

$$k_\Gamma = k_0\left(\frac{\Gamma[Mm]_0}{[RX]_0}\right)^{-\left(0.65+0.02\frac{\Gamma[Mm]_0}{[RX]_0}\right)},$$

where k_Γ is the current k value at a given degree of polymerisation Γ, expressed as the $[Mm]/[Mm]_0$ ratio ($\Gamma = \Delta[Mm]/[Mm]_0$), and k_0 is the k value at $\Gamma = 0$. Calculations performed using this model gave reasonable agreement with the experimental data.

Taking into account the known data on the diffusion kinetics,[267, 268, 271–290, 292–294] the necessity of considering the diffusion-controlled character of quadratic chain termination reactions seems to be quite natural. Rather it is unclear why the neglect of this factor in the description of the mechanism of 'living' radical polymerisation in the presence of alkoxyamines causes no discrepancies between the calculated and the experimental data.

Clearly, there is no basic distinctions between the mechanism of the action of alkoxyamines and TMH (*cf.* Schemes 7 and 5). In both cases, pseudo-'living' chains (growing free radicals) are formed. At regular intervals, they are 'revived' and can react both with the monomer and with one another (unlike true 'living' chains which never react with one another).

It seems likely that the main distinction between TMH and alkoxyamines as agents for 'living' polymerisation has a purely quantitative character and lies in the fact that for TMH the rate constants for activation of 'dormant' chains are two orders of

magnitude higher than the corresponding rate constants for alkoxyamines. Because of this, the repetition frequency of the dissociation ⇄ recombination cycle responsible for the initiation of 'living' radical polymerisation increases substantially in the presence of TMH (see Scheme 7). This leads to a decrease in the 'sensitivity' of the polymerisation process to additional initiation (*e.g.*, thermal initiation in the case of styrene) and to reduction of the polydispersity ($M_w/M_n \simeq 1$). Probably, the increase in the 'sensitivity' of the process to the dependence of the rate constants for quadratic chain termination reactions on the degree of conversion is also due to an increase in the repetition frequency of the cycle, which necessarily requires consideration of the diffusion control of the rates of these reactions.

Detailed studies of the mechanism of ATRP showed first of all that, generally, the reaction follows a radical mechanism. It was found that introduction of strong inhibitors (galvinoxyl) results in complete suppression of polymerisation, whereas the additives of poisons of anionic and cationic polymerisation (alcohols and water) have no effect on the process.[213, 295] This undoubtedly confirms that ATRP follows the radical mechanism.

The question may also arise as to whether the polymer chain propagation occurs in this case by insertion of the monomer molecule into the $R-M^{n+1}Y_nL_mX$ bond (a conventional mechanism involves homolysis of the $R-M^{n+1}$ bond followed by the reaction of the released free radical with the monomer). Obviously, it is impossible to answer this question experimentally; however, most of investigators believe that chain propagation occurs in a normal manner rather than involving the monomer insertion.[213, 231, 296]

It should also be noted that, according to Scheme 7, the reaction of chain termination should result in a polymer with halogen atoms as the end groups. This was observed experimentally.[295, 297] In addition, it was shown that polymerisation of a fresh portion of the monomer can be initiated by introducing the polymers with Cl or Br atoms as the end groups (of course, in the presence of catalytic amounts of $M^nY_nL_m$).[295]

An interesting study aimed at elucidating the mechanism of ATRP was carried out by Matyjaszewski and co-workers [298] who investigated a catalytic system based on $CuBrL_m$. The addition of finely dispersed copper to the components of the system resulted in the transformation of $CuBr_2$ formed in the course of the reaction into active CuBr which rapidly reacted with RX (RBr).

$$Cu^{2+} + Cu^0 \longrightarrow 2Cu^+.$$

This redox reaction promoted a substantial increase in the initiation rate. As a result, the rate of polymerisation increased by more than an order of magnitude and complete conversion was reached after 55 min. The redox reaction between Cu^{2+} and Cu^0 was confirmed by ESR spectroscopy. There is no question that this approach and related investigations into the processes of activation of 'living' radical polymerisation are also technologically important.

3. Catalytic systems based on transition-metal halides and the assortment of polymeric products formed

Studies on 'living' polymerisation using TMH are primarily dedicated to the search for the most efficient catalytic systems using semiquantitative evaluation procedures. It was found that the most efficient systems are based on copper bromide.[212, 219, 231] It is these catalytic systems that allowed the synthesis of polymers with $M_w/M_n = 1.04-1.05$ and molecular masss $M_n = (50-100)\times 10^3$. This has initiated intensive search for novel catalytic systems without accompanying detailed kinetic studies. However, systems based on other transition metals appeared to be less efficient as regards both the polydispersity index, M_w/M_n, and the molecular mass M_n. Currently, catalytic systems containing chlorides and bromides of Cu(I) and Cu(II),[4, 212–214, 217–249, 299, 300] Fe(II),[250, 301–303] Ni(II),[304–310] Ru(II),[215, 295, 296, 311–320] Rh(II),[221, 321] acetates of Pd(II) [322] and Cr(II),[323] as well as ReO_2 (see Ref. 324) have been studied (Table 3). For all the salts, except for CuBr and CuCl, the polydispersity indices, M_w/M_n, lie between 1.1 and 1.3.

Syntheses of polymers with $M_w/M_n = 1.04-1.05$ have clearly demonstrated that quadratic chain termination contributes insignificantly to the MMD of the polymers. A semiquantitative procedure developed for the analysis of experimental results is based on the determination of the dependences of $\ln([Mm]_0/[Mm]_t)$ on t, where $[Mm]_0$ and $[Mm]_t$ are the initial and running concentrations of the monomer, respectively. The results of testing were accepted if both dependences were linear.

This procedure was used to analyse a large number of catalytic systems. For instance, organic ligands (L) were varied in studies of the catalysts based on CuBr. If both the above-mentioned dependences were linear, the effect of the nature of the ligand on the polydispersity index was followed and those ligands were chosen which gave polymers with the smallest M_w/M_n ratios. The effect of ligands on the solubility of TMH in the monomers (solvents) was also taken into account [212, 213, 231] and then the ligands which were the best to stabilise the ions of metals in the highest oxidation state were chosen from the group of preliminarily selected compounds. This made it possible to choose the systems with the highest concentrations of active intermediate $R-M^{n+1}Y_nL_mX$. As follows from the data listed in Table 3, bipyridines and polyamines appeared to be the best ligands, whereas triphenylphosphine appeared to be the worst one. This is likely due to the fact that triphenylphosphine *per se* can be involved in the redox cycle.

Apparently, ligands can also suppress a number of possible side reactions such as (presumably) oxidative chain termination (for simplicity, the ligands at TMH are not shown):

$$R_n^{\bullet} + M^{n+1} \longrightarrow P_n(=) + M^n + H^+$$

and (or) hydride transfer:

$$R_n^{\bullet} + M^{n+1} \longrightarrow P_n(=) + HM^{n+1},$$

where $P_n(=)$ is the polymer with the end group containing a double bond. Such radical reactions are known for transition-metal salts and complexes.[325] Both reactions result in chain termination and, hence, in broadening of MMD and an increase in M_w/M_n. (Scheme 7 discussed in the previous subsection ignores these reactions since it corresponds to the case M = Cu where the neglect of these side processes is well substantiated.)

A similar procedure was used for studying and choosing alkyl halides (RX). In this case, the results of bulk polymerisations and polymerisations in solvents were compared. The M_w/M_n ratio was analysed as a function of the degree of conversion.

Almost all catalysts listed in Table 3 make it possible to obtain better values of M_n and M_w/M_n than TEMPO. In addition, these catalytic systems allow polymerisation of almost all vinyl monomers at lower temperatures.

In addition to catalytic systems, activators have also been studied. Aryl and sulfonyl halides were found to be the best activators of 'living' polymerisation, alkyl halides are less efficient. In the latter case, the role of activator is played by the second component of the binary system, which 'works in pair' with the catalyst ($M^nY_nL_m$ or $M^{n+1}Y_nL_mX$). For compounds $M^nY_nL_m$, alkyl halide RX acts as activator (the initial pair is $RX + M^n$), whereas for compounds $M^{n+1}Y_nL_mX$ this role is played by the source of free radicals, such as azodinitrile, *etc.* (the initial pair is $R^{\bullet} + M^{n+1}$).

It is believed [212, 213, 231] that the rate of the redox reaction between the activator and catalyst should be high enough to provide nearly simultaneous initiation of all chains; this is one of the main conditions for the preparation of polymers with narrow MMD and very low polydispersity M_w/M_n. The choice of compounds to be used as activators is performed to meet this condition.

Table 3. Catalytic systems for ATRP based on transition-metal compounds.

Metal compound and its concentration/mol litre^{-1}	Ligands (L) and their concentrations /mol litre^{-1}	Activator (A) and its concentration/mol litre^{-1}	T/K	t/h	Main characteristics of polymer				Ref.
					type of the monomer (Mm)[a]	conversion (%)	M_n	M_w/M_n	
CuBr 3×10^{-2}	4,4′-di(nonan-5-yl)-2,2′-bipyridine $6\cdot10^{-2}$	diphenylethyl bromide 6×10^{-2}	383	5	MA	95	17 000	1.05	219
					St	95	50 000	1.05	
CuBr 5.53×10^{-2}	2,2′-bipyridine 5.53×10^{-2}	2-bromopropionitrile 5.53×10^{-2}	317	23	AN [solution in ethylene carbonate (5.25 mol litre^{-1})]	38.3	10 000	1.04 – 1.06	240
$CuBr_2$ 4.5×10^{-2}	4,4′-di(nonan-5-yl)-2,2′-bipyridine 9×10^{-2}	azobis(isobutyronitrile) 4.5×10^{-2}	383	16	St	90	50 000	1.15	224
			383	10	MA	90	9 000	1.1 – 1.15	
			383	8	MMA		16 000	1.2 – 1.4	
CuCl	2,2′-bipyridine	$MeSO_2Cl$	363	5 – 6	MMA	89		1.35	225
[Mm] : [CuCl] : [A] : [L] = 200 : 1 : 1 : 3			403	5 – 6	St	89		1.49	
			493	5 – 6	BMA	98		1.27	
CuBr 1.05×10^{-2}	4,4′-di(nonan-5-yl)-2,2′-bipyridine 2.01×10^{-2}	*p*-toluenesulfonyl chloride	363	5	MMA (solution in biphenyl ether)	85	184 000	1.5	236
[CuBr] : [Cu^0] = 1 : 10	4,4′-di(nonan-5-yl)-2,2′-bipyridine	methyl 2-bromopropionate	363	0.9	St	96	50 000	1.1 – 1.3	298
[A] : [CuBr] : [L] = 1 : 2 : 0.4									
CuCl	4,4′-di(nonan-5-yl)-2,2′-bipyridine	4,4′-di(chlorosulfonyl)-biphenyl	413	2.5	BA		30 000	1.5	213
[Mm] : [A] : [CuCl] = 200 : 1 : 2									
CuBr 9×10^{-2}	1,1,4,7,10,10-hexamethyltriethylenetetraamine 4.7×10^{-2}	1-phenylethyl bromide 9×10^{-2}	363	8	MMA	90	20 000	1.1	224
			383	8	MA	80	20 000	1.2	
			383	8	St	80	20 000	1.15	
$FeBr_2$ 10^{-2}	4,4′-di(nonan-5-yl)-2,2′-bipyridine	1-phenylethyl bromide	353	15	MMA		75 000	1.24	303
			383	12	St	64	7 000	1.27	
$FeCl_2$ 10^{-2}	triphenylphosphine 0.1	CCl_4 10^{-2}	353	60	MMA	90	2 000	1.3 – 1.4	302
$RuCl_2$ 10^{-2} (aluminium isopropoxide as a co-activator)	triphenylphosphine 0.1	$PhCOCHCl_2$	353	81	MMA	97	10 000	1.3	296, 314
$[NiCl_2] = 10^{-2}$ (aluminium isopropoxide as a co-activator)	triphenylphosphine	CCl_3Br 2×10^{-2}	353	12	MMA [solution in benzene (2 mol litre^{-1})]	48	5 200	1.21	306
CuBr 0.1	4,4′-di(nonan-5-yl)-2,2′-bipyridine 2×10^{-2}	benzyl bromide 0.1	363 – 373	–	MMA	95	10 000	1.2	217
ReO_2 (aluminium isopropoxide as a co-activator)	triphenylphosphine	MeCH(Ph)I 6×10^{-2}	373	8	St	94	40 000	1.15	324
ReO_2	triphenylphosphine	–	353	25	St	98	9 900	1.4	324
$[ReO_2(PPh_3)_3] = 6\times10^{-2}$			333	25	St	93	9 900	1.32	
			303	25	St	83	8 500	1.6	
$Pd(OAc)_2$	triphenylphosphine	CCl_4	343	24	MMA	74	30 000	1.6	322
$[Pd(OAc)_2] : [CCl_4] = 10 : 1$									
CuBr	2,2′-bipyridine	methyl 2-bromopropionate	363	15	2-hydroxyethyl acrylate	~100	6 270	1.2	
CuCl 10^{-2}	*N*,*N*′,*N*″,*N*″,*N*‴-pentamethyldiethylenetetramine 10^{-2}	1-phenylethyl bromide 10^{-2}	313	8	VP	85	15 500	1.17	230

[a] Notations: MA is methyl acrylate, St is styrene, AN is acrylonitrile, MMA is methyl methacrylate, BMA is butyl methacrylate, BA is butyl acrylate and VP is vinylpyridine.

4. 'Living' radical polymerisation performed in emulsions, suspensions and with the use of immobilised catalysts

As was mentioned above, intensive studies on 'living' radical polymerisation have led to the discovery of relatively simple and cheap catalytic systems which make it possible to accomplish the polymerisation process in several hours and to obtain well-defined polymers with molecular masses as high as 10^5 monomer units and narrow MMD ($M_w/M_n \simeq 1.05 - 1.1$).

It is obvious that bulk polymerisation faces some problems associated with fast heat transfer from the reaction zone and with

an increase in the viscosity of the reaction media during the process. Additionally, catalysts should be removed from the polymer after completion of the process, since usually they have an intense colour and can oxidise polymers under operating conditions.

Polymerisation in solvents also has essential drawbacks such as fire hazard, necessity of solvent regeneration and environmental costs.

Suspension or emulsion polymerisation in water-borne systems seems to be best suited to overcoming all the above-mentioned problems.

However, no studies on the emulsion [214, 326] and suspension [215] 'living' radical polymerisation had been reported until 1999. The results obtained recently are encouraging, since emulsion polymerisation is at least as efficient as bulk polymerisation.

Matyjaszewski *et al.*[214] found that emulsion polymerisation of butyl methacrylate using $CuBr_2L$ as catalysts allows reduction of the temperature of the process from 363 to 343 K and shortening of the polymerisation time from 20 to 4–5 h. The monomer conversion reached $\sim 90\%$, as is the case of bulk polymerisation. However, it should be noted that MMD was somewhat broader and varied between 1.1 and 1.2 instead of being equal to 1.05.

The new approach has of course posed some problems associated with the choice of initiators and emulsifying agents, buffer solutions, *etc.*, including the problem of stability of the latex species against aggregation as well as the problem of confining the catalysts to the monomer phase. Nevertheless, there is reason to believe that all these problems will be successfully solved since the mechanism of the action of catalysts in binary systems remains essentially the same.

'Living' radical polymerisation in suspensions have also been studied by investigators from Japan.[215] Polymerisation of MMA was performed at 353 K using $RuCl_2(PPh_3)_3$ as the catalyst. Monomer suspensions in a toluene–water mixture as well as in alcohols with additives of CH_2Cl_2 and water were used. Fairly good results were obtained, the polymers were characterised by $M_n \simeq 10^5$ and $M_w/M_n = 1.1-1.3$. Stability of suspensions was achieved by vigorous stirring of the mixtures.

Finally, Matyjaszewski [213] attempted to immobilise $CuBr_2L_2$-based catalytic systems using silica gel and cross-linked polystyrenes as catalyst's supports. However, polymerisations of styrene in the presence of immobilised catalysts were unsuccessful, namely, the M_w/M_n ratio varied in different experiments between 1.5 and 10 (for $M_n = 10^4-10^5$). The reasons why MMD is so broad are likely associated both with the diffusion from the matrix supporting the immobilised catalyst and with the increase in the molecular mass of 'living' chains during conversion. Despite the failure, the author intended to continue his studies since immobilisation of catalysts results in considerable reduction of contamination of the polymeric products by metal-containing impurities.

5. Synthesis of block, graft, star and hyperbranched copolymers using atom transfer radical polymerisation

It is well known that block copolymers, as well as star and other copolymers were first synthesised using a 'living' cationic and anionic polymerisation of vinyl monomers (their number is limited, however). Obviously, 'living' radical polymerisation would favour the extension of the assortment of different types of copolymers and, correspondingly, the broadening of the spectrum of their consumer properties.

A procedure for the preparation of block copolymers by 'living' chain polymerisation is simple. First, polymerisation of a monomer A is performed until complete conversion. Then, the other monomer (B) is introduced into the reaction system to yield a block copolymer AB. The blocks can alternate in any manner.

Star copolymers are synthesised using polyfunctional activators (alkyl halides, sulfonyl halides, *etc.*) with more than one active halogen atom. In the reaction with a catalyst (*e.g.*, Cu^IBrL_2), these halides are transformed into 'living' chains so that each polyfunctional (with respect to the halogen) molecule becomes the initial point for the growth of several polymer chains which form a star-like structure. Synthesis of star copolymers with two, three, five [213, 311] and even eight arms has been reported.[212]

Graft copolymers are prepared using the reaction of chain transfer to polymer. In this case, the monomer simultaneously plays the role of an activator since halogen atoms are constituents of the monomer molecules. Almost all of them can be the initial points for chain propagation. A number of studies on the synthesis of this type of polymers has been reported.[223, 327, 328]

It is known that both anionic and cationic polymerisation require extremely pure reagents and solvents with complete exclusion of water. 'Living' radical polymerisation allows nearly complete elimination of these limitations. Recently, numerous syntheses of almost all types of copolymers by 'living' radical polymerisation of a broad spectrum of monomers have been reported.[229, 231, 235, 305, 306, 311, 329, 330] For instance, diblock and triblock copolymers of alkyl methacrylates,[305, 331] styrene and acrylates,[213, 312] polysulfones and styrene [222] and some other linear copolymers have been prepared.[212, 213, 296, 314]

An interesting procedure for the synthesis of block and graft copolymers involves a combination of cationic polymerisation with ATRP.[233, 246, 249, 332–334] In the first stage, cationic polymerisation of a monomer A is used to grow the chains with halogen-containing end groups (macromonomers), which are then involved in the ATRP process which proceeds in the bulk of a monomer B. This procedure was used for the preparation of various diblock copolymers of the AB type, where A is poly(tetrahydrofuran),[246] ε-caprolactone,[332] vinyl ethers,[233] norbornene or cyclopentadiene,[249] as well as bicyclic alkenes such as bicyclo[2.2.1]heptene and bicyclo[2.2.1]heptadiene [333] (cationic polymerisation), and B is polystyrene or poly(meth)acrylates (ATRP process).

VII. Three-dimensional 'living'-chain radical polymerisation

Polyfunctional unsaturated oligomers are compounds the molecules of which contain more than one double bond (glycol dimethacrylates, divinylbenzene, oligoester acrylates,[335–338] oligoester maleates,[339] *etc.*). Polymerisation of these compounds results in the formation of polymer networks (three-dimensional structures). Unlike linear polymerisation of conventional vinyl monomers, three-dimensional radical polymerisation proceeds according to a specific (the so-called microheterogeneous) mechanism [336, 337] to give a specific type of topological and supramolecular (morphological) structure of the polymeric product. A salient feature of the topological structure of the polymer is that a large number of small rings is formed in the polymer network.[144–146] These rings play the role of defects in the continuous network. A peculiarity of the morphology is that a 'grain' structure is formed in the polymer and the inter-'grain' spacings are considered as defects of the supramolecular structure.

The appearance and development of topological and morphological defects during three-dimensional radical polymerisation is due to the chain character of the polymerisation process.[336, 337] That is, the chains initiated upon decomposition of the initiator rapidly (nearly instantaneously in the time scale of complete conversion) grow until the final length and undergo termination. The reaction system built of branched, cross-linked and aggregated polymer chains is thermodynamically and kinetically unstable in the bulk of the initial oligomer. Because of this, microphase separation occurs in the system, enhanced by a local gel effect. Eventually, this is the reason for the formation of defects, which affects physicomechanical characteristics of this type of polymer and materials based on them.

Since unsaturated oligomers have found wide and technologically important use,[335–339] investigators are in continuous search for the ways of eliminating the reasons for the formation of defects during their polymerisation. In this regard, 'living' chains play a special role. Actually, transformation of a conventional three-dimensional chain polymerisation into 'living' chain polymer-

isation makes the process stepwise, which is typical of such well-known oligomers as epoxides, urethanes and polycondensation resins. A small distinction between 'living'-chain polymerisation and stepwise process is only that each initiation act causes the propagation of growing polymer chains by several monomer units rather than one unit. Thus, the increment value for stepwise 'living' radical polymerisation exceeds unity (one monomer unit), which makes it possible to call this process a pseudostepwise one. In this case, the reasons for intense formation of defects, inherent in three-dimensional radical polymerisation, are eliminated.[336, 337]

Only a few studies on three-dimensional 'living'-chain radical polymerisation have been reported to date.[72, 143, 340–343]

Ide and Fukuda [72, 340] studied three-dimensional 'living' radical copolymerisation of styrene with 4,4-divinylbiphenyl at 398 K in the presence of alkoxyamine synthesised from styrene and a TEMPO-like nitroxide. They determined the copolymerisation constants including that of styrene with 'pendent' double bonds of 4,4′-divinylbiphenyl, $r_p = k_{ll}/k_{lp} = 1.0 \pm 0.1$ (the subscripts 'l' and 'p' correspond to styrene and divinyl oligomer, respectively). Since $r_1 = k_{11}/k_{12} = 0.38$, it was concluded that intense cyclisation on 'pendent' bonds, inherent in conventional radical chain polymerisation in this system, ceases nearly completely upon transformation of the process into 'living' polymerisation. It was also found that the end product, a cross-linked polystyrene (or a polystyrene network), was almost free from small-cycle topological defects.

A comparative study of the properties of polystyrenes cross-linked with 4,4′-divinylbiphenyl synthesised using conventional radical polymerisation (without TEMPO) and 'living' radical polymerisation (in the presence of TEMPO) has been reported.[340] Specimens of identical composition prepared in the presence and in the absence of TEMPO possessed substantially different properties. These differences were interpreted in terms of the microheterogeneous model.[340] The specimens synthesised by 'living'-chain polymerisation were identified as 'homogeneous'. They were characterised by nearly random distribution of cross-link points of the polymer network in the bulk of the copolymer. The specimens prepared in the absence of TEMPO were identified as 'microheterogeneous'. Their structure comprised a loose network built of highly cross-linked microgel aggregates. It was also found that, for the same concentration of cross-link points of the polymer network per unit volume, 'homogeneous' specimens had appreciably larger modulus of elasticity and greater swelling and, hence, longer fragments between the cross-link points of the polymer network (calculations by the Flory–Renner method) than 'microheterogeneous' specimens.

'Living' three-dimensional radical homopolymerisation and copolymerisation of diethyleneglycol dimethacrylate with different monomers and oligomers in the presence of *p*-xylylene-bis(*N*,*N*-diethyl dithiocarbamate), which undergoes reversible dissociation upon photoirradiation ($\lambda = 365$ nm), has been studied.[341–343] Temperature and frequency dependences of the modulus of elasticity and the loss factor tan δ, as well as the spectra of relaxation times and thermal characteristics of the homo- and copolymers were measured using dynamic mechanical analysis. Judging from the pattern of the distribution of relaxation times, it was concluded that microheterogeneity in the specimens increases as the density of the three-dimensional polymer network increases.

However, it is impossible to evaluate the extent to which the defectiveness of the specimens prepared by 'living' polymerisation decreases using the results obtained in these studies. An indirect confirmation of the efficiency of 'living'-chain polymerisation can be obtained from the results of ESR measurements of the concentrations of stabilised methacrylate radicals (chain carriers). According to ESR data, the concentration of chain carrier radicals in the specimens of highly cross-linked methacrylates is low, while specimens prepared by conventional radical polymerisation are characterised by high concentrations of methacrylate radicals. Moreover, these radicals do not recombine at room temperature over a long time (days and even months). Such a high stability of methacrylate radicals is due to inhomogeneous distribution of the cross-link points of the polymer network in the bulk of the material and to the presence of microscopic domains with extremely dense polymer network in which stabilisation ('freezing') of chain carrier radicals occurs.[336, 337, 344]

Three-dimensional radical copolymerisation of styrene with dimethacrylates in the presence of alkoxyamines was also studied.[143] It was established that the process under study was 'living'-chain polymerisation and specimens were synthesised for studying their microheterogeneities using the known procedure [336, 337] and for measuring their physicomechanical characteristics. It is believed that further comparison of these polymers with related materials obtained by conventional radical polymerisation will make it possible to solve the problem of the efficiency of three-dimensional 'living'-chain polymerisation of unsaturated oligomers.

VIII. Other agents for 'living' radical polymerisation

Most of the studies discussed in the previous Sections have been devoted to two (the main, in our opinion) investigation lines in the area of 'living' radical polymerisation. These are implementation of 'living'-chain polymerisation in the presence of (i) alkoxyamines (or stable nitroxyl radicals introduced into the polymerisation system in order to synthesise alkoxyamines *in situ*) and (ii) halide transition-metal complexes with organic ligands (or their components for the *in situ* synthesis). The choice of the investigation lines to be reviewed was dictated by two reasons, namely, the number of studies reported to date and, which is more important, the reliability of experimental results (all the data mentioned above were repeatedly reproduced by several independent research groups). This made it possible to give reliable formulations of the main kinetic features and the mechanism of the polymerisation processes under study. However, the list of studies carried out in these two investigation lines is far from being exhaustive. Below, we will outline some other lines of scientific exploration in the area of 'living' radical polymerisation.

Currently, studies of 'living' radical polymerisation have been carried out for a wide range of compounds capable of forming reversible adducts with labile bonds (*e.g.*, C–S,[345–348] C–Co,[10, 349] C–Al [350–352] and C–X (X = Cl, Br, I) [313, 353–356] bonds) upon reactions with growing polymer chains.

Compounds with the C–S and C–X bonds were called iniferters, since they simultaneously act as the chain *initiators*, *transfer* agents and *terminators*. Thermal and photo-iniferters are known; their studies began in the 1980s.[357]

In writing the review 'living' radical polymerisation in the presence of iniferters was deliberately excluded from consideration. The development of this investigation line is associated with the studies by Otsu (Japan) who seems to be the pioneer of this area. Our decision was due to the fact that a comprehensive review covering the problem was published in 1998.[358] All classes of iniferters were considered which were found to be the most efficient agents for 'living' polymerisation. The review concerns mono-, di-, tetra- and polyfunctional iniferters which reversibly dissociate being exposed to light (photo-active agents) or on heating, as well as monomeric, polymeric or microdisperse (microgel) iniferters used for the synthesis of monofunctional, telechelic or polyfunctional polymers, block and graft copolymers, branched (dendritic), star and cross-linked polymers. Thermally active iniferters were considered taking phenylazotriphenylmethane and tetraphenylethane derivatives as examples. The group of photo-active iniferters was represented by organosulfur compounds. Mention was made that compounds with the *N*,*N*-diethyldithiocarbamoyl groups were found to be the most efficient.[359]

The use of macrocyclic cobalt compounds (MCCC) appeared to be quite efficient for performing a 'living' radical polymerisation of acrylic monomers. This procedure was used for the synthesis of, *e.g.*, well-defined poly(methyl acrylates) with

$M_n \simeq 50\,000$ and $M_w/M_n = 1.1$.[349] It was found that the mechanism of the action of MCCC is essentially different from that of mixed-valence metal compounds (see Section VI) since cobalt is not involved in the redox reactions during reversible formation and decomposition of the labile adducts of MCCC with growing polymer chains.

Detailed study of porphyrin-based MCCC showed that the active intermediate R–CoPorph formed upon trapping by cobalt porphyrin complexes can decompose in different ways depending on the type of trapped radical and reaction conditions. Possible pathways of the decomposition are three catalytic reactions described in a monograph [10] (see also Refs 6–9 and 11–33).

$$R_n^{\cdot} + \text{CoPorph} \longrightarrow [R_n \ldots \text{CoPorph}] \longrightarrow \text{HCoPorph} + P_n(=), \quad (30)$$
$$\text{HCoPorph} + \text{Mm} \longrightarrow R_1^{\cdot} + \text{CoPorph};$$

$$R_n^{\cdot} + \text{CoPorph} \longrightarrow [R_n \ldots \text{CoPorph}] \longrightarrow \text{HCoPorph} + P_n(=), \quad (31)$$
$$\text{HCoPorph} + R_m^{\cdot} \longrightarrow P_m + \text{CoPorph};$$

$$R_n^{\cdot} + \text{CoPorph} \rightleftharpoons [R_n \ldots \text{CoPorph}] \overset{\text{Mm}}{\rightleftharpoons} [R_{n+1}^{\cdot} \ldots \text{CoPorph}]. \quad (32)$$

Here, CoPorph is a cobalt porphyrin (phthalocyanine, or glyoxime) complex; R_n, R_m and R_l are radicals with the degree of polymerisation equal to n, m and 1, respectively; Mm is monomer, $P_n(=)$ is macromolecule with the double bond in the end group, $[R_n\ldots\text{CoPorph}]$, $[R_{n+1}\ldots\text{CoPorph}]$ are reactive intermediates with the C–Co bond and [HCoPorph] is porphyrin cobalt hydride.

Reactions (30)–(32) were called catalytic chain transfer, catalytic inhibition and reversible inhibition reactions. The last-named reaction was observed in the polymerisation of acrylates; however, the process showed some but not all features of 'living' polymerisation, apparently because it was accompanied by side reactions (30) and (31). More recently,[349] suppression of side reactions by introducing axial ligands into CoPorph was reported by researchers from the United States.

Porphyrins and related ligands seem to be of limited use in the polymerisation of acrylates only. At least, our studies showed that effective control of chain propagation can be achieved only in this case.

Vigorous catalytic chain transfer reactions were observed in the case of polymerisation of MMA and styrene. Using this reaction, one can obtain oligomers up to a dimer (at CoPorph concentrations of $\sim 10^{-2}$ mol litre^{-1}). At first glance, introduction of axial ligands into CoPorph could promote transformation of this reaction into reversible inhibition. However, polymerisation of both MMA and styrene in the presence of CoPorph with axial ligands (quinoline, pyridine, *etc*.) revealed the catalytic inhibition reaction. The nature of the radical seems to play the key role in the reactions with CoPorph and related compounds, so that only the nature of the polymer radical dictates which of reactions (30)–(32) will actually occur.

In conclusion, mention may be made that studies concerned with purely technological problems, except for a few references in the Sections concerning emulsion, suspension and solution polymerisation, have not been covered in this review.

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