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## CHAIN-GROWTH CONTROL IN FREE RADICAL POLYMERIZATION<sup>1</sup>

DANIEL COLOMBANI<sup>2</sup>*Institut Charles Sadron (UPR 22 CNRS), 6 rue Boussingault, F-67083 Strasbourg Cedex, France*

**Abstract** – The present review relates generally to improved processes in which it is possible to control the growth steps of a radical polymerization to produce relatively monitored chain-length homopolymers and copolymers, including block, star and graft copolymers. The review, which contains more than 360 references to original works, has only to be taken as a snapshot of this rapidly developing area. Investigations summed up in this article are mainly those carried out by ‘polymer synthesis schools’ over the world over the past 20 years, with a detailed analysis of results obtained over the past three years. Indeed, works pertaining to the possibility of continuous radical polymerization to be achieved through the complexing and stabilization of free radicals, often called ‘living’ radical polymerizations, have witnessed an explosive growth in the past decade. These latter are chain-growth polymerizations, free from chain transfer, termination and other side reactions, and are promising methods for the synthesis of well-defined polymers. Despite the inherent instability of the growing macroradicals, ‘living’ radical polymerizations of vinyl monomers have recently been investigated based on the general principle of ‘radicophilic stabilization of the growing macroradical’. Three approaches have been followed in efforts to develop radical polymerization systems exhibiting living characters:

- The first uses physical methods to prevent radicals from contacting each other, thereby preventing their termination. The process is generally conducted in a heterogeneous medium.
- The second involves chain-growth control by chemical stabilization of the growing macroradical in homogeneous polymerization.
- The third approach, which involves no living process but exhibits some living characteristics, is based on the repeated reinitiation of polymer chains either by homolysis (thermo- or photolysis) of weak and/or reversible linkages that are built into the chains or by addition–fragmentation processes on macromonomers.

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<sup>2</sup>Tel: + (33) 3 88 41 40 74; fax: + (33) 3 88 41 40 99; e-mail: colomban@janus.u-strasbg.fr

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## ABBREVIATIONS

|                  |  |
|------------------|--|
| Ac               | acetyl   |
| AFCT             | addition-fragmentation chain transfer                    |
| AFM              | addition-fragmentation monomer                           |
| AFP              | addition-fragmentation polymerization                    |
| AIBN             | 2,2'-azobis( <i>isobutyronitrile</i> )                   |
| AN               | acrylonitrile  |
| AOS              | 1-oxo-4-methoxy-2,2,6,6-tetramethylpiperidinium salt     |
| ATRP             | atom transfer radical polymerization                     |
| BA               | <i>n</i> -butyl acrylate                                 |
| BDE              | bond dissociation energy (or enthalpy)                   |
| BMA              | <i>n</i> -butyl methacrylate                             |
| BPO              | dibenzoyl peroxide                                       |
| <i>t</i> -Bu     | <i>tertio</i> -butyl                                     |
| CSA              | camphorsulphonic acid                                    |
| CTA              | chain transfer agent                                     |
| DBPO             | di- <i>tertio</i> -butyl peroxide                        |
| DMF              | dimethyl formamide                                       |
| DMSO             | dimethyl sulphoxide                                      |
| DOXYL            | 4,4-dimethyl-3-oxazolidinyloxy                           |
| $DP_n$           | number-average degree of polymerization                  |
| Dpy              | 2,2'-dipyridyl   |
| $\Delta G^\circ$ | standard free energy                                     |
| $\Delta H^\circ$ | standard enthalpy  |
| $\Delta S^\circ$ | standard entropy   |
| eacac            | ethyl acetoacetate                                       |
| ESR              | electron spin resonance                                  |
| Et               | ethyl  |
| <i>I</i>         | polydispersity (= MWD)                                   |
| Ini              | initiator  |
| <i>k</i>         | rate constant  |
| M                | monomer  |
| MA               | methyl acrylate  |
| MAA              | methacrylic acid   |
| MCA              | methyl $\alpha$ -chloroacrylate                          |
| Me               | methyl   |
| MMA              | methyl methacrylate                                      |
| $M_n$            | number-average molar mass                                |
| $M_w$            | weight-average molar mass                                |
| MWD              | molecular weight (molar mass) distribution (= <i>I</i> ) |
| NMAm             | N-methyl acrylamide                                      |
| NMMAm            | N-methyl methacrylamide                                  |
| P $\cdot$        | polymer radical  |
| PAA              | poly(acrylic acid)                                       |
| PAN              | poly(acrylonitrile)                                      |
| Ph               | phenyl   |
| PMA              | phenyl methacrylate or poly(methacrylic acid)            |
| PMMA             | poly(methyl methacrylate)                                |
| PP               | poly(propylene)  |
| PROXYL           | 2,2,5,5-tetramethyl-1-pyrrolidinyloxy                    |
| PS               | poly(styrene)  |
| $R_p$            | rate of propagation (i.e. polymerization)                |
| $R_t$            | global rate of termination reactions                     |

|                  |   |
|------------------|---|
| SEC              | size-exclusion chromatography   |
| SFR              | stable free radical   |
| St               | styrene   |
| T <sup>*</sup>   | reversible terminator radical   |
| TEMPO            | 2,2,6,6-tetramethyl-1-piperidinyloxy  |
| TMP              | tetramesityl porphyrinato   |
| TMPEP            | 2,2,6,6-tetramethyl-1-(1-phenylethoxy)piperidine  |
| VA               | vinyl acetate   |
| [ ] <sub>0</sub> | refers to initial molar concentrations (at the onset of the reaction)                                     |
| [ ]              | refers to molar concentrations of reagents or active species, whenever the reaction medium is homogeneous |

## 1. INTRODUCTION

Polymers are widely used in all walks of human life and play a vital role in shaping modern man's activities to be as sophisticated and comfortable as they are today. The advances in science and technology made in recent decades owe much to the development of polymer science. Thus, the time when a polymer was an ill-defined and often insoluble material with limited structural information has passed. The technological challenges for the near future in all areas of science and technology, ranging from domestic appliances, microelectronics and automobiles to advanced aeroplanes, biomedical science and the space shuttle, forecast a parallel development in polymer technology to cope with the exponential growth in these fields. Indeed, polymers do play a crucial role in one phase or other of their development.

The synthesis and design of new polymeric materials to achieve specific physical properties and specialized applications, and the attempt to find interesting applications involving advanced structures and architectures, are in continuous and parallel development in the era of polymer science. However, it is essential now that, after the initial period of discovery and investigation of fundamental polymerization principles, new or advanced technologies are pursued by an intensive search to ensure that the materials reach their fullest potential. As the performance requirements of polymeric materials become more demanding, the ability to control architecture, i.e. the physical properties of polymers through the polymerization process, becomes increasingly important. A thorough understanding of numerous structure-property relationships has helped us to design polymers that are tailored for specific applications. Depending on particular needs, polymeric materials have to satisfy certain requirements in terms of their processability, durability, resistance to environment, cost effectiveness, mechanical performance, and so on. New applications and modern technologies have required the preparation of tailor-made macromolecules with precisely controlled dimensions, polydispersities, microstructures (sequences, tacticities) and terminal functionalities. Novel phenomena and properties can be observed for well-defined polymers and copolymers. These include mechanical, electrical, optical, surface and other properties.

Basically, a polymerization process is based on a repetitive reaction in which a monomer is converted into a polymer segment. To achieve such a goal, polymer chemists have a variety of synthetic processes to choose from and can often fine-tune reactions with very high selectivity when planning a particular synthesis. However, each method has its strengths and its weaknesses, and often requires high-purity reagents and special conditions. Indeed, the need for high-purity monomers and solvents, reactive initiators and anhydrous conditions

has dramatically limited the industrial application of many techniques based on ionic and group-transfer polymerization processes.

Organic radicals play an important role in polymer syntheses. Free radical polymerization is very important in the field of industrial polymer synthesis and is the preferred route to commercial polymers. Industrially, more than 50% of all plastics produced in the world are synthesized through radical polymerization processes because this method has a number of merits for vinyl polymer syntheses. Indeed, free radical polymerization is very easy to perform and is adaptable to many types of monomer under mild conditions using convenient equipment, and often shows substantial reproducibility. In most cases, monomer purification is not required to a high extent and initiator residues need not be removed from the polymer because they have little or no effect on polymer properties. Moreover, free radical polymerization processes can be readily and economically performed in the bulk and in suspension—distinct advantages from an industrial point of view.<sup>1,2</sup> However, the preparation of some well-defined polymers from unsaturated monomers has been limited by the technology available for conventional free radical polymerizations. Indeed, such processes inherently do not allow for precise control over molar masses and tend to give broad polydispersity species because not all the polymeric chains are initiated at the same time and because of a lack of control over chain-breaking reactions; i.e., both termination and the transfer steps greatly limit the ability to control polymer architecture. Thus, such polymers tend to contain significant amounts of high and very low molar mass chains, which can give unattractive properties to the polymer composition.

Moreover, the synthesis of block copolymers is practically impossible via the sequential addition of monomers in a conventional free radical polymerization. This leads to a mixture of homopolymers since there are often no living radicals at the end of each monomer addition step and new radicals need to be produced to start the new monomer polymerizing. Therefore, the development of techniques to control the largest negative feature of free radical processes, i.e. to breathe 'livingness' into radical polymerizations, has become the focus of recent free radical polymerization research.

Anionic, cationic and step-growth polymerizations are well suited for the controlled growth of polymer chains since these reactions proceed one step at a time and can be stopped after a few steps if desired. Therefore, it would be desirable if the control achieved by step-growth polymerization techniques could also be achieved in free radical polymerizations, but without the disadvantages of stringent reaction conditions. Typically, a radical is essentially neutral. Hence, it is generally less sensitive to the nature of the reaction media when compared to ionic species which are much more sensitive to the media, e.g. solvent and counter ions. Therefore, the possibilities for the control of kinetic and thermodynamic stabilities and orientations of radicals are limited. The reactivity control of monomers and their radicals on the one hand, and an accurate understanding of the contribution of side reactions in polymerizations, coupled with chemoselectivities, regioselectivities and stereoselectivities, on the other hand, are the important factors in designing well-defined polymer architectures with controlled molar mass, molar mass distribution, monomer sequences, chain end groups, branching, and so on.

The construction of tailor-made polymers, especially through a living radical mechanism, may be achieved by the control of radical stabilization, i.e. chemically or physically stabilized radicals. A variety of methods has been developed to control the reactivity of macroradicals. There are primarily two ways of regulating radical stabilization in a polymerization, i.e.

chemical and physical regulation. Persistent macroradicals can bring about the *quasi-living radical polymerization* of standard vinyl monomers either through a covalently bonded propagating species (**chemical regulation**, proceeding by the capping of the propagating end by a persistent radical through a thermo- or photoreversible covalent bond); or stabilization can be achieved by **physical regulation** via complex assemblies or 'supramolecules'. In such a state, polymerization generally becomes slow because of a restriction in the mobility of the reactants, but can become more rapid when the system is arranged in a suitable orientation.

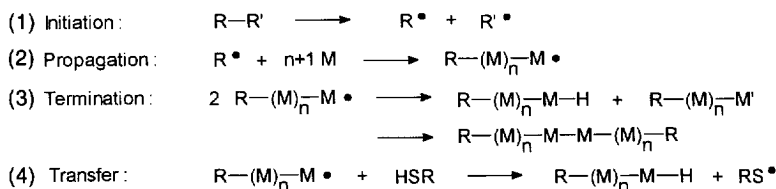
## 2. GENERALITY

### 2.1. Basics of radical polymerization

Radical polymerization is probably the most important commercial process leading to high molar mass polymers. This is due to the large variety of monomers which can be polymerized and copolymerized radically and to the relatively simple experimental conditions which require the absence of oxygen but which can be carried out in the presence of water, e.g., as in suspension or emulsion polymerizations, and within a convenient temperature range, typically 0–100°C.

The four processes of importance in vinyl polymerization by free radical mechanisms are: (1) initiation, the creation of the radical; (2) growth, the successive additions of monomer to the radical; (3) termination, the mutual reaction of two radicals to produce inactive polymer; and (4) transfer, the termination of a polymer chain and the subsequent initiation of a new polymer chain (for example, by abstraction of a hydrogen atom by a radical from some other molecule or by addition to a CTA to produce a polymer molecule and a new radical) (Scheme 1).

Polymerization systems that involve propagating free radicals are likely to involve very short-lived intermediates. Free radical termination reactions are very fast, being diffusion controlled even for the smallest of radicals.<sup>3</sup> They exhibit a pronounced inclination to recombine or disproportionate, in contrast to cationic or anionic chain ends in ionic polymerizations which do not react with one another because of electrostatic repulsion. Indeed, unlike anions or cations, radicals recombine and/or disproportionate with rate constants approaching the diffusion-controlled limit; i.e.,  $k_t \approx 10^8 \pm 1 \text{ (M s)}^{-1}$ , which is much higher than the corresponding propagating rate constant,  $k_p \approx 10^3 \pm 1 \text{ (M s)}^{-1}$ . Moreover, the initiation is usually incomplete due to slow decomposition of classic radical initiators; i.e.,  $k_d \approx 10^{-4} \sim 10^{-6} \text{ s}^{-1}$ . These are the kinetic reasons why classic radical polymerization processes yield ill-defined polymers with uncontrolled molar mass, broad molar mass distribution and



Scheme 1.

uncontrolled structures. Moreover, the properties of the polymer produced in the polymerization reaction can be adversely affected by a high incidence of initiator or chain transfer fragments residing on the polymer chains. Such behaviour presents a severe challenge to chemists who would hope to control the growth of free radical polymerization systems.

The synthesis of polymers having relatively low molar masses (i.e. oligomers) has recently become of increasing interest since such polymers have been found to be useful in a variety of products such as high solids or solvent-free coatings, in adhesives, as plasticizers in polymeric compositions, and as reactive intermediates for the production of a wide variety of other materials such as surface-active agents. While various polyesters, polyethers, polyamides and polyurethanes having molar masses in the range 500 to 2500 can be conveniently prepared by step-growth polymerizations, it has not been possible to produce similarly sized polymers satisfactorily by free radical polymerizations. The synthesis of such polymers with controlled structures requires that these reactions proceed with high chemoselectivity, regioselectivity and stereoselectivity. For example, in order to obtain a polymer with a polymerization degree  $DP_n \approx 100$ , the chemoselectivity of the chain-building reaction must be at least 99%, whereas chemoselectivity should exceed 99.99% for the preparation of a higher polymer with  $DP_n \approx 10^4$ .<sup>4</sup> The most important chain-breaking reaction in radical systems is not transfer but rather termination between two growing radicals.<sup>4</sup> Normally, all radical processes are proceeding at once and the molar mass of the resulting polymer is determined statistically by the competition of process (2) with processes (3) and (4) (see Scheme 1). The resulting molar mass distribution is generally quite broad. Theoretical calculations suggest that the lowest polydispersity that could be achieved by a free radical polymerization process is at least 1.5.<sup>5</sup> In most cases, polydispersities close to 2–3 are obtained for poly(vinyl monomers) synthesized on a small or an industrial scale. For radical synthesis of copolymers, the polydispersities are generally much higher. Such behaviour precludes the preparation of polymers with complex architectures. The primary reasons for this difficulty include the high reactivity or low stability of free radicals and their facile coupling and/or disproportionation reactions.

Because the propagating radical in a radical polymerization is very short lived in homogeneous systems, it is impossible to obtain long-lived (living) propagating radicals except for the case in which mobility decreases markedly. Propagating radicals are actually detected in polymerization systems in precipitation, microgel, microsphere, highly viscous medium, and frozen state.

The traditional methods of producing block copolymers, whether by living polymerization (by ionic, coordination or group-transfer mechanisms) or by the linking of end-functional polymers, suffer from many disadvantages. They have limitations both for economic reasons (due to stringent requirements on reaction conditions and monomer purity) and because of the limited range of monomers that are compatible with this technique.<sup>6</sup> The end-linking method suffers from problems associated with producing pure end-functional polymers and difficulties associated with conducting reactions between polymers. These problems have brought about a marked growth in interest in methods for controlling polymer architecture by free radical polymerization. Recent approaches were developed that afford the polymer chemist many of the synthetic advantages that living polymerization systems provide. These include the synthesis of polymers with narrow molar-mass distributions, block copolymers and polymers with star or radical-block architectures. Thus, various forms of 'living' radical polymerization have been reported.<sup>7–12</sup>



Scheme 2.

Synthesis of high molar mass polymers requires slow initiation to produce a low momentary concentration of growing radicals ( $[P^\bullet] \approx 10^{-7} \text{ mol l}^{-1}$ ) which terminate in a bimolecular process. The ratio of the rate of propagation to that of termination ('livingness') decreases with  $[P^\bullet]$  because propagation is a first-order process but termination is a second-order process with respect to  $[P^\bullet]$ . The proportion of chains marked by termination increases with chain length. Therefore, well-defined polymers from radical polymerization may be formed only if chains are relatively short and the concentration of free radicals is low. These two requirements are in apparent contradiction but can be accommodated via reversible deactivation of growing free radicals in a way similar to the deactivation of growing carbocations.

Up to now, the precision with which polymer architecture can be controlled by living radical polymerization is not as high as that obtainable with living ion polymerizations. Moreover, living radical polymerizations involving tertiary radical propagating species (e.g., those based on methacrylate ester monomers) are complicated by side reactions that limit conversion and block purity. Disproportionation of the propagating species with  $T^\bullet$  produces a macromonomer and the hydride (TH) of the stable radical (see Scheme 2).<sup>13,14</sup> The species TH may then terminate additional chains by hydrogen atom transfer.

A further disadvantage which limits the commercial application of the methodology is the requirement for an equimolar amount of the (often expensive) reagent  $T^\bullet$  or its precursor. Nevertheless, the greater versatility of free radical polymerizations and copolymerizations compared to ionic polymerizations somewhat compensates for this limitation. For example, free radical polymerization can be conducted over a wide temperature range, using a variety of solvents, and it enables a wide range of monomers to be (co)polymerized.

The classical reaction scheme of living polymerizations comprises initiation and propagation, with no spontaneous termination or transfer reactions.<sup>15</sup> A polymerization process is said to be fully living when each polymer unit contains an active site where chain growth occurs indefinitely without termination or chain transfer reactions.<sup>5,8,16</sup> The number of active sites in a batch is constant and equal to the number of initiator molecules introduced at the onset of the reaction. As a consequence, the number-average degree of polymerization is determined by the molar ratio of monomer converted to initiator that is used. Under such conditions, the molar mass distribution within a prepared sample is expected to be rather narrow (as in a Poisson distribution).<sup>17</sup> Once the polymerization reaction is completed, the sites remain living, granting opportunities to functionalize the chain ends upon induced deactivation or to initiate the polymerization of a second monomer to yield block copolymer.

Szwarc et al.<sup>18</sup> were the first to apply the living processes concept to anionic polymerization. Up to now, this polymerization technique is one of the most used to access precisely defined polymer architectures.<sup>19</sup> In carbocationic polymerization, living polymerization conditions were not so easily attained and living polymers were not generally expected to be possible ten years ago. The control of chain growth has long been considered very difficult due to the instability of the highly reactive carbocationic growing species (short lifetimes) and the well-known importance of transfer reactions.<sup>20-22</sup> In recent years, very extensive



research carried out in the field of carbocationic polymerization has led to the synthesis of well-defined (co)polymers by the cationic process,<sup>20,23,24</sup> and many articles asserting the existence of living conditions in various polymerizing systems have been published. In these living cationic processes, the unstable growing carbocations were 'stabilized' via the reversible formation of the corresponding covalent or dormant species that rapidly exchange with their ionic counterparts.<sup>25</sup>

The most general feature of these systems is the linear growth of the number-average molar mass with polymer yield, with sometimes a further growth on new monomer addition. But since the distribution of molar masses is often wide ( $M_w/M_n \geq 2$ ) and the molar masses low, there has been no definite proof of the absence of termination and transfer, and it may be shown that the results might often be compatible with significant termination and with transfer constants sometimes as high as  $k_t M/k_p = 10^{-3}$ . However, it seems that in many of the systems studied and as assumed by many authors, it is possible to have a reversible termination, growth being possible on most polymer end-groups. Living radical polymerization has long been expected to be even less possible in view of the strong tendency for radicals to react together to give rapid termination reactions. However, some attempts at block copolymerization have been successful, with polymeric radicals trapped in crosslinked or other very viscous media. But the most interesting idea seems to be that of using systems with reversible termination.

In an effort to combine the attributes of ionic living polymerization systems with the economic advantages of free radical polymerization, new processes were developed to 'breathe life' (as Georges et al. proposed<sup>11</sup>) into free radical polymerization processes. Thus, by analogy with living cationic polymerization, one could expect that living-type radical polymerization would also be realized if the growing radical were reversibly stabilized by a covalent species, such as one with a C–O bond (with nitroxide) or with a C–halogen bond (systems with halocompounds). Moreover, drawing an analogy from anionic polymerization processes, one can assume that reaction conditions for taming 'living' radical polymerization could be met if all the chains were initiated at the same time and premature termination and chain transfer processes were prevented.

The living character in radical polymerization was achieved by using a combination of one radical that only initiates polymerization and a second that only reversibly binds with the growing polymer radical. Thus, if a non-symmetrical initiator R–R' is split into two radicals R\* and R', and if the monomer is initiated only by R\*, the growing polymer chains R–M<sub>n</sub> may react either with themselves, leading to termination, or with R', giving R–M<sub>n</sub>–R', which may also be capable of initiation and further growth. If the cross-termination giving R–M<sub>n</sub>–R' is favoured compared to the symmetrical ones, a system more or less similar to a living one might be obtained.

Carbon-, sulphur- and oxygen-centred radicals that function as reversible radical capping agents were utilized in illustrating the potential of this strategy, and polymer products with relatively small polydispersities have recently been obtained by using stable aminyloxyl-type radicals as radical capping groups. Detailed knowledge of organometallic reactivity patterns and mechanisms has also resulted in the design of well-characterized living organometallic systems that initiate and propagate the polymerization of alkenes<sup>26,27</sup> and alternating copolymerization of alkenes with CO.<sup>28</sup> Unfortunately, up to now, there were only a few examples of initiators and monomers that seemed to behave in this way (particularly with styrene, MMA and acrylates), because secondary reactions occur and no perfect system has

yet been described. Achieving near ideal properties for a living radical polymerization has proven to be elusive.<sup>16</sup> Well-defined, highly versatile living radical polymerizations are still beyond our reach, and no general principles have been established to achieve living or controlled radical polymerizations.

The investigation of the field of controlled radical polymerization, that is, assemblies of polymer molecules formed by radical polymerization which may grow without chain-breaking reactions and may react subsequently with other monomers and various reagents through their end-groups, has led to great progress in the knowledge of the mechanism of radical polymerization and to the synthesis of a large variety of well-defined block copolymers, graft copolymers and polymers with functionalized end-groups. Systems making polymerization possible at temperatures higher than those used for many anionic and most cationic polymerizations would be particularly interesting.

At present, controlling radical polymerization (chain-growth control and chain-length control) is a major problem in the field of polymer science. In this review, various approaches which enhance the control of growth of radical polymerizations are described. These methods provide routes to polymers with low polydispersities and, in some instances, to block copolymers. Chain-length control in free radical polymerization was recently reviewed by Colombani and Chaumont with respect to addition-fragmentation processes on chain transfer agents.<sup>29,30</sup>

The various definitions of living polymers, the problems of detection of possible termination and transfer reactions, and the influence of the relative rates of initiation and propagation are discussed in the first part of the review. Questions concerning the radical or pseudo-radical nature of various active species are also discussed briefly. The general characteristics of living polymerizations are analysed, and a proposition is made on this basis for the classification of existing living polymerizations. The following discussion therefore refers to these systems as living, quasi-living, pseudo-living or controlled systems.

## 2.2. Note on terminology

### 2.2.1. *Stable, persistent and transient radicals*

The stability of a system is both a kinetic and a thermodynamic notion. From a thermodynamic point of view, a system will be called *stable* if the variation in the standard free energy of the system ( $\Delta G^\circ$ ), dealing with any evolution in the system, is positive:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \gg 0$$

The apparent stability of a system can also be due to a very slow reaction rate, and it is necessary to separate the stability of a system into two contributions: kinetic and thermodynamic. Thus, a radical is termed *persistent* if its lifetime is significantly higher than those for a transient radical such as methyl radical (typically  $<10^{-3}$  s) under the same conditions. A radical is called *stable* if it is particularly persistent, not reactive with air and not moisture sensitive, and is stockable without any specific conditions. The persistence of a radical depends more closely on kinetic factors (especially steric effects) than on electronic ones. It is a concept relevant to kinetics whereas stabilization is more of a thermodynamic notion. The latter term is an intrinsic property of the radical and depends on electronic factors. Therefore, for example, captodative substituted radicals may belong to a class of radicals

with a kinetic persistence between that of transient radicals, such as 1-methylcarbonyl-1-methyl radical generated from the decomposition of the corresponding azo esters, and that of persistent radicals such as some aryl radicals.

### 2.2.2. Termination reactions

The problem of termination reactions and of the interaction between polymer radicals remains one of the most complicated questions in the kinetics of radical polymerization.<sup>31</sup> It is customary to assume that radical polymerization is characterized by rather intensive chain termination reactions between two radicals, most often polymer radicals, that decay via either recombination or disproportionation<sup>32</sup> and display a short time for the propagation of one chain as compared to the time of polymerization. When a homopolar bond is formed by recombination, the single electrons of the free radical sites of two chains are pairing. When a disproportionation occurs, whereby a hydrogen atom is transferred from one chain to the other, two molecules of 'dead' polymer are formed, one of them bearing a double bond at the chain end. Nearly zero activation energies (values between 1.3 and 1.7 kJ mol<sup>-1</sup>) are reported for termination reactions proceeding through recombination. Disproportionation requires an activation energy of about 17 kJ mol<sup>-1</sup> (the activation energy for termination reactions in the bulk polymerization of MMA was reported to be up to 12.6 kJ mol<sup>-1</sup> because it proceeds via recombination and disproportionation<sup>33</sup>). The ratio between recombination and disproportionation reactions therefore increases with changing temperature. In both cases, the reaction involves mutual destruction of radicals, and kinetically these two processes cannot be distinguished. But their consequences on the molar mass distribution and polydispersity of the polymers formed are different.<sup>34</sup>

The termination process is customarily regarded as a diffusion-controlled step.<sup>35,36</sup> Its rate constant is inversely proportional to the viscosity of the reaction medium. This, among other considerations, explains the decreasing termination rate and the increasing polymerization rate in the course of the process, i.e., with the accumulation of the polymer in solution and the increasing diffusive hindrances which prevent the macroradicals from approaching and reacting with one another. In this case, according to numerous theories in which an attempt is made to describe quantitatively the termination reaction in radical polymerization, the recombination rate constant of radicals must depend on their degree of polymerization and must decrease with the growing macroradical length. The dependence of termination rate on macroradical chain length results in a broadening of the polymer molar mass distribution.<sup>37</sup> Thus, solvent viscosity will retard termination of propagating radicals with longer chains more than those with shorter chains. The formation of complexes between propagating radicals and solvent or other additives affects the rate of termination of polymerization, though generally less significantly than the rate of the propagation reaction. Indeed, the solvent has a direct effect on the conformation of a polymer coil of the propagating radical. However, the effect of a poor solvent on the termination of propagating radicals is observable only if the degree of polymerization is higher than 10<sup>3</sup>.<sup>38,39</sup>

When termination involves only recombination, the polymerization process gives a polymer with initiator fragments at both chain ends. However, in ordinary radical polymerizations, termination by disproportionation and chain transfer reactions both occur, and it is impossible to control the ratio of recombination and disproportionation which is determined by the structure of the polymer radicals (i.e., structure of monomers) and temperature. The

rate of termination increases with the second power of the concentration of radicals, but the rate of propagation increases with the first power. Thus, the contribution of termination reaction and the proportion of terminated chains increases with the concentration of free radicals:

$$R_t/R_p = k_t[P']^2/k_p[P'][M]$$

The control of macromolecular structure requires low  $R_t/R_p$  ratios and low  $[P']$ . Thus, a first approximation is that termination as a chain-breaking process cannot be completely avoided in radical polymerization; i.e., a truly living radical polymerization cannot be realized.

In this review, we will examine certain radical polymerization processes in which chain termination reactions are considerably inhibited or almost excluded. For example, a reversible termination reaction involving end-capping of macroradicals is not considered to be a classical termination process because it only temporarily deactivates growing chains. Thus, the determination of the average degree of polymerization has to include not only the active but also the dormant, temporarily deactivated species as well:

$$DP_n \approx \Delta[M]/([P'] + [P-T *])$$

(where \* symbolizes either a radical or not). The above equation is accurate provided that exchange between both species is fast and the contributions of termination and transfer are small.

### 2.2.3. Transfer reactions

The transfer reaction in free radical polymerization is generally a transfer of the radical centre from the propagating radical to another molecule, i.e. initiator, monomer, polymer, solvent or other compound that is often added to the reaction medium as a regulator of the relative molar mass of the polymer. However, the termination of the growth of the polymer molecule by a transfer reaction is not automatically the end of the kinetic chain because the new radical formed by transfer may start the growth of a new polymer chain.<sup>40</sup>

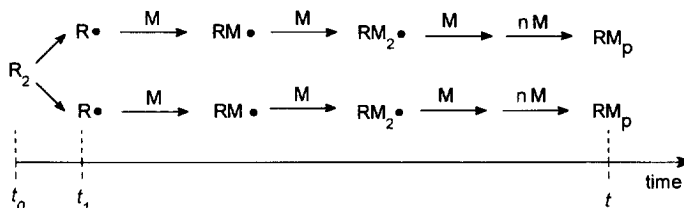
The transfer reaction is quantitatively determined by a transfer constant, denoted  $C_{tr}$  and defined as the ratio between the transfer rate constant,  $k_{tr}$ , and the propagation rate constant,  $k_p$ , of the growing macroradicals. This transfer constant is defined by a simplified relationship as derived by Mayo<sup>41</sup>:

$$1/DP_n = 1/DP_{n0} + C_{tr}[CTA]/[M]$$

where  $DP_n$  and  $DP_{n0}$  are number-average degrees of polymerization in the presence and absence of the chain transfer agent (CTA), and  $[CTA]$  and  $[M]$  are concentrations of the chain transfer agent and monomer, respectively. The relation was derived on the assumption that  $C_{tr}$ , i.e. the ratio of the rates of transfer to CTA and propagation reactions, results from the mutual ratio of the reactivity of solvent and monomer with respect to the propagating radical.

### 2.2.4. Classification of 'living' systems

The rapid progress on chain-growth control in the field of free radical polymer science<sup>3</sup> has led to the reconsideration of many general concepts of living polymerization. These involve questions over the definition and criteria for living polymerizations, and mechanistic and

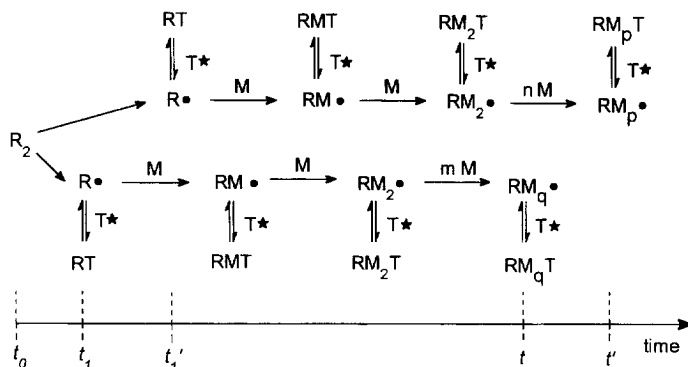


kinetic uncertainties in novel living polymerization systems. Due mainly to individual interpretations or in order to distinguish new living polymerizations from more 'classical' living anionic polymerization processes, numerous terms such as quasi-, pseudo-, truly or apparently living system, livingness enhancement or enhanced livingness system and controlled polymerization have been used in the literature to describe these growth-controlled polymerization systems. This diversity in terminology might indicate that fundamentally different living polymerizations exist, and in such a case it would seem difficult to provide a general description and classification for these polymerization systems.

2.2.4.1. *Various types of living polymerization* — The field of living polymerizations has undergone a rapid development during the last few years. New polymerization techniques have been developed, based on the discovery of new initiating systems for existing growth-controlled polymerizations (see e.g. ref.<sup>42</sup>) and on the development of suitable polymerization conditions for suppressing or inhibiting side reactions, i.e. termination and transfer reactions. These include: group transfer polymerization (GTP),<sup>43–47</sup> carbo-cationic polymerization,<sup>48,49</sup> ring-opening cationic polymerization,<sup>50–52</sup> ring-opening metathesis polymerization (ROMP),<sup>53–55</sup> immortal polymerization,<sup>56,57</sup> and Ziegler–Natta polymerization.<sup>58,59</sup> The majority of these living polymerization systems involve quasi-living equilibria between active (propagating) and dormant (non-propagating) polymer chains.

2.2.4.2. *Living and quasi-living polymerizations* — Only two steps, initiation and propagation, are mechanistically involved in an ideal living polymerization. Initiation is followed by propagation as long as monomer is present in the polymerization system, and addition of a new charge of monomer (or a second monomer) leads to further propagation. There are no chain-breaking reactions, such as termination or chain transfer, and after consumption of the initiating species only propagation occurs. In other words, all the chains formed by initiation are in an active form; i.e., all the growing chain ends are permanent 'living' chain carriers for propagation during polymerization at any time (Scheme 3).

A wide range of opportunities for obtaining polymers with well-defined structures and molar masses, and in many cases narrow molar mass distributions, may be offered by the use of ideal living polymerization processes. However, by analysing the existing living polymerization systems which meet the required experimental criteria (see Section 2.4), or at least the majority of them, it appears that ideal living polymerization is a very rare process. Anionic polymerization of olefins, such as styrene in polar solvents, belongs to this category (see e.g.



ref.<sup>60</sup>). In the majority of reported 'living' polymerizations, only a portion of chain ends are active and these are in equilibria with inactive 'dormant' chains. These systems, for which not all chains in the system are active at one time due to slow initiation or slow exchange between dormant and active species, are named '*quasi-living polymerization systems*' to distinguish them from '*ideal living*' systems (which exhibit fast initiation and exchange reactions).

The term '*quasi-living radical polymerization*', which implies partial regulation of the molar mass and/or its distribution throughout the polymerization, is often used to distinguish it from the well-known '*true (or ideal) living radical polymerization*', which implies complete regulation of both  $M_n$  and  $M_w/M_n$ , i.e. increasing molar mass with increasing conversion with monodispersity of the polymer throughout the polymerization. However, since the system is 'living' in terms of the rigorous definition given by Quirk and Lee,<sup>61</sup> a more accurate terminology is '*living polymerization with reversible deactivation*'. If an equilibrium exists between propagating and non-propagating species in the absence of permanent chain transfer and termination, systems exhibit similar kinetic behaviour to ideal living polymerizations, i.e., linear number-average molar mass ( $M_n$ ) vs monomer conversion plots and linear  $[P^*]$  vs  $t$  relationships, respectively. A general model for polymerizations with an active  $\leftrightarrow$  dormant equilibrium is shown in Scheme 4.

Most of the differences between ideal and quasi-living systems arise from the possibility of chain-breaking processes in the system, the rate of initiation (fast or slow compared to the propagation rate) and the efficiency of exchange reactions between active and dormant species. Thus, ideal living polymerization may be considered as a special subclass of quasi-living polymerization.<sup>42,62</sup> When the equilibrium constant between active and dormant species is equal to zero, the kinetics of quasi-living polymerization is reduced to that of ideal living polymerization.

Due to the ambiguous meaning of the word 'quasi' in some languages, there is opposition to the use of the term 'quasi-living' for living polymerizations with active  $\leftrightarrow$  dormant equilibria between species. Quirk and Lee<sup>61</sup> have suggested the terms '*living polymerization with reversible termination*' or '*living polymerization with equilibrium between propagating single polymer chains and non-propagating aggregates*', etc. On the other hand, a trend in all areas of science is the use of simple terms or expressions for describing and referring to complex phenomena. Since the 'quasi-living' term has been used during the last decade for

defining living carbocationic polymerizations with reversible termination (see e.g. refs.<sup>21,63</sup>), it can also be selected to denote living polymerizations in which not all the chains are propagating but exhibit dynamic equilibrium with the active propagating macroradicals.

2.2.4.3. *Controlled and pseudo-living polymerizations* — Well-defined homopolymers and block copolymers can be prepared not only in living systems but also in systems with chain-breaking reactions. On the other hand, polymers with uncontrolled molar masses and high polydispersities can be formed even if chain-breaking reactions are absent but when initiation and exchange between sites of different reactivities are slow in comparison with propagation. Matyjaszewski<sup>4</sup> proposed recently to distinguished controlled and living polymerization on the basis of the possibility of controlling the design of the polymers. Controlled polymerization is a synthetic method leading to well-defined polymers and copolymers. It can be based on either step-growth or chain-growth mechanisms. Chain-breaking reactions are possible but initiation and exchange have to be fast. Often molar masses should be limited, accounting for the contribution of chain-breaking reactions. On the other hand, living polymerizations are chain-growth processes without chain-breaking reactions, according to the original definition.<sup>60</sup> Well-defined polymers are obtained only if initiation and exchange reactions are fast.

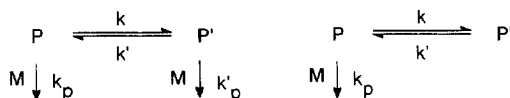
Pseudo-living polymerizations are controlled systems which involve no living processes (absence of stabilized radicals) but which exhibit some 'living characteristics', i.e. narrow polydispersities, molar masses increasing linearly with conversion, etc. Classical termination and transfer reactions are generally operative in such polymerizations, but repeated reinitiation of inactive polymer chains by homolysis of initiators in the backbone of the chain, or by addition-fragmentation chain transfer on macromonomers, involve a continuous growth of the polymer chain length. Examples of such radical polymerization processes are reported in Section 5.

### 2.3. Concept of reversible deactivation in radical polymerization

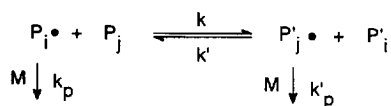
In ionic reactions, active species with various reactivities coexist (free ions, ion pairs, aggregates, covalent species, etc.). If they propagate simultaneously but with different rate constants, then polymodal molar mass distributions may result. The polydispersity in these cases will depend on the rate of exchange between these species. In the case of exchange being faster than propagation, very narrow distributions are expected.

Thirty years ago, it was shown<sup>64</sup> that an equilibrium between species of different reactivities can lead theoretically to a considerable broadening of the MWD if the rate of interconversion is slow or comparable to the rate of propagation (Scheme 5).

The concept of living polymerization allows the presence of species with various reactivities and, in the extreme case, even entirely dormant (inactive) species. A broadening of the MWD due to slow exchange was observed for several living processes. Müller et al.<sup>65</sup> showed



Scheme 5.

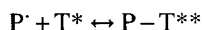


Scheme 6.

the formation of inactive aggregates in anionic polymerization, and mentioned the existence of non-activated silyl ketene acetals in group transfer polymerization.<sup>66</sup> The existence of non-ionic species in living carbocationic polymerization was also reported.<sup>67,68</sup> When one of the species involved in the above-mentioned equilibrium is stable enough not to involve a propagation step with monomer, the two-state system can be called a *reversible deactivation system*, based on the reversible formation of inactive or 'dormant' species ( $k'_p = 0$ , Scheme 5). Besides this indirect mechanism of activity exchange, i.e. by activation/deactivation, a direct exchange called '*degenerative transfer*' between active and dormant chain ends is also feasible (cf. Scheme 6, where the indices  $i$  and  $j$  denote different chain lengths and  $i = 0$  or  $j = 0$  denote the initiator) for living processes exhibiting reversible deactivation.<sup>69,70</sup> The concept of reversible deactivation was applied recently to radical polymerization, and applications of various systems of this type have been published.

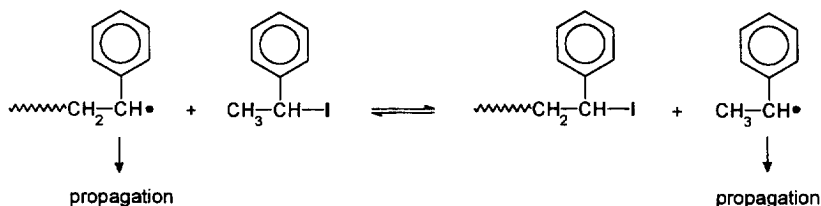
### 2.3.1. Reversible homolytic cleavage of non-radical or persistent radical species

Most of the reported radical polymerization systems are based on the reversible termination of growing radicals with various terminators,  $T^*$  (where  $*$  symbolizes either a radical or not). The reversibility involves the coexistence of a large number of deactivated chains, denoted  $P-T^{**}$  (also called inactive or dormant) and at the same time a low, stationary concentration of growing macroradicals,  $P^*$ . There are two ways of deactivation of growing radicals  $P^*$ , depending on the terminator  $T^*$ , which can bear an even or an odd number of radicals. The first one is with a scavenging radical  $T^*$ :  $T^*$  reacts with  $P^*$  but not with monomer ( $M$ ), and does not initiate polymerization (addition to  $M$ ). There is formation of non-radical species  $P-T$ . The second approach is based on the use of a covalent scavenger  $T$  which provides reversibly persistent ('dormant') radicals  $P-T^*$ .



Non-radical and persistent radical species can reversibly and homolytically cleave to release one or two reactive organic radicals ( $P^*$  and terminator  $T^*$ ). In order to ensure a controlled radical polymerization, the equilibrium should be strongly shifted towards the dormant polymer chain. The release of organic radical  $P^*$  may react with monomer and return to the dormant state  $P-T^{**}$  after several propagation steps. The repetition of this process will provide continuous growth of all chains and well-defined polymers. In the ideal case, the concept of reversible cleavage of covalent or persistent radical species results in the continuous growth of all chains but at a rate much slower than that of a classical radical polymerization, since the fraction of active species is much smaller than the total number of polymer chains. Polymers with low polydispersities can be produced if exchange of activity between the active and dormant chain ends is fast enough, in order for all the chains to grow. To control molar masses in a sufficient way, the initiation rate should also be comparable to





Scheme 7.

that of propagation and, therefore, the structure of the initiator should be similar to that of the dormant species  $P-T^*$ .

From the point of view of the synthesis of well-defined polymers, block copolymers and end-functional polymers, any chain-breaking is disallowed. Nevertheless, in the reversible deactivation concept, the recombination of  $[P^*]$  with  $[T^*]$  is not considered to be chain-breaking because it is reversible. The stationary concentration of growing radicals is nearly constant because, although some chains are terminated, the radicals are easily reformed from the large pool of dormant species. On the other hand, irreversible termination produces entirely inactive chains by either coupling or disproportionation of growing radicals  $P^*$ . However, termination and transfer lead to different deviations from the behaviour of ideal systems (either lower rates or lower degrees of polymerization). Thus, whatever the method involved, the synthesis of well-defined polymers by radical polymerization requires a low stationary concentration of growing radicals. The kinetic requirements for each case are identical to each other. The first approach is best realized with nitroxyl radicals and the second with organometallic compounds. However, in the latter case, some of the reported systems display a high affinity toward hydrogen and may lead to undesired and uncontrolled transfer side reactions.

### 2.3.2. Degenerative transfer

Bimolecular exchange is well known in synthetic organic chemistry.<sup>71,72</sup> An ideal degenerative transfer process is based on a thermodynamic neutral bimolecular exchange between a growing radical  $P^*$  and a dormant species bearing a fragment structurally similar to the active macroradical, denoted  $P-T$ .<sup>73</sup> The potential advantage of the bimolecular exchange system is that it may be based on a classic initiator added in small amounts to an efficient transfer agent. A successful degenerative transfer agent also involves stability to homolytic cleavage but a sufficient lability of the  $P-T$  bond, otherwise a unimolecular process will take place.<sup>74</sup>

Matyjaszewski et al.<sup>75,76</sup> reported the successful controlled polymerization of styrene and butyl acrylate in the presence of 1-phenylethyl iodide as degenerative transfer reagent (Scheme 7). Molar masses of the polymers increase with conversion and drop to levels approximately equal to  $DP_n = \Delta[M]/[\text{iodide}]$ . Radical initiators such as AIBN or BPO are needed to initiate the polymerization. Alkyl bromides or chlorides are reported to be inactive under such conditions.

### 2.4. Experimental criteria and diagnostics for growth-controlled polymerizations

Since no polymerization is perfectly living, Szwarc stated that ‘‘polymers are considered to

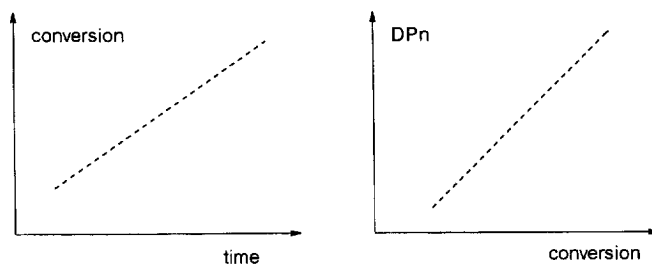
be living if they retain their capacity for growth for a time needed for the completion of a desired task'.<sup>16</sup> A large number of polymerization systems can thus be considered 'living' in terms of this definition, on the basis of the rates of both termination and transfer reactions, which have to be negligible compared to the rate of propagation.

Matyjaszewski also proposed a ranking of livingness of the various systems, based on the values of the ratios of the termination/transfer to the propagation rate constant ( $k_t/k_p$  and  $k_{tr}/k_p$ ).<sup>77</sup> This ranking enables the upper limit of the  $DP_n$  of the well-defined polymer to be determined by the ratio of the corresponding rate constants. If only a  $DP_n \approx 100$  is planned, the well-defined polymer can be prepared even at a ratio of  $k_{tr}/k_p \approx 10^{-4} \text{ mol l}^{-1}$ , but if the goal is  $DP_n \approx 10^4$  this value should be nearer to  $10^{-6} \text{ mol l}^{-1}$ . Living polymerization should provide well-defined polymers with a negligible amount of chain breaking (<5%) at high conversion (>99%).

Living polymerization is generally evaluated from experimental evidence, such as the agreement between observed  $M_n$  values and those calculated from  $[\text{monomer}]/[\text{initiator}]$ , a narrow molar mass distribution, and the capacity for post-polymerization after all of the initial monomer is consumed. Control of molar masses in the living process additionally requires fast initiation. However, most of them lead to considerably broader MWDs than a Poisson distribution. Indeed, if initiation is much slower than propagation, then higher than expected degrees of polymerization will be observed. The theoretical lower limit for the molar mass distribution of a conventional free radical polymerization is 1.5.<sup>78</sup> (The limiting  $M_w/M_n$  value of 1.5 was obtained with assumptions of 100% coupling termination and conversion.) The preparation of polymers with polydispersities less than 1.5 is often considered as one line of direct evidence for living conditions. Recently, there have been several pioneering works in achieving polydispersities lower than 1.5 via various approaches.

Recent papers by Penczek et al. and Quirk and Lee are useful in order to understand more detailed experimental criteria for living polymerization. Penczek et al.,<sup>79</sup> and especially Quirk and Lee,<sup>61</sup> have reviewed the scope and limitations of the experimental criteria for living polymerizations. Limitations of the use of linear plots of number-average molar mass  $M_n$  (or  $DP_n$ , the number-average degree of polymerization) vs conversion and plots of the number of polymer molecules (conversion) vs time (Scheme 8) as criteria for living polymerization systems were shown.

Penczek et al.<sup>79</sup> examined the diagnostic criteria of the livingness of polymerizations. The authors comment that the linearity of the number-average degree of polymerization vs conversion plot is not a sufficient criterion for a system to be 'living'. Indeed, the only requirement needed for the linearity of the plot  $DP_n = f(\text{conversion})$  is that there is no transfer ( $k_{tr} = 0$ ),



Scheme 8.

but this does not provide any information on the non-existence of a termination reaction. Thus, termination may take place and the plot will still remain linear on the condition that there is at least one macromolecule growing when complete conversion is achieved. The linearity of the plot  $R_p$  or  $\text{conv.} = f(\text{time})$  shows only that there is no termination reaction, i.e., that the number of growing chains is constant throughout the polymerization. It does not, however, eliminate the existence of transfer reactions. Both termination and transfer reactions lead to broadening of the molar mass distribution (MWD). A Poisson MWD is sufficient proof that the system is living, but Penczek et al. suggest that the latter criterion has to be related to high-conversion polymerization.

Penczek et al.<sup>79</sup> also proposed the use of a unique criterion by combining the dependence of  $DP_n$  on conversion with the dependence of  $R_p$  on time. For a living process with  $k_i > k_p$ :

$$\ln \left( 1 - \frac{[\text{Ini}]_0}{[\text{M}]_0} \overline{DP}_n \right) = -k_p [\text{Ini}]_0 t$$

The linearity of the corresponding plot was claimed as a necessary and sufficient criterion for termination and transfer reactions to be excluded.

### 3. CHAIN-GROWTH CONTROL BY PHYSICAL STABILIZATION OF RADICALS

#### 3.1. General considerations

When vinyl monomers are polymerized by conventional techniques, the random nature of the chain initiation and termination processes results in a polymer whose molecules have a wide range of molar masses. For the rate of chain termination to be reduced, it is necessary to decrease sharply or arrest completely the progressive diffusion of radicals. Radicals generated in an environment where motion is physically restricted have shown unusual reaction behaviour.<sup>80</sup> In such homogeneous and heterogeneous restricted systems, stability and selectivity of the radicals are changed significantly in comparison with unrestricted homogeneous systems. Thus, rate acceleration and retardation and variation of the product distribution have been observed. Particularly, such environmental effects are expected to be much larger for macroradicals than for small radicals, and long-lived propagating radicals have often caused peculiar polymerizations. This section deals with studies on the stabilization and activation of the radicals generated in the polymerization of vinyl monomers packed in matrix. This includes polymerizations in the presence of inclusion compounds, emulsifiers, template polymers and absorbents.

#### 3.2. Polymerization of vinyl monomers trapped in a matrix

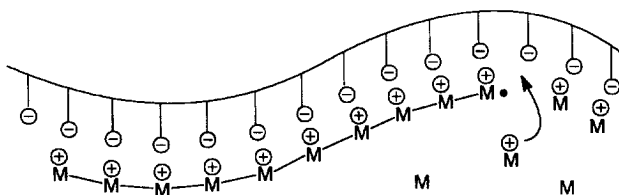
In the usual radical polymerization, the propagating polymer radicals are generally highly reactive, and hence short lived. However, some polymerization systems were reported to involve long-lived (living) propagating radicals.<sup>81</sup> Among such processes are some heterogeneous polymerization reactions where the polymer formed is not dissolved but separates in an individual, e.g. crystal, phase, and where the mobility of the occluded radicals is not high.

### 3.2.1. Precipitation polymerizations

The effect of molar mass distribution on most of the physical properties of polymers is of great importance. The method of purification of polymers via fractionation by precipitation from solution has, of late, been widely used for narrowing the molar mass distribution of the resulting polymers. However, such a technical procedure is inconvenient when more than minimal quantities of material are to be handled, and usually is of unknown effectiveness. As an adaptation from this experimental process, it was recognized fifty years ago<sup>82</sup> that it was possible for polymer particles formed during polymerization reactions to contain trapped radicals which could remain present for months. A precipitation polymerization is an extreme example of the viscosity effect. Such radicals, detected by ESR studies, were used to initiate the polymerization of monomers allowed to swell into the polymer particles. When certain vinyl monomers are polymerized in poor solvents, the propagating radicals are buried alive within the resulting polymers. A typical example is the bulk polymerization of acrylonitrile (AN). The photosensitized polymerization of AN with DBPO was reported to form living PAN radicals in a yield of about 13%, based on the initiating *tert*-butoxyl radicals.<sup>83</sup> The PAN radicals reacted with other vinyl monomers to produce block copolymers.<sup>84,85</sup> Vinyl chloride was also converted to its living polymer radicals, a process similarly used to prepare block copolymers.<sup>85</sup>

Another interesting example is tetrafluoroethylene polymerization.<sup>86</sup> Poly(tetrafluoroethylene) is a highly crystalline polymer which is insoluble in nearly all solvents. As a result of radical polymerization, or with irradiation of the polymer, a considerable number of free radicals are formed and remain sufficiently stable when stored in a vacuum in the absence of the monomer. These radicals are detected by the ESR method and identified as chain propagation radicals. Brought into contact with the polymer which contains radicals, the monomer is polymerized. Moreover, during photoinitiated polymerization, a prolonged post-polymerization period is observed for hours and even days after the light has been switched off. This indicates a considerable lifetime for propagation radicals in solid poly(tetrafluoroethylene). The post-polymerization rate, however, decreases with time and is possibly the result of either the annihilation (chemical transformation) of the radicals or their 'immurement' in the polymer formed (physical deactivation).

Seymour et al. have also applied the heterogeneous polymerization method to the synthesis of many kinds of block copolymer.<sup>87-89</sup> They have emphasized that the solubility parameters are useful for finding the optimum conditions for block copolymerization.<sup>90</sup> Block copolymers can be made efficiently by this process, provided that proper attention is paid to differences in solubility parameters. The absolute difference between the solubility parameters of the polymer and the polymerization medium should be at least 1.8 to obtain a polymer precipitate



Scheme 9.

or dispersion containing entrapped radicals, and the absolute difference between the solubility parameters of precipitated polymer and the second monomer must be less than 3.6 for efficient grafting in the second step.<sup>90</sup> For example, block copolymers can be prepared by adding acrylonitrile to entrapped PS radicals, but not by adding styrene to entrapped PAN radicals. Extensive ESR and block copolymerization studies on living radicals derived from substituted acrylamides have been reported.<sup>81</sup>

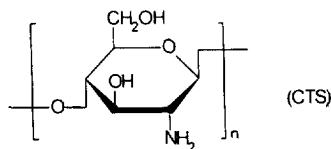
$\gamma$ -ray irradiation of solid monomers such as acrylamide derivatives<sup>91</sup> and acrylic acid<sup>92</sup> also yielded the corresponding living polymer radicals. Such polymer radicals were allowed to react with second monomers to give block copolymers.<sup>93</sup>

### 3.2.2. Template polymerizations

Template polymerizations can be defined as polymerizations in which polymer chains are able to grow along template macromolecules for the greater part of their lifetime. A well-chosen template is generally able to affect the rate of polymerization as well as the molar mass and microstructure of the formed polymer (daughter polymer). The molar masses of the polymer formed by template polymerization are up to 70 times greater than those of polymers produced in the absence of the template and can be higher in molar mass than the templates themselves. This was satisfactorily explained by the retardation of the termination for template-associated radicals and by hopping of a radical to the neighbouring template after reaching the end of a template polymer.

PAA and PMA form complexes with a large number of polymers, including poly(N-vinylpyrrolidone), poly(ethylene oxide), poly(vinyl pyridine) and poly(ethylene imine).<sup>94</sup> For example, rate enhancements with respect to the bulk polymerization were observed up to a factor of 6 in the polymerization of N-vinylimidazole along a poly(methacrylic acid) template in water.<sup>95,96</sup> The rate of polymerization could be further enhanced by using templates of higher molar mass. A mechanism was proposed in which rate enhancements arise from the propagation of template-associated radicals in an adsorbed mobile monomer (Scheme 9).

When these complexes are formed from growing polymer radicals and co-complexing polymer, the mobility of the radicals is decreased substantially, termination rate constants are reduced, and living polymer behaviour may be possible. Thus, Kataoka and Ando<sup>97</sup> reported the matrix-trapped living radical polymerization of the sodium salt of methacrylic acid in aqueous solution in the presence of chitosan (CTS) acetate, using potassium persulphate as an initiator. The growing macroradicals were considered to survive due to complexation with CTS. Polymer radicals were observed after 150 h in a potassium persulphate initiated system at 30°C, and the addition of styrene after the complete polymerization of the MA resulted in a 67% yield of an MA–St block copolymer.<sup>98</sup>



A long-lasting reactivity of radicals was also observed in the photopolymerization of methacrylic acid with poly(N-vinyl-2-pyrrolidone) template after switching off the

lamp,<sup>99,100</sup> suggesting a stabilization of the propagating radical along the template. A model kinetic study indicated that the rate constant for the complexation between oligomeric radical and template polymer strongly affects the overall polymerization rate enhancement. However, it has to be taken into account that since polymer–polymer complexes are often insoluble, the template polymerization approach to living radical polymerization may actually be a special case of precipitation polymerization in many cases.

### 3.2.3. Emulsion polymerizations

Emulsion polymerization of vinyl monomer in the presence of a surfactant is accompanied by the isolation of the polymer-producing area from the solution containing the initiator. It represents an efficient method of obtaining surviving polymer radicals which were isolated in micelles.<sup>101</sup> The living radicals in micelles were also available for block copolymer synthesis.<sup>102,103</sup>

Mutual termination between two growing chains can be practically eliminated by using a water emulsion system in which each growing chain is in its own separate micelle,<sup>104</sup> and ESR measurements show that polymer radicals can exist in polymer latices for long periods. According to the simplest model for emulsion polymerization, one half of the monomer–polymer particles present at any given time in an emulsion polymerization system can contain propagating polymer radicals. Such radicals are terminated by the entry of other, generally small, radicals into the monomer–polymer particles. When the generation of new radicals stops, those that remain in the monomer–polymer particles can live for long periods. They can continue to grow as monomer diffuses into them, or add to different monomers to form block copolymers.

The key to obtaining living polymerization behaviour is to control the radical initiation step. This has been attempted in two ways: by photochemical initiation (external control), and by removing from the system those components that are required for initiation (internal control). Ingenious use was made of photochemical external control in a manner that enables all of the latex particles to be involved and affords up to 50% conversions of polymers with narrow molar-mass distributions.<sup>105</sup> The approach involves exposing the polymerization mixture at regular intervals to bursts of radiation, causing the monomer–polymer particles to be flooded with small radicals at the end of each interval. Each burst of small radicals causes the immediate termination of any growing polymer radicals and the initiation of a new set of growing polymer chains. Thus, all polymer chains grow for the same length of time and narrow molar-mass distribution products are obtained. The molar masses, which range from 5 to  $25 \times 10^5$  g mol<sup>-1</sup>, are controlled by the time between bursts. The time of growth for polymerizing styrene radicals was controlled by adding overwhelming amounts of free radicals at intervals to an emulsion polymerization system. The styrene chains initiated in one addition are mostly terminated in the next addition, so that their growth time is the interval between additions. Polymers with molar masses of most of the molecules very narrowly concentrated around selected values were prepared in this way. UV light plus 2,2'-azobis(*isobutyramide*) were found to be a practical initiation system for preparing PS in this way with molar masses greater than  $5 \times 10^5$ . The upper limit of the molar mass obtainable was determined by the rate of chain transfer on the polymer. For styrene, this upper limit appeared to be a few million. In detailed studies<sup>106,107</sup> of styrene polymerization by this process, it was noted that the process is complicated by polymer radicals escaping

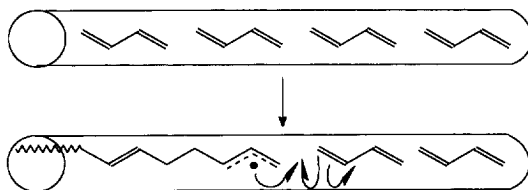
termination during bursts, by chain-transfer effects, and by polymerization occurring outside the latex particles.

An original idea was also developed to control the radical initiation step by internal control in redox emulsion polymerization. A stabilization of the propagating radical towards the termination reaction was obtained by Mikulàsovà et al.<sup>101,102,108,109</sup> who used oxidized isotactic polypropylene powder as a heterogeneous initiator and some reducing agents, e.g. triethylenetetramine, as activators. When the initiating system was used for the emulsion polymerization of styrene, living propagating radicals were studied by the ESR method after heterogeneous initiator had been separated from the reaction mixture. Peroxidized PP is insoluble and radical generation can easily be stopped by filtering the polymer from the polymerization mixture. For example, polymerization of styrene initiated by oxidized polypropylene and triethylenetetramine proceeds through quasi-living radical polymerization, i.e. increase of molar mass of the resulting polymer with increasing conversion, and potential production of block copolymers.<sup>102</sup> It is worth noting that the resulting PS has ultra-high molar mass ( $M_n$  up to  $10^7$  g mol<sup>-1</sup>) and narrow molar mass distribution ( $I = 1.01-1.13$ ). Mikulàsovà et al. also prepared block copolymers of styrene-*b*-MMA,<sup>101</sup> but the mechanism of the mode of stabilization of the propagating radical toward termination has not been cleared up. The interaction between propagating radical and the reaction products of the activator is still obscure.

Such a process was used by other groups to prepare diblock and triblock copolymers.<sup>103,110,111</sup> However, it has been suggested that this method works because peroxidized PP breaks down into small fragments that are incorporated into the polymers.<sup>110,111</sup> The fragments later decompose and serve as radical sources for subsequent polymerizations. The approach may thus be an example of a pseudo-living radical polymerization (other examples of pseudo-living polymerization are presented in Section 5). Similar results were reported when systems of some alkyl peroxides and amines were used as initiators.<sup>112</sup> These living polymer systems were used as initiators to prepare block copolymers.

### 3.2.4. Polymerizations in inclusion compounds

Inclusion polymerization using various hosts, e.g. clathrate channels, was reported as an effective and convenient method for hindering radical-termination reactions, obtaining living polymerization behaviour and controlling the microstructures of polymers.<sup>113</sup> Dienes and some vinyl monomers form inclusion (clathrate) compounds with urea, thio-urea, deoxycholic acid, perhydrotriphenylene, and other molecules that form crystals with open channels.<sup>60</sup>Co-irradiation of such inclusion compounds induces radical polymerization. The structures of the propagating radicals formed in the polymerization of pentadiene derivatives in a



Scheme 10.

deoxycholic acid canal were studied by ESR.<sup>114</sup> Polymer radicals formed within the channels are unable to diffuse to other radicals and terminate (Scheme 10).

Because of the remarkably restricted mobility in a canal, the propagation rate constant becomes very low, e.g.  $\sim 10^{-3} \text{ l (mol s)}^{-1}$  in the polymerization of 1-chlorobutadiene<sup>115</sup> in deoxycholic acid as host molecule, which corresponds to 1/100–1/1000 of the rate constant in homogeneous solution polymerization. The termination rate constant is also surprisingly low, ca.  $10^{-9} \text{ l (mol s)}^{-1}$ . The activation energies for propagation and termination were determined to be 49 and 46 kJ mol<sup>-1</sup>, respectively. The former value is close to that for butadiene polymerization (38–42 kJ mol<sup>-1</sup>), whereas the latter appeared to be very high, suggesting a restricted mobility of the macroradicals.<sup>115</sup>

Block copolymers of butadiene and isoprene were prepared by exposing perhydrotriphenylene crystals to <sup>60</sup>Co-irradiation to generate radicals, allowing butadiene to diffuse into the crystal channels and then to polymerize. This was followed by allowing isoprene to diffuse into the crystal channels to polymerize at the ends of the polybutadiene chains.<sup>113</sup>

### 3.2.5. Polymerizations in inorganic intercalation compounds

Synthetic zeolites were used as efficient stabilizing matrices for free radicals, even at relatively high temperatures. Radicals can be generated by the thermal homolysis of peroxide initiators, which are adsorbed in the zeolite alone or with the monomer. In large pores (silica gel), monomer diffusion becomes relatively easy, whereas mobility of the polymer radical is still restricted. Consequently, a monomer can be converted into polymer at a relatively high rate to give a long-lived polymer radical.<sup>116</sup> ESR spectra of some oligomer radicals, obtained from the polymerization of *n*-BA, allyl methacrylate and styrene, indicated that the propagating radical was stabilized by adsorption on synthetic zeolites (faujasite of the NaX type),<sup>117</sup> rather than by entrapment of the polymer in the secondary porous structure of the zeolite.

### 3.2.6. Miscellaneous polymerizations

3.2.6.1. *Polymers with rigid backbones* — Although the termination rate constant for methyl acrylate polymerization is in the order of  $10^7 \text{ l (mol s)}^{-1}$ , the corresponding value for diisopropyl fumarate is  $0.84 \text{ l (mol s)}^{-1}$ .<sup>118,119</sup> This very low value for diisopropyl fumarate, a consequence of the rigidity of poly(diisopropyl fumarate) chains, enables it to be polymerized to high molar masses even though it is highly hindered. ESR and post-polymerization studies on diisopropyl fumarate polymerization mixtures indicate that radical activity can exist in such mixtures for several hours.

3.2.6.2. *Polymerization of (meth)acrylamide derivatives* — Sato and Otsu<sup>81</sup> studied the radical polymerization of (meth)acrylamides and their derivatives such as N-methyl (meth)acrylamides. These monomers produce long-lived propagating polymer radicals when they are polymerized in good solvents for the monomers and poor solvents for the polymers, such as 1,4-dioxane and benzene, with a peroxide as radical initiator under UV light irradiation at room temperature.<sup>120</sup> As the polymerizations proceed, the systems become heterogeneous and give polymer microspheres which contain the very stable propagating radicals of the amide monomers in high concentrations.

In the polymerization of NMMAm in benzene with AIBN, the cyanopropyl radicals



escaping from the solvent cage are converted to living polymer radicals PNMMAm in high yields, *ca.* 90%. In degassed benzene, PNMMAm remains unchanged for several years at normal temperatures. However, the radical reacts easily with oxygen to convert to a peroxy radical. The polymer radical can also be allowed to react with a second monomer to give a block copolymer.<sup>121,122</sup> Thus, methyl acrylate was converted into polymer with a 100% yield.<sup>121</sup>

3.2.6.3. *Polymerization of  $\alpha$ -fluoroacrylamide* —  $\alpha$ -fluoroacrylamide was reported by Kamachi et al.<sup>123</sup> as a monomer which underwent quasi-living radical polymerization when initiated by AIBN in dimethyl sulphoxide. The rate of polymerization, expressed by  $R_p = [\text{AIBN}]^{0.95}[\text{amide}]^{1.1}$ , followed an abnormal rate dependence on the initiator concentration which was interpreted by the authors on the basis of a unimolecular termination mechanism. The presence of long-lived propagating radicals was monitored by ESR and revealed that the radical concentration increased linearly with time. The reason the long-lived radicals existed in solution was supposed most likely to be due to the poor solubility of high molar mass poly( $\alpha$ -fluoroacrylamide) in the dimethyl sulphoxide solution. When the propagating polymer radicals reach the molar mass where they verge on insolubility in the solvent, they become tightly coiled, and thus two such radical centres cannot easily react with each other.

## 4. CHAIN-GROWTH CONTROL BY THE CHEMICAL DEACTIVATION OF RADICALS

### 4.1. *Stabilization of radicals by coordination to metal complexes*

Metal-assisted radical polymerization was studied in connection with the control of growth of a polymerization reaction by resonance stabilization and polarization of monomer and radical. It has been shown<sup>124</sup> over the past years that in radical polymerization the chain termination rate constant is observed to decrease with the introduction of complexing agents in the polymerization systems. Complexation of propagating radicals with anions or polar molecules of organic or inorganic origin results in a remarkable increase in the lifetime of radicals because such radical complexes hinder termination either by mutual ionic repulsion or by steric hindrances near the radical. This type of radical stabilization was first known for small radicals.<sup>72</sup> In radical polymerization, whatever the mode of stabilization used, one usually speaks of 'living radical polymerization or copolymerization' or 'growth-controlled radical polymerization'.

It must be stressed that polymerizations with organometallic compounds may proceed not only by radical but also by ionic or coordinative mechanisms. In fact, a number of very similar initiation systems have been ascribed to anionic/coordinative polymerization.<sup>125</sup> It is imperative in these cases to use various scavengers, and to study the solvent effects and the copolymerization relationships, in order to elucidate the mechanism in an unambiguous way.

#### 4.1.1. *Polymerizations in the presence of protonic acid*

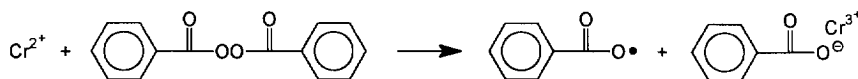
It is noteworthy that quasi-living radical polymerization by complexation with protonic acid was claimed in the homogeneous polymerization of MMA with  $\text{H}_3\text{PO}_4$ .<sup>126</sup> An especially

sharp decrease of the termination rate, up to the formation, under certain conditions, of 'living' radical polymerization centres, was noted in the MMA–orthophosphoric acid system. The molar mass increased with increasing monomer conversion, but the chain length of the resulting polymer and its dispersity were not controlled. At continuous photoinitiation, the MMA polymerization rate was shown to increase considerably with the introduction of  $\text{H}_3\text{PO}_4$ . The reaction was shown to be inhibited by a typical radical scavenger, viz. *p*-benzoquinone, and the values of the propagation rate constant appeared similar both with and without  $\text{H}_3\text{PO}_4$ . Thus, the role of the complexing agent seemed essentially to reduce the chain termination rate. Under conditions of continuous initiation, the observed order with respect to the initiation rate of radicals was close to 0.5; i.e., most radicals were still being annihilated in the course of their bimolecular interaction. When the post-polymerization was studied with the light off, it turned out that the polymerization rate was at first somewhat decreased; then, for a long time, it remained constant, with the yield reaching 100%. The molar mass of the polymer grew, while the number of chains remained almost constant. The introduction of benzoquinone reduced the post-polymerization rate and, at a certain concentration, completely inhibited the process. The variations of polymer molar mass distribution were explained by the assumption that, with the growing degree of macroradical polymerization, the probability increases of its being entrapped in a certain associate as a result of complexing. Such a phenomenon reduces its mobility and consequently decreases the rate constant of its interaction with other radicals. While continuous initiation exists, termination is actualized through the interaction of low-molar-mass radicals with high-molar-mass radicals. After all the radicals have reached a certain length, the chain termination practically stops.

Systems such as MMA/ $\text{H}_3\text{PO}_4$ , AN/ $\text{H}_3\text{PO}_4$  and methyl  $\alpha$ -chloroacrylate (MCA)/ $\text{H}_3\text{PO}_4$  have also been used to produce block copolymers, graft copolymers and graft block copolymers on solid organic (cellophane film) and inorganic (silica gel) substrates.<sup>127</sup> The method applied was the one previously developed<sup>60</sup> for ionic systems, i.e. the successive introduction of new portions of comonomers. At first, it was shown that after all the monomer has been consumed in the  $\text{H}_3\text{PO}_4/\text{MMA} = 3:1$  (molar ratio) system in post-polymerization (initiation with UV light) with a new portion of MMA introduced, the amount of the polymer increases, along with a proportional rise in the molar mass. The introduction of another monomer in the second stage results in the formation of two fractions: a block copolymer with a higher molar mass formed on the living radicals, and a homopolymer (the dead polymer) of the first stage of the process. It should be noted that a homopolymer is never formed in the second stage of the process; i.e., the 'living' radicals initiate the polymerization of the second portion of the monomer exclusively through addition.

Of special interest is the possibility of producing a considerable amount of graft polymers on solid substrates (see Section 3.2.5). Acrylic monomers (MMA or MCA), along with orthophosphoric acid, were applied to previously  $\gamma$ -irradiated cellophane films or silica gel in vacuum. A graft polymer was observed to form, but almost no homopolymer was formed in this case. Without a complexing agent, polymerization does not take place under the same conditions. It seems that in this case as well, in the absence of a structure-forming agent, the mobility of the radicals on the surface is too high and they can rapidly recombine. Successive introductions of portions of different monomers made it possible to produce double and triple block copolymers, e.g. PMMA–PMCA–PMMA or PMCA–PMMA–PMCA.

'Living' radical processes open up new possibilities for synthesis, previously characteristic



Scheme 11.

of ionic 'living' systems, i.e. the production of block copolymers, and the established possibility, in principle, of obtaining structures with narrow molar mass distributions. However, the formation of 'living' radical systems was accompanied by a partial annihilation of radicals, i.e., the formation of 'dead' polymer, which corresponded to a broadening of MWD.<sup>127</sup>

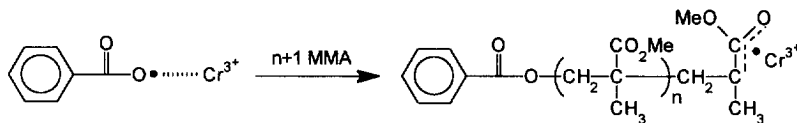
#### 4.1.2. Polymerizations in the presence of Lewis acids

For a long time, there has been hope that a way may exist of stabilizing radicals by forming complexes with metal ions and thus converting propagating polymer radicals into complexes that would be reluctant or unable to participate in termination reactions. This would, of course, provide an important entry into living radical polymerization. In one approach along these lines, Lee et al.<sup>128,129</sup> used a binary initiator system of  $\text{Cr}(\text{OAc})_2$ /benzoyl peroxide to initiate a living-type polymerization of MMA in DMF at 30°C or below. Intensive structuring of macromolecules in such a radical polymerization in the presence of complexing agents<sup>124</sup> results in a decreasing termination rate and the formation of practically 'living' polymers. The initiating mixtures were allowed to 'age' at -20°C for several days to generate species that exhibited living radical behaviour (Scheme 11).

Increases in molar mass with conversion for MMA polymerization at low temperatures, and degrees of polymerization up to  $10^4$ , were observed. These initiating systems have, however, been unsuccessfully used in the polymerization of other vinyl monomers such as VA or St. Lee et al.<sup>128,129</sup> also synthesized block copolymers by adding acrylonitrile to living PMMA chains.

The effect of metal salts has scarcely been defined in most polymerization reactions and the mechanism for controlled polymerization with chromium compounds is not yet clear. These polymerizations are not controlled by the classical kinetic laws of conventional radical polymerizations. Lee et al. previously proposed that Cr(III) species were complexing with the growing PMMA radicals to form long-lived complexes.<sup>128</sup> In any case, the coordination of functional charged groups such as carbonyl and nitrile to Lewis acids (formation of  $\sigma$ -complex) is in any event the first step of the promotion of metal-assisted radical reactions. Such a  $\sigma$ -complex will formally complex growing radicals to form Cr(III) species. In that case, Cr(II) will have a dual role: as a redox co-initiator and as the reversible scavenger of growing species.

The structure and the stability of this complex could be similar to those reported for the complex formed by BPO in the presence of  $\text{Cr}^{2+}$  (Scheme 11). The propagation mechanism could proceed through insertion of monomer into the benzoyloxy-Cr(III) complex formed during initiation. The resistance to termination of the propagating radical complexed with  $\text{Cr}^{3+}$  would be explained by the fact that carbon macroradical also interacts with  $\text{Cr}^{3+}$  and would be stabilized by conjugation with a carbonyl group. The screening of the active centre (e.g. long-lived benzoyl and PMMA radicals) by  $\text{Cr}^{3+}$  would inhibit the bimolar termination of propagating polymer radicals because of electrostatic repulsion<sup>130</sup> (Scheme 12).



Scheme 12.

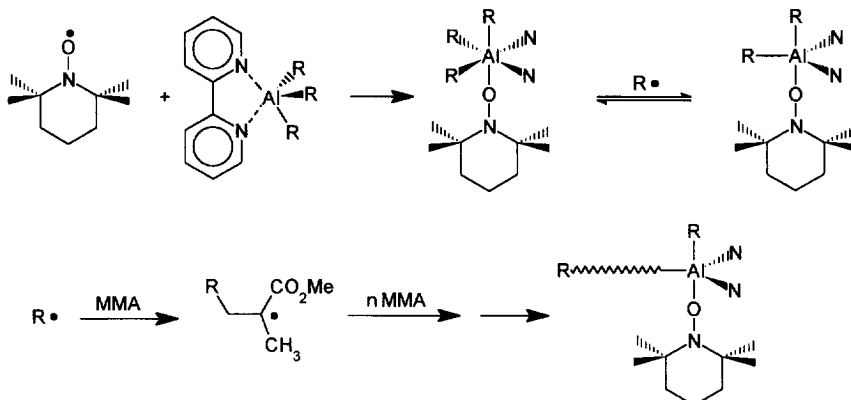
However, on the other hand, it is now generally accepted that the termination reaction is not influenced by the metal salt. Nevertheless, it is only to be expected that the selectivity of the bimolar termination, e.g. the ratio of recombination to disproportionation, varies with end-capping of the growing radical, especially at high concentrations of metal salt.<sup>131</sup> Additional experiments have posed questions about this abnormal polymerization. Hungenberg and Bandermann<sup>132</sup> claimed that the polymerization of MMA reported by Lee et al.<sup>128</sup> involved the development of several uncomplexed initiating species in the reaction and proceeded also with uncomplexed macroradicals. They proposed a more conventional explanation: the higher rate of this polymerization could be attributed to the higher rate of BPO decomposition in the presence of  $\text{Cr}^{2+}$  and DMF, and the increment in the  $DP_n$  vs conversion could be ascribed to the gel effect. However, Hungenberg and Bandermann<sup>132</sup> do not explain the formation of block copolymers effectively observed by Lee et al.<sup>129</sup>. In spite of considerable efforts, unequivocal proof of any of the proposed mechanisms is still lacking.

Gaylord et al.<sup>133-135</sup> have also reported the existence of 'living radicals' in alternating copolymerization of styrene with MMA in the presence of  $\text{ZnCl}_2$  or ethylaluminium chloride with different contents of chlorine and ethyl groups in the molecule. Quasi-living radical polymerization by complexation with metal was also claimed for BMA with  $\text{ZnCl}_2$ ,<sup>126</sup> AN with  $\text{EtAlCl}_2/\text{VOCl}_3$ <sup>136</sup> and ethylene with  $\text{AlEt}_3$ .<sup>137</sup> The  $DP_n$  increased with increasing monomer conversion, but the molar mass of the polymer and its dispersity were not controlled.

Recently, Sivaram et al.<sup>138</sup> investigated the photopolymerization of MMA induced by a mixture of linear and cyclic oligomeric methylaluminumoxanes. Methylaluminumoxanes form a weak complex with MMA, affording polymerization to high molar mass polymers when irradiated with UV (350 nm) at 30°C. Both conversion and molar mass were shown to increase linearly with time, and the plot of  $M_n$  vs conversion was also fairly linear up to 60%. At the moment, this unusual behaviour of the radical propagating species has only been checked by NMR for tacticity.

#### 4.1.3. Polymerizations in the presence of organometallics complexed with ligands

4.1.3.1. *Use of aluminium complexes activated with TEMPO* — About fifteen years ago, organoaluminium compounds complexed by various N- or O-based donor ligands, such as pyridines,<sup>139</sup> dipyrityl<sup>140</sup> and semiquinones,<sup>141</sup> were reported to initiate radical polymerization, but, in each of these systems, no control of polymerization was mentioned. More recently, Matyjaszewski et al.<sup>142-144</sup> reported the use of a trialkylaluminium complex in association with a nitroxyl radical to synthesize a variety of polymers with narrow polydispersities.<sup>145</sup> The tricomponent system was based on



Scheme 13.

organoaluminium compounds coordinated to 2,2'-dipyridyl ligands as stabilizing groups and activated by TEMPO for the polymerization of MMA, St and VA. It was surmised that the action of TEMPO displaces an alkyl radical from the aluminium complex. The addition of TEMPO to  $R_3Al$  coordinated by Dpy causes the reversible displacement of an alkyl radical  $R'$  with the formation of  $R_2Al-TEMPO$  and a new Al–O bond. The alkyl radical initiates polymerization and the aluminium atom coordinates reversibly with the growing chain, enabling the polymerization to behave in a living manner. The mechanism is described as being via an alkyl radical from hexacoordinated aluminium–SFR. The departing radical reacts with incoming monomer, and the resulting polymeric radical may recombine reversibly with the pentacoordinate aluminium species (Scheme 13).

This system has the advantage of the fast generation of propagating radicals. It has maximum activity when the ratio  $[TEMPO]/[Al] = 2-3$ , and was claimed, as a hypothesis, to be based on the presence of an equilibrium between active and dormant centres, i.e. the reversible formation of hypercoordinated aluminium radicals which release reversibly propagating radicals. Unfortunately, no molecular schemes were depicted by the authors and it is difficult to fully understand the mechanism. This system appeared, however, extremely sensitive to moisture and oxygen, and its activity strongly depended on the monomer structure and on the nature of the organoaluminium compounds involved. For example, polymerization of VA in benzene at 20–60°C initiated by the tricomponent system, *iso*Bu<sub>3</sub>Al/Dpy/TEMPO (1:1:2), proceeded according to first-order kinetics in the monomer and exhibited an apparently constant concentration of growing species. The molar mass increases linearly with conversion in the following examples: *i*Bu<sub>3</sub>Al/Dpy/2TEMPO, *i*Bu<sub>3</sub>Al/(PhC(O)OCH<sub>2</sub>)<sub>2</sub>/2TEMPO and Et<sub>2</sub>AlCl/Dpy/2TEMPO, with polydispersities of 1.15–1.25 for molar masses up to  $5 \times 10^4$ . Depending on the monomer involved, the polymerization rate was much faster with activated monomers (e.g. MMA) than for VA and polymerization was completed in a few minutes rather than in a few hours under similar conditions. Typically, 90% conversion of vinyl acetate occurs over 24 h at ambient temperatures.

The preparation of block copolymers involving MMA, St and VA was also allowed by using the same initiating system for each of these monomers. The authors observed, however, that better results were obtained using VA as the first monomer, due to a slower and better

controlled polymerization, than when using MMA. It represents the first successful synthesis of block copolymers containing vinyl acetate.

The challenge of understanding the mechanisms of these new reactions promises to be of great interest for years to come. Matyjaszewski reported some ESR evidence to support a radical mechanism and described the activation of monomer by coordination with aluminium–TEMPO species as analogous chemistry to immortal polymerization.<sup>143</sup> However, reactions with organometallic compounds may proceed not only via homolytic cleavage of the metal–carbon bond but also by heterolytic cleavage leading, for example, to enolate anions in polymerization of MMA. The coordinative polymerization and insertion of monomer into the metal–carbon bond is also feasible. Thus, studies based on scavenger and copolymerization radical reactions are necessary to prove the nature of the growing species involved in the reaction. The nature of the initiator is also complex and is illustrated by a time dependency of initiator efficiency, reported as an ‘ageing effect’. The pentacoordinated aluminium is thought to react with TEMPO with the expulsion of an *isobutyl* radical, which initiates polymerization, leaving a pentacoordinated aluminium species which end-caps the propagating polymer chain in a six-coordinate metal complex. However, solvent effects in these Lewis acid–Lewis base reactions are very important. Haddleton and Davis<sup>146</sup> have shown that the reaction of *triisobutylaluminium* with Dpy yields a mixture of species, including radicals centred on the Dpy ligand, and reduction side-products of the Dpy to give tetracoordinated aluminium complexes. A large amount of radicals are thus produced in the absence of added TEMPO, which was claimed by Haddleton to explain that the system does not afford 100% initiator efficiency.<sup>146</sup> At present, the exact mechanism is still unclear and the reader can refer to papers cited therein for a more detailed mechanistic hypothesis.

4.1.3.2. *Use of organochromium complexes* — Poor control of molar masses and facile chain transfer processes were noticed in preliminary studies on metal-stabilized propagating radicals based on Co and Cr. Such phenomena were attributed to the reversibility of the redox couples  $\text{Co}^{3+/2+}$  and  $\text{Cr}^{3+/2+}$  due to their positive redox potentials and to  $\beta$ -hydrogen abstractions in the formation of metal hydrides.<sup>147</sup> The controlled polymerization of VA and MMA in THF was achieved by using redox initiator systems based on BPO and  $\text{Cr}(\text{OAc})_2$  complexed with different N-based ligands, i.e. Dpy, 18-ane-6 trisulphate, and hexamethyl 18-ane-6. The highest conversion, up to 90%, obtained in the shortest time, 30 h, was found in the presence of 18-ane-6 trisulphate as ligand. On the other hand, polymerization rates were reduced and lower conversions were observed in the presence of ligands known to stabilize the lower oxidation states, e.g. Dpy and hexamethyl 18-ane-6. A divergence from linearity was also observed in the plot of molar masses vs conversion, indicating a poor control of chain growth in the absence of any ligands.

4.1.3.3. *Use of organocobalt complexes* — The radical activity of cobalt complexes to control the free radical polymerization of vinyl monomers depends on structure and on the monomer involved. The presence or absence of a  $\beta$ -hydrogen on the monomer causes either a catalytic chain transfer process or quasi-living radical polymerization, respectively.

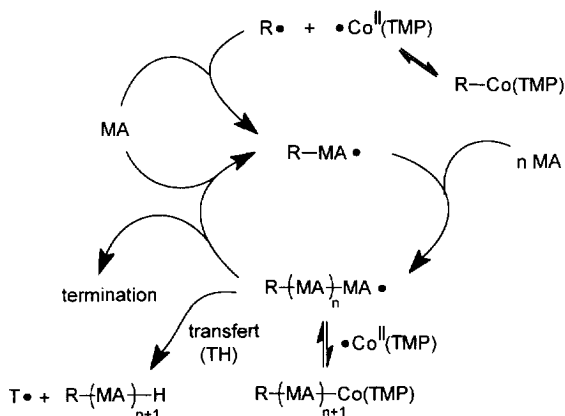
Bis(dimethylglyoximato) complexes of cobalt, commonly known as cobaloximes, have been widely investigated as efficient catalytic CTAs in order to regulate molar masses of PMMA and PS synthesized by radical processes.<sup>148–150</sup> The difference in catalytic chain transfer constants between St and MMA is believed to be due to the preferential formation

of adducts between propagating  $PS^*$  radicals and cobaloxime. Indeed, the cobalt catalyst was shown to act as a radical trapping agent for  $PS^*$ , involving the formation of a carbon–cobalt bond at the end of the polymer chain. In the case of MMA, the instability of the cobalt–(tertiary carbon) bond prevents the formation of the adduct and, thus, only catalytic chain transfer was observed.<sup>151</sup>

The polymerization of MMA involving the use of a binary initiator system in acetonitrile, a cobaltocene/bis(eacac)copper(II) system, also showed some features of a living character; i.e., the molar mass of the resulting polymer increased with increasing polymer yield<sup>152</sup> and was also used in preparing an MMA–St block copolymer.<sup>153</sup> More recently, the use of cobaloximes as photoinitiators<sup>154</sup> or of organocobalt porphyrins as thermal initiators<sup>155</sup> for polymerization of acrylates was reported. The mechanism of polymerization involves, respectively, a photo- or thermolytic cleavage of the cobalt–carbon bond, insertion of monomer units, and cage recombination.

Harwood et al.<sup>154</sup> used alkyl cobaloximes as photoinitiators for free radical polymerization of ethyl acrylate, and showed that polymerization proceeded almost quantitatively with continued conversion upon second addition of monomer and that molar mass increased linearly with conversion. The cobalt–carbon bond breaks into an alkyl radical and  $Co^{2+}$  species when irradiated with visible light, which reinitiates polymerization of the monomer, and rapid recombination occurs. The mechanism was first thought to involve a living-type polymerization. However, the kinetics clearly differ from the normal free-radical case, and the authors stated that the true mechanism of polymerization with these reagents remains obscure.

Wayland et al.<sup>14,155</sup> reported that organocobalt derivatives (e.g. tetramesityl porphyrinato cobalt(III)–organo complexes,  $(TMP)Co-R$ ) initiate and control chain growth in the polymerization of acrylates to form homopolymers and block copolymers.  $(TMP)Co-R$  provides both a thermal source for the initiator radical ( $R^*$ ) and a persistent radical  $(TMP)Co^{II}$  that reversibly binds with the growing polymer radical and controls the polymerization process. Linear increase in the polymer number-average molar mass with monomer conversion, relatively small polydispersity ( $M_w/M_n = 1.1-1.3$ ), formation of block copolymers and observation of  $(TMP)Co$ –organopolymer complexes are all signatures of a living polymerization process.



Favorable kinetics of polymerization, suppression of polymer radical termination by the persistent radical effect of  $(\text{TMP})\text{Co}^{\text{II}}$  and steric inhibition of  $\beta\text{-H}$  abstraction by  $(\text{TMP})\text{Co}^{\text{II}}$  combine in this system to accomplish an effective controlled radical polymerization of acrylate monomers (Scheme 14).

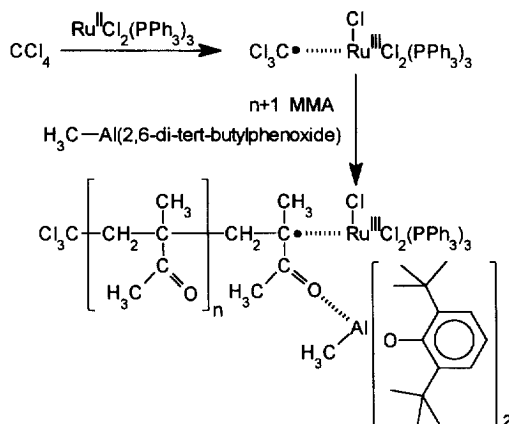
The living nature of MA polymerization induced by  $(\text{TMP})\text{-Co}$  organocomplexes was illustrated by formation of MA-co-BA block copolymers. The real polymerization process cannot be fully living because of inherent bimolecular radical termination processes and H transfer reactions with monomer, polymer, solvent and  $(\text{TMP})\text{Co}^{\text{II}}$  which result in non-living polymer chains. At least 95% of the polymer chains are living, even at relatively high conversions. The scope and limitation of the methodology developed by Wayland et al.<sup>14,155</sup> and Harwood et al.<sup>154</sup> in achieving quasi-living radical polymerization of acrylate monomers was recently discussed in terms of the kinetic and thermodynamic factors that govern the processes. Davis et al.<sup>156</sup> proposed an explanation for the selectivity of the C-Co termination process over classical radical-radical termination reactions, based on the works of Fischer<sup>157</sup> and Daikh and Finke.<sup>158</sup> Davis et al.<sup>159</sup> proposed also a model of 'living' radical polymerization reaction based on a persistent radical process. The authors demonstrated that the living nature of the reaction is enhanced if the ratio of stable  $\text{Co}^{\text{II}}$  to polymer radical is greater than 1, but the rate of polymerization is decreased. Moreover, the extent of control exerted over the living reaction is tempered by the choice of solvent used for the polymerization.<sup>154</sup>

4.1.3.4. *Use of  $\text{CCl}_4/\text{Cl}_2\text{Ru}^{\text{III}}(\text{PPh}_3)_3$  initiating system activated with methyl bis(2,6-di-tert-butylphenoxide) aluminium* — Sawamoto et al.<sup>160</sup> proposed a well-controlled polymerization of MMA in the presence of the ternary initiating system consisting of  $\text{CCl}_4$ ,  $\text{Ru}^{\text{III}}\text{Cl}_2(\text{PPh}_3)_3$  and methyl bis(2,6-di-tert-butylphenoxide) aluminium (denoted  $\text{MeAl}(\text{ODBP})_2$ ) via such a mechanism in which the dormant intermediate with a carbon-chlorine terminal bond might reversibly be converted into a radical growing species by organometallic compounds. However, the roles of  $\text{RuCl}_2(\text{PPh}_3)_3$  and  $\text{MeAl}(\text{ODBP})_2$  have to be clarified. Some experimental evidence has suggested that the polymerization proceeds by a radical mechanism in which the transient radical intermediate is confined in the coordination sphere of the ruthenium complex and is thereby stabilized. When the carbon-chlorine bond of the polymeric adduct is dissociated into an active growing radical by the  $\text{RuCl}_2(\text{PPh}_3)_3/\text{MeAl}(\text{ODBP})_2$  system, the resulting radical species successively react with MMA without undesirable side reactions to induce quasi-living radical polymerization. Sawamoto et al.<sup>160</sup> employed  $\text{MeAl}(\text{ODBP})_2$  as a bulky Lewis acid to activate the carbon-chlorine bond of the  $\text{CCl}_3\text{-PMMA-Cl}$  adduct (see Scheme 15) by coordination of the  $\alpha$ -ester carbonyl function.

## 4.2. Polymerization in the presence of aminyloxyl-type radicals

A longstanding goal of polymer chemistry has been the development of practical living radical polymerization methods. An increasing number of reports on the syntheses of polymers with complex architectures, such as block and graft copolymers and star polymers, has appeared in recent years. The development of living free-radical processes that meets the challenging test of providing polymers with narrow polydispersities was attempted by the design of reversible termination agents that balance the competing requirements of rapid





Scheme 15.

propagation and no new initiation (reaction enthalpies for the addition of terminating radicals to monomers have to be positive) once all the living chains have been generated.

Free radical polymerizations involving the addition of stable aminyloxyl-type radicals (denoted T<sup>\*</sup>) to the polymerization feed were developed to minimize termination by radical coupling and to allow for control of end-group structure. The radicals formed during the initiation step are trapped by the stable radical T<sup>\*</sup> to reversibly terminate polymer chains by radical–radical combination. According to the counter-SFR involved, the formation of the reversible termination between the active centre and the counter-radical can be obtained by photoactivation or thermal activation. The bond formed between the coupled radicals is labile, allowing further monomer to add. A most notable example of living-type radical polymerization involves the concept developed by several research groups, which takes advantage of the stability of oxygen-centred nitroxyl and (aryloxy)oxyl radicals. Long recognized as inhibitors of radical polymerization reactions,<sup>161</sup> stable nitroxyl free radicals would not be expected to initiate new polymeric chains. These counter-radicals have also been examined as stable terminators to end-cap macroradicals. The use of these aminyloxyl radicals was investigated to allow the polymerization reaction to proceed at a faster rate than those involving the thiocarbonyl or arylmethyl SFRs by making the bond between the radical chain end and the stable free-radical fragment more labile.

Moreover, in order to initiate all living chain ends in a very short time span, it is essential to operate under conditions which lead to very rapid initiator fragmentation. Consequently, reaction conditions must be chosen such that the initiator half-life is very short. The nitroxyl–adduct bond homolysis increases dramatically with the temperature of polymerization, independently of the increase in  $k_p$ . The nitroxyl radical concentration is also critical to quasi-living polymerization: only a very small amount of living radical chain results if the concentration of nitroxyl radical is too high, and uncontrolled free radical polymerization can occur if it is too low.<sup>162</sup>

Molecular orbital calculations were used to determine the strength of the bond between a propagating macroradical chain-end and a free radical species that reversibly reacts with it. The determination of the reaction enthalpy for the addition of these SFRs to monomer (styrene) was also investigated. Kazmaier et al.<sup>163</sup> have used semiempirical molecular

calculations to model stable free-radical-mediated living polymerization reactions, and estimated  $150 \text{ kJ mol}^{-1}$  as the upper limit of the bond dissociation enthalpy for the homolysis of the end-capping fragment for a convenient propagation rate of polymerization. Kazmaier et al.<sup>163</sup> calculated BDEs on the assumption that termination reactions by recombination of radicals occur without an activation energy (cf. Section 2.2.2).<sup>164</sup> Moreover, Kazmaier et al.<sup>163</sup> did not take into account the transition state step. They also estimated, as a first approximation, that solvent effects on radical reactions could be ignored. Such a latter approximation has to be made with great care considering numerous studies on solvent effects indicating variation of termination and propagation rate constants in the radical polymerization of vinyl monomers.<sup>165</sup>

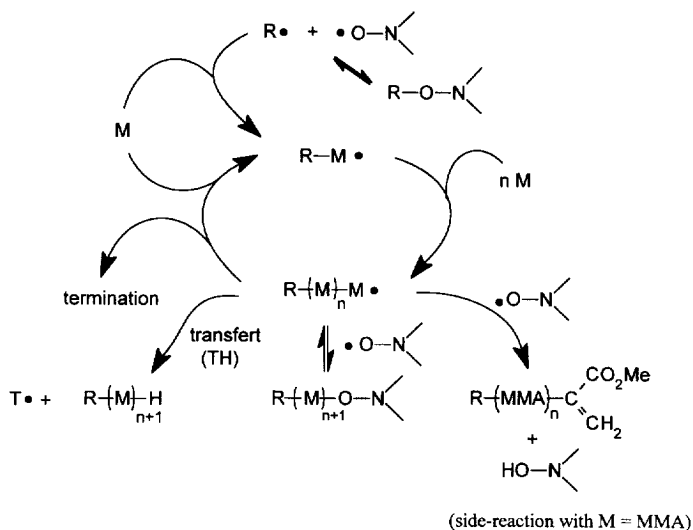
Kazmaier et al.<sup>163</sup> showed that intermediates with very high BDEs, such as the benzoyloxyl derivatives (*ca.*  $336 \text{ kJ mol}^{-1}$ ), do not form living systems. Dithiocarbamyl derivatives have generally lower BDEs ( $160 \text{ kJ mol}^{-1}$ ) but were predicted to react slowly. Their calculations suggested that the BDEs could be lowered substantially by going to very stable free radicals, such as TEMPO adducts ( $111 \text{ kJ mol}^{-1}$ ) or PROXYL adducts ( $112 \text{ kJ mol}^{-1}$ ), as the reversible capping agent.

In a conventional radical polymerization reaction, high molar mass polymer chains are obtained almost immediately and their  $DP_n$ s remain relatively constant throughout the reaction. However, polymerization in the presence of SFR initially provides materials with low molar masses, which increase with time. More importantly, the polydispersities of the corresponding polymers are considerably less than 1.5, which is the theoretical lower limit calculated for a conventional free radical polymerization process. However, in all cases, the published data consistently show the lack of truly narrow polydispersities, and the polydispersity obtained is generally proportional to the molar mass being produced.

#### 4.2.1. Use of nitroxyl radicals

Free radical polymerization processes involving the addition of stable nitroxyl radicals to the polymerization feeds have been developed to minimize termination by radical coupling and to allow control of end-group structure. The radicals formed during the initiation step are trapped by the nitroxyl radicals. The bond formed between the coupled radicals is labile, allowing further monomer to add. Polymers prepared by this process are generally oligomers which have functional groups capable of undergoing further chemical reactions to form useful materials. They have a terminal oxyamine group at one end of the chain and an initiator residue at the other end, and, depending upon the monomers used, may have chemically reactive functional groups along the chain. Removal of the oxyamine end-group may also be achieved to yield a stable functional group at the end of the polymer chain. For example, reduction by Zn/AcOH gives both an  $\omega$ -hydroxy terminated polymer and hydroxylamine, which can be reoxidized to the nitroxyl radical. Reaction with hydrogen donors, e.g. thiols, gives the corresponding  $\omega$ -hydrogenated polymer. When the last monomer unit is MMA, the  $\omega$ -aminyloxyl polymer can also decompose to form an  $\omega$ -(2-methoxycarbonyl-2-propenyl) macromonomer. Another key feature of the  $\omega$ -aminyloxyl polymers is that they can be isolated, stored at room temperature, and then subsequently used for further reaction, as, for example, in chain extensions to prepare higher molar mass polymers.

The use of nitroxyl SFRs to trap carbon-centred radicals<sup>166–168</sup> and the extension to radical polymerization to trap growing polymer chains were first demonstrated by Solomon



Scheme 16.

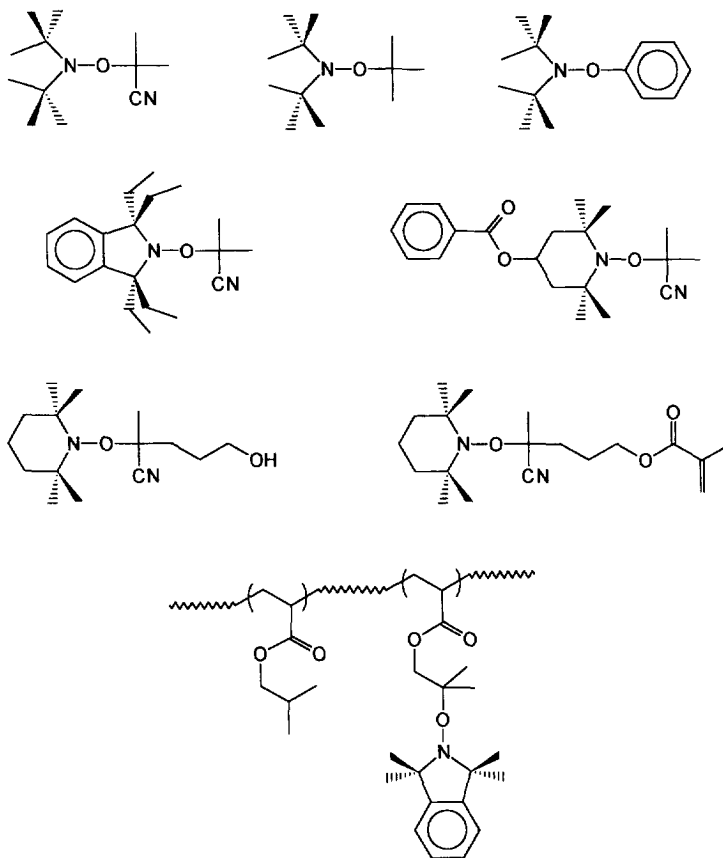
et al.<sup>169-172</sup> for the synthesis of oligomers, primarily acrylates. TEMPO was used in most of the work, but other stable nitroxyl radicals were also used. Nitroxyl radicals may be readily prepared by the oxidation of the appropriate secondary amine or hydroxylamine, reduction of the appropriate nitro or nitroso compound, or by the addition of free radicals to nitrones. Alternatively, the alkoxyamine initiators can be either prepared or generated in situ by the addition of a source of free radicals to a suitable nitroxyl radical, either in the presence of an unsaturated monomer or with the monomer being added after the free radicals have reacted with the nitroxyl SFR. The free radicals can be generated by any of the methods well known in the art, e.g. by decomposition of an azo compound, by scission of an alkoxy radical or by H atom abstraction from a suitable monomeric or polymeric compound, or by addition of a free radical to an olefin (macroradicals). While nitroxyl radicals do not react with oxygen-centred radicals, they do react with carbon-centred radicals with bimolecular kinetics to form stable adducts, and the rates of these reactions are nearly diffusion controlled.<sup>173</sup>

The quasi-living polymerization scheme<sup>161,171</sup> based on nitroxyl radicals is believed to proceed according to Scheme 16. It consists of first forming an initiator-nitroxyl adduct, R-O-N<, where R• is an initiating radical fragment derived from an azo initiator, such as AIBN, and •O-N< represents the nitroxyl SFR. The R-O-N< adduct is optionally isolated and purified, then added to monomer to initiate polymerization by thermal homolysis of the R-O bond. For several years, this process has been used to synthesize end-functional and narrow polydispersity homopolymers<sup>162,171,174-176</sup> and various block copolymers<sup>13,171,177</sup>. Detailed computer calculations of the kinetics of these polymerizations were also performed, based on acrylate polymerization.<sup>176</sup> It appeared possible to control the polymerization processes by selecting alkoxyamines with appropriate substituents, the polymerization temperature, and the amount and type of monomer(s) added at any one time. The lability of the C-ONR<sub>2</sub> bond depends essentially on the substituents on the carbon atom. Polar substituents, such as those encountered in the polymerization of acrylics and vinyl

acetate, as well as sterically crowded tertiary species, led to homolytic cleavage at temperatures below 100°C. However, with the polymerization of styrene, temperatures above 120°C were required in order to ensure sufficient dynamics of the exchange process, but thermal polymerization of styrene was also observed at this temperature. To decrease self-initiation, the best solution is to increase the lability of the C–ONR<sub>2</sub> bond in order to perform the polymerization at sufficiently low temperatures. Several methods were attempted to increase the rate of homolytic cleavage and to shift the position of the equilibrium between active and dormant species without increasing the reaction temperature. Homolysis rates increase with ring size of the nitroxide fragment (for the cyclic nitroxides). Alkoxyamines based on the open chain nitroxyl moiety, i.e. di-*tert*-butyl nitroxyl radicals, offer the fastest homolysis rates. An increase in size of the substituents  $\alpha$  to the nitroxide nitrogen was also shown by Moad and Rizzardo to result in enhanced homolysis rates.<sup>178</sup> The effects of additives or structural changes within the nitroxyl radical can be checked by comparison of the overall rates of polymerization (which are proportional to the concentration of the growing radicals) and by the analysis of the evolution of molar mass vs conversion. TEMPO-type, PROXYL-type and DOXYL-type nitroxyl adducts were predicted to exhibit rather fair BDEs (59–109, 71–113 and 105–121 kJ mol<sup>-1</sup>, respectively), involving an efficient livingness for the corresponding radical polymerization.<sup>163</sup> A major advantage of the alkoxyamines process over other end-capping techniques is also that nitroxyl radicals are completely inert toward most monomers under classical polymerization conditions.<sup>172</sup> Indeed, nitroxyl adducts were estimated to be endothermic with regard to addition to styrene (4–42, 8–30 and –4–33 kJ mol<sup>-1</sup>, respectively).<sup>163</sup>

Solomon, Rizzardo and Caccioli<sup>171</sup> pioneered and patented the use of thermally unstable alkoxyamine initiators involving various nitroxyl radicals as end-capping agents. They are generally prepared by decomposition of an azo compound in the presence of these nitroxides. Polymerization proceeds on thermal activation, the terminal C–O bond being homolysed to release carbon-centred radicals, which initiate polymerization, and a stable alkoxy radical. These reactions generally operate at temperatures close to 80–100°C (for di-*tert*-butylnitroxyl derivatives) and higher temperatures, which are determined by the half-life of the alkoxyamine involved. Typically,  $t_{1/2}$  lies between 8 and 120 min at 60°C, depending on the solvent employed. Suitable groups for N–O–R include *t*Bu, cyanopropyl, phenyl, methyl and others. A wide range of alkoxyamines is reported, including functionalized initiators and polymer supported, grafted initiators (Scheme 17). The patent proceeds to describe the preparation of (co)oligomers of MMA, acrylates, styrene, VA and methacrylonitrile, as well as the production of block and graft architectures. Typically, low yields of polymer are obtained, e.g. < 20% of an oligomeric product. Thus,  $\omega$ -nitroxyl oligomers are first isolated from the reaction mixture and then added to a second monomer. A range of graft copolymers was also prepared by the use of polymers containing alkoxyamine side-groups, including poly(MA-*g*-St), poly(MMA-*g*-St), poly(butadiene-*g*-MA) and poly(isoBMA-*g*-EA). The chain ends can also be functionalized to produce macromonomers (Scheme 17).

The key to such SFR-moderated living polymerizations is the enhancement of reversible termination between the SFR and the living chain. The polymerization kinetics were predicted for different values of the propagation rate constant and other experimental conditions. Moad, Solomon et al. showed that, while the dissociation of the SFR–polymer adduct has a rate constant of 10<sup>-2</sup>–10<sup>-5</sup> (M s)<sup>-1</sup> for the polymerization of acrylates, the larger value gives the fastest rate and the narrowest polydispersity.<sup>176</sup> However, even when the rate constant is

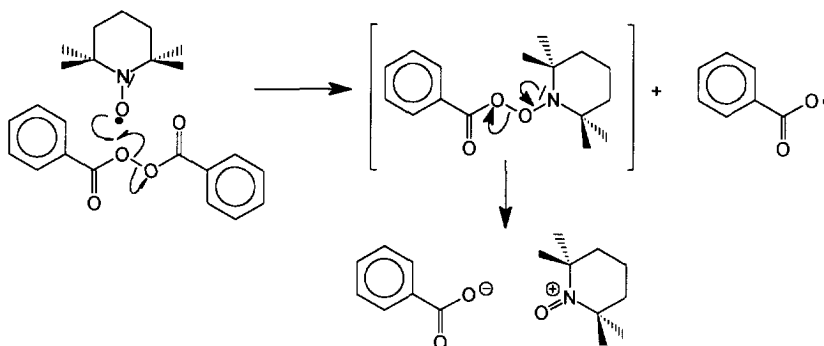


Scheme 17.

close to  $10^{-2} \text{ (M s)}^{-1}$ , there is initial formation of high molar mass polymer since polymerization is very fast at first (when the concentration of SFR is still low).

The system proposed by Solomon and Rizzardo exhibits some severe limitations. Indeed, the values of the rate constants for initiation and propagation are of the same order of magnitude, resulting in higher polydispersities than those obtained with living anionic polymerization. Fair yields are obtained in each polymerization step and there is need for multiple separations. Moreover, some characteristics of 'living' systems have been shown only for low conversions and should be extended to polymerizations conducted at useful higher conversions (cf. the criteria for growth-controlled polymerization in Section 2.4).

Georges et al.<sup>162</sup> also described the use of stable free nitroxyl radicals in the production of narrow molar-mass polystyrene and poly(styrene-*co*-butyl acrylate)<sup>179,180</sup>. Polymerizations were carried out in bulk, solution or suspension. Benzoyl peroxide was used as the initiator for the majority of the work, yielding conversions of 90% in bulk. Narrow polydispersity PS was obtained when the reaction mixture was heated at 125°C for 21–69 h, with a TEMPO to BPO ratio of 1.3<sup>179</sup>. Samples removed from the reaction mixture over the course of the reaction showed increasing molar masses  $M_n$  (from 1.7 to  $8.7 \times 10^3 \text{ g mol}^{-1}$ ) and with fairly

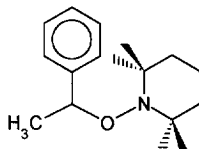


Scheme 18.

constant polydispersity (*ca.* 1.2–1.3). Growing PS chains were proposed to be reversibly deactivated by scavenging TEMPO radicals, thus substantially reducing irreversible termination that prematurely stops chain growth. It was also assumed that new initiating radicals generated by thermal processes have some effect on molar masses and polydispersities. The kinetics of the polymerization do show a linear increase in  $M_n$  with time, after an induction period. The rate of reaction between the propagating chain and TEMPO is nearly diffusion controlled, while the rate of breakage of the TEMPO–styrene O–C bond is slow. Thus, 69 h at 133°C was necessary to reach 90% conversion,<sup>162</sup> suggesting that the rate constant for the release of TEMPO (and growing chains) is *ca.* 3 (M s)<sup>-1</sup>, which is much larger than the 10<sup>-2</sup> (M s)<sup>-1</sup> upper limit suggested for the quasi-living polymerization of acrylates based on SFR-terminated initiator.<sup>176</sup> The unusually narrow polydispersity can be attributed to the fast initiation by a redox process in which phenyl radicals are formed by decomposition of BPO promoted by TEMPO. Georges et al.<sup>181</sup> determined the activation energy for the SFR-induced BPO decomposition close to 40 ± 5 kJ mol<sup>-1</sup>, which must be compared to about 120 kJ mol<sup>-1</sup> for thermal decomposition. Thus, the TEMPO-promoted decomposition of BPO dominates over the thermal BPO decomposition under the conditions of the first step of the quasi-living polymerization (Scheme 18). After 3.5 h at 95°C the TEMPO radical concentration remained constant, suggesting that all the BPO had been consumed.

Georges et al. hypothesized that the lack of ability to make truly monodisperse PS with nitroxyl-mediated styrene polymerization was caused by continuous initiation of new PS chains during the polymerization. Indeed, autopolymerization of styrene was shown to occur at temperatures above 100°C, even in the presence of TEMPO.<sup>182–184</sup> To achieve narrow polydispersity, Georges et al. added organic acids such as benzoic acid or camphorsulphonic acid (CSA) to inhibit the spontaneous polymerization of styrene. Benzoic acid appeared even more effective than CSA at controlling the polydispersity. Indeed, protonic acids reduce the rate of self-initiation of styrene and lead to more well-defined systems.<sup>185,186</sup> The acid/peroxide ratio is critical: if too much acid is used, the MWD broadens significantly. Moreover, Georges et al. discovered that CSA did more than just inhibit spontaneous styrene polymerization. CSA appears to make the nitroxyl–polystyryl adduct more labile. Moreover, acids can also catalyse the formation of Diels–Alder adducts and may lead to cationic polymerization and/or the formation of indan-type dimers.

Recently, Georges et al.,<sup>187,188</sup> concerned over environmental problems, developed an

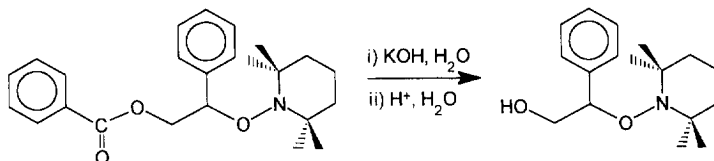


Scheme 19.

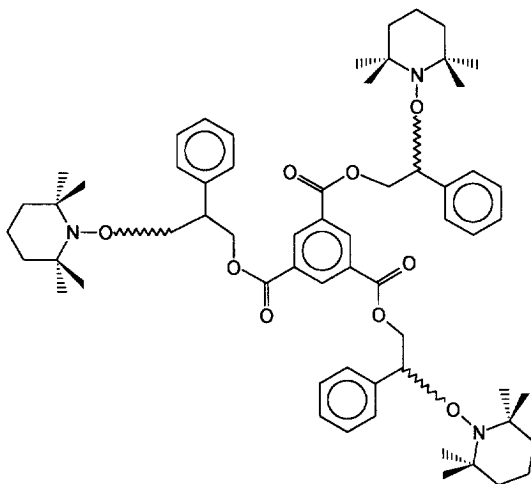
SFR-type polymerization process that allows access to narrow-polydispersity water-soluble poly(styrenesulphonate, sodium salt)–TEMPO terminated polymers. Narrow polydisperse water-soluble polymers cannot be prepared directly by conventional living polymerization systems. Functional groups which impart water solubility to monomers and polymers are not compatible with ionic polymerization systems, which requires these groups to be protected prior to polymerization and deprotected thereafter. Solution polymerizations involving the sodium salt of styrenesulphonic acid were performed in the presence of TEMPO, in water/ethylene glycol solution (20/80 w/w), at 125°C. The molar mass of polymers can be varied from very low to very high (e.g., from 8 to  $900 \times 10^3 \text{ g mol}^{-1}$ ) while maintaining narrow polydispersities (ca. 1.12–1.33), with conversions in the range 25–97%.

Priddy et al.<sup>189,190</sup> studied the kinetics of decomposition of 2,2,6,6-tetramethyl-1-(1-phenylethoxy) piperidine (TMPEP, Scheme 19). They determined that TMPEP decomposed following first-order kinetics with activation energies of 119 and 101  $\text{kJ mol}^{-1}$  in 1,2,4-trichlorobenzene and DMSO-*d*<sub>6</sub>, respectively. Implications of TMPEP for nitroxyl-mediated styrene polymerization were also examined in both neutral and acidic conditions.

Hawker et al.<sup>174,191</sup> also developed numbers of functionalized unimolecular initiators containing a covalently attached TEMPO unit, which are also capable of accurate macromolecular control in the preparation of telechelics by quasi-living radical polymerization. Initially, Hawker<sup>174</sup> prepared the unimolecular initiator 2,2,6,6-tetramethyl-1-(2-benzoyloxy-1-phenylethoxy) piperidine (TMBPEP) by reaction of benzoyl peroxide and TEMPO in a large excess of styrene, and also 2,2,6,6-tetramethyl-1-(2-hydroxy-1-phenylethoxy)-piperidine (TMHPEP) by hydrolysis of the former initiator (Scheme 20). Telechelic polystyrenes containing hydroxy, carboxy or carbonyl groups were prepared. Accurate control of the chain ends is a result of essentially all chains being initiated by TMBPEP or TMHPEP and the capping of the corresponding growing macroradicals by a TEMPO unit. These polymers were also employed to form graft and triblock systems with condensation polymers such as polyimides. Hawker<sup>192,193</sup> also prepared multifunctional initiators to form complex architectures, such as star and graft polymers, with a high degree of structural control. Thus, a trifunctional initiator was recently reported and used in the polymerization of styrene to yield the corresponding 3-arm star ( $M_n = 16\,500$ ,  $M_w/M_n = 1.20$ ) (Scheme 21).

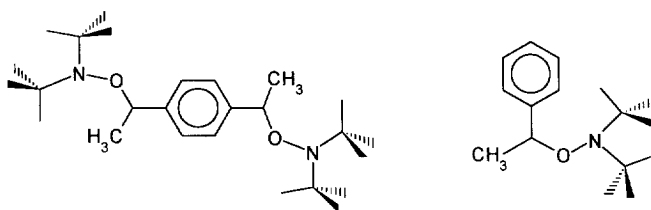


Scheme 20.



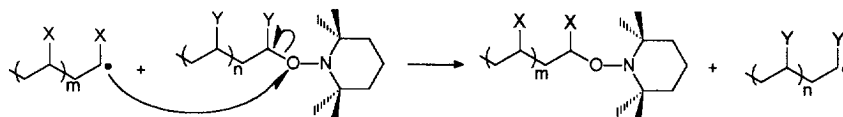
Scheme 21.

Catala et al.<sup>194,195</sup> polymerized styrene in bulk at 90°C in the presence of either a mono or a diradical initiator containing thermoreversible bonds, i.e. one or two di-*tert*-butyl nitroxyl adducts (Scheme 22). Di-*tert*-butyl nitroxyl adduct provides a significantly faster polymerization reaction than with the TEMPO system under the same reaction conditions (more than three times faster per growing chain) while maintaining a narrow polydispersity. BDE and reaction enthalpies for addition of di-*tert*-butyl nitroxyl radical to styrene were calculated to be between 71 and 92 kJ mol<sup>-1</sup> and between 21 and 33 kJ mol<sup>-1</sup>, respectively.<sup>163</sup> The propagation reaction occurred at both ends of the polymer chain to yield difunctionalized oligomers. The authors considered the radical process as ‘living’ on the basis of the linear evolution of monomer consumption and the monotonic variation of molar mass with time. The conversion vs time plots point to a particular behaviour of the radical mechanism: the same straight line was obtained for different initiator concentrations, implying that the polymerization rate stays independent of the initiator concentration. Catala et al.<sup>194</sup> proposed the possibility of a high degree of association between the dormant species through their chain ends; a degree of association higher than 10 was hypothesized to explain the behaviour of the kinetics. The possibility of such an association seems, however, difficult to understand if one



Scheme 22.



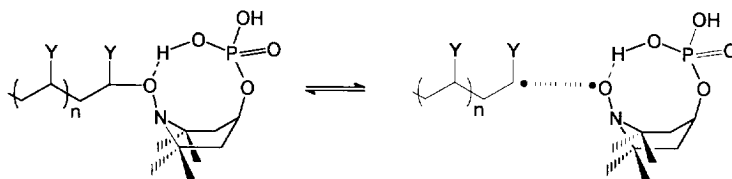


Scheme 23.

considers the low difference of polarity of species involved (this behaviour has been very recently discussed by Matyjaszewski and Fukuda; see Section 6).

Matyjaszewski et al.<sup>8,196</sup> investigated the system proposed by Georges by using nitroxyl radicals in the thermal autopolymerization of styrene, in the absence of any added radical initiators. The radicals generated thermally were initially scavenged by TEMPO, forming alkoxyamines bonded by oligomeric PS growing chains. When the concentration of thermally generated radicals became comparable to, or exceeded,  $[\text{TEMPO}]_0$ , polymerization could proceed. With increase of  $[\text{TEMPO}]_0$ , induction periods increased and the reaction became slower, following a typical pattern for inhibition. Alkoxyamines are thermally unstable at temperatures higher than  $120^\circ\text{C}$  and can reversibly decompose, generating PS radicals and releasing TEMPO. After addition of the first monomer molecules, polystyryl radicals were reversibly trapped by TEMPO to form dormant alkoxyamines. Because radicals are continuously generated, it is also possible that they may react with dormant alkoxyamines in the degenerative transfer processes (Scheme 23). Indeed, Matyjaszewski et al.<sup>8,196</sup> believed that the rather narrow polydispersity obtained by the addition of TEMPO to spontaneous styrene polymerization was not due to homolysis of the TEMPO–polystyryl adduct but, instead, the radicals formed continuously during styrene conversion, reacting in a transfer process with the polymeric oxyamines (Scheme 23). Such a process would result in an averaging of chain lengths. A finding that tends to support this hypothesis is that the dispersity actually narrows with increasing polymerization temperature.<sup>8</sup>

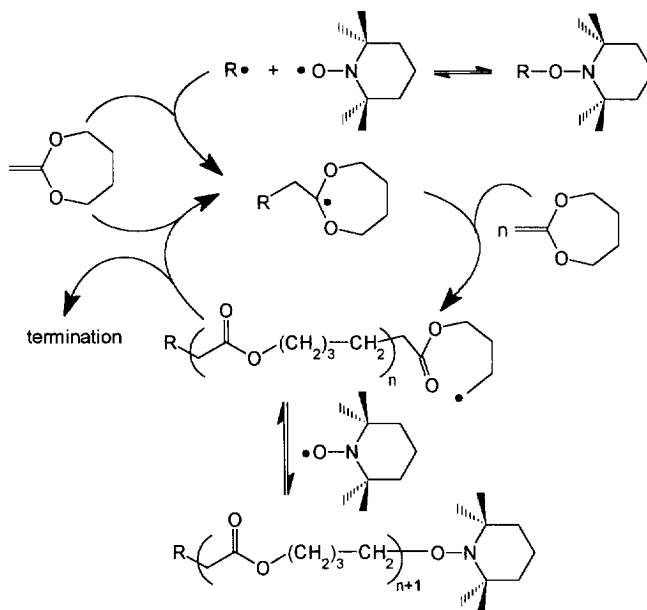
The unimolecular and bimolecular exchange reactions allow the simultaneous and almost linear growth of all chains with conversion and the preparation of polymers with low polydispersities. However, Georges et al.<sup>182</sup> claimed recently that broad polydispersity PS ( $I \sim 1.9\text{--}2.6$  for 10 to 32% conversion) is always obtained when St is heated above  $100^\circ\text{C}$  in the presence of TEMPO with no added acid. Matyjaszewski et al.<sup>197</sup> have used different solvents and found that increasing solvent polarity from decaline to bulk styrene and to diglyme had very small effects on both the kinetics and molar masses. However, addition of H-bonding species such as alcohols greatly affected the rate of polymerization. This phenomenon was explained by the H-bonding to alkoxyamine, facilitating homolytic cleavage. The authors also suggested that the nitroxyl radical may have become less reactive because of the H-bonding, which would be facilitated by a partial negative charge on the oxygen atom in the nitroxyl radical. Matyjaszewski et al.<sup>197</sup> followed this observation by using nitroxyl radicals with an attached phosphoric acid moiety. Thus, the rate of polymerization of styrene increased significantly when TEMPO was substituted as 4-(TEMPO)phosphoric acid. At the same time, molar masses did not change substantially, indicating a similar number of chains in the dormant state. On the other hand, 4-hydroxyTEMPO does not act in a similar manner, probably because both N–O $\cdot$  and –OH substituents are in equatorial positions and cannot provide efficient H-bonding. The potential explanation of the hydrogen bonding in both systems is shown schematically in Scheme 24.



Scheme 24.

Matyjaszewski et al.<sup>197</sup> investigated another approach based on the complexation of nitroxyl radicals with Lewis acids and with transition metal complexes. However, the rates of polymerization for styrene and MMA initiated by AIBN in the presence of 4-phenyl-2,2,5,5-tetramethyl-3-imidazolin-1-yloxy-3-oxyl free radicals were reported to be only very weakly affected by the addition of transition metals such as manganese (II) hexafluoroacetylacetonate. The rate of MMA polymerization was reported to be accelerated twofold by the addition of an equimolar amount of the manganese salt, but the rate of styrene polymerization was reduced in the presence of manganese salts.

Georges et al.<sup>175,183</sup> also studied the kinetics of the high temperature SFR-moderated polymerization of styrene. The first step of the quasi-living polymerization supports the coupling of a TEMPO radical with an initiated free-growing polymer chain. It involves the reaction of benzoyl peroxide, styrene and TEMPO at  $[\text{TEMPO}]_0/[\text{BPO}]_0$  ratios close to 1.2 at 95°C. TEMPO and BPO disappear rapidly by a bimolecular reaction to furnish the corresponding adduct (see TMBPEP, Scheme 20), with a rate given by  $k_{id}[\text{TEMPO}][\text{BPO}]$ , where  $k_{id}$  is the rate constant for this induced decomposition. This promoted decomposition occurs in addition to the usual thermal decomposition of BPO (with a rate given by  $k_d[\text{BPO}]$ ).<sup>162,181</sup> The initial rate of disappearance of TEMPO in the presence of BPO was also determined in styrene or toluene (as a control).<sup>83</sup> TEMPO couples with carbon-centred radicals with a rate constant  $>10^{-9} (\text{M s})^{-1}$ , while initiating radicals from BPO are produced with  $k_d < 10^{-1} \text{ s}^{-1}$  even at 150°C. Thus, the kinetics are consistent with the following picture: a TEMPO radical immediately couples to each initiated polymer chain, so that there is only a very small steady-state concentration of free polymer chains. Furthermore, it is preferable to work at high temperatures, where  $k_d$  is much larger than  $k_{id}$ , thereby consuming less TEMPO. The second step of the quasi-living polymerization, which takes place at higher temperatures (propagation occurs at 125°C), is controlled by the reversibility of polymer chain termination by TEMPO. As the reaction temperature is increased, the lability of the bond between TEMPO and the polymer chain increases, resulting in the production of free polymer chains that can undergo polymerization and add monomer with a rate constant,  $k_p$ , supposedly unaffected by the presence of TEMPO radical. Moreover, further experiments demonstrated that if TEMPO, BPO and styrene are directly heated to higher temperatures than 120°C, narrow polydispersity polymers still result.<sup>162</sup> Indeed, at high temperatures, induced decomposition is no longer important since thermal decomposition is extremely rapid. At 133°C, the half-life of BPO is only 3 min, and it is less than 20 s at 150°C. Also, there is a comparatively large amount of TEMPO at the start of the reaction, as TEMPO is present in a greater than 1.2:1 molar ratio with BPO, whereas very little of the BPO has initiated growing chains. Thus, unlike the SFR-adduct-initiated system proposed by Solomon, Rizzardo et al.,<sup>171,176</sup> Georges



Scheme 25.

et al. claimed that there is no formation of high molar mass material at the start of the reaction.

Free radical addition–fragmentation polymerization (also incorrectly termed ring-opening polymerization) has been the focus of great interest because functional groups such as esters, amides and carbonates can be incorporated into the backbone of chain polymers and a low volume shrinkage from monomer to polymer can be achieved.<sup>29,80,198</sup> Wei et al.<sup>199</sup> recently proposed the first example of quasi-living free radical addition–fragmentation polymerization of a cyclic ketene acetal using the method involving stable nitroxyl free radicals (TEMPO). They demonstrated that 2-methylene-1,3-dioxepane undergoes a free radical polymerization with quantitative ring opening in the presence of TEMPO with di-*tert*-butyl peroxide (DBPO) as initiator to yield polyesters with a good control of the growth of the polymer chain. Wei et al.<sup>199</sup> observed a clear trend of decreasing polydispersity with increasing [TEMPO]/[DBPO] ratio. At [TEMPO]/[DBPO] ratios of 1.4, 1.6 and 1.8, polydispersities of the polymers were found to be 1.5, 1.3 and 1.2, respectively. These observations were explained according to the mechanism shown in Scheme 25.

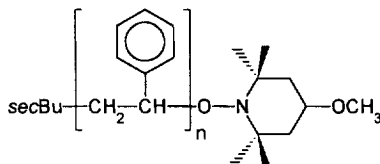
Initiation of the addition–fragmentation polymerization of the ring monomers is accomplished by homolysis of DBPO to *tert*-butoxyl free radicals, which afford propagating chain radicals after addition to the ring monomers. These chain radicals are believed to be reversibly capped with TEMPO radicals, and an equilibrium between dormant (capped) and activated (uncapped) chain ends is reached (see Scheme 25). The bond between the propagating radical and TEMPO is sufficiently labile at the high polymerization conditions (125°C) to allow for polymer growth mainly by the reaction of the activated chain ends with incoming monomers. At high concentrations of TEMPO, the stationary concentration of activated

radicals remains low and the occurrence of chain transfer and termination reactions is believed to be negligible.

Wei et al.<sup>199</sup> also observed that the molar mass of the polymer progressively increases with the conversion of monomer and that both  $M_w$  and  $M_n$  of the polymers initially increased as the [TEMPO]/[DBPO] ratio was increased, reaching a maximum at the ratio 1.0, and then decreased as the ratio increased further. The initial increase can be attributed to the occurrence of conventional, non-living chain propagation at the low TEMPO concentrations. That is, an insufficient amount of TEMPO is present in the system to cap all the propagating chain ends. Since uncapped chains propagate at much faster rates than their capped counterparts, the majority of the monomer in these systems is probably consumed by the uncapped chains. Thus, the polymerization effectively becomes a conventional free radical polymerization with TEMPO serving only to decrease the initiator efficiency, leading to an increase in molar mass. Further, the probability of chain transfer and termination reactions occurring in these systems is high which would explain the initially broad polydispersity. As the concentration of TEMPO is increased, the stationary concentration of uncapped chains decreases until finally, at a ratio of approximately 1.0, all the propagating chains become capped and the polymer propagates mainly by the quasi-living mechanism. After this point, the molar mass begins to decrease due to an increase in initiator efficiency. Because the chain ends have to be activated by the thermal uncapping process for further growth, the overall rate of propagation becomes slower relative to initiation. This expected decrease in the propagation rate is consistent with the observed decrease in the polymer yield as the [TEMPO]/[DBPO] ratio is increased. It has to be noticed that the availability of these living polymers could provide the synthesis of new and well-controlled polymeric materials (especially functional block copolymers) by the combination of addition-fragmentation monomers and conventional ones, e.g. vinylic monomers.

Several investigations on the transformation of living anionic to free radical polymerization have been performed by modification of the anionic propagating end. Richards et al. reported that reaction of the anionic living PS with triethyllead chloride<sup>200</sup> or with bromine<sup>201</sup> led to free radical species. However, these radical polymerizations do not exhibit any living characteristics. Endo et al.<sup>202</sup> recently proposed the synthesis of  $\omega$ -aminoxyl following the reaction of various cationic poly(vinyl ether)s with 1-oxo-4-methoxy-2,2,6,6-tetramethylpiperidinium salt (OAS). However, no block copolymer was produced upon heating the resulting functionalized polymer with MMA, due presumably to thermal stability of the primary C–O bond located between the aminoxyl and the end of the poly(*isobutyl vinyl ether*).

To verify such a hypothesis, the aminoxyl fragment was quantitatively grafted to a PS chain-end by the reaction of 4-methoxyTEMPO with poly(styryl-lithium) having a controlled molar mass and a very narrow molar mass distribution.<sup>203</sup> The  $\omega$ -aminoxyl PS caused the homolytic scission at the C–O terminal bond upon heating, due to the relatively stable benzyl radicals produced (Scheme 26). Thus, radical polymerization of MA, EA, and *n*BA were carried out with PS–O–N< (Scheme 26) as a macroinitiator in benzene, at 120°C for 6 h, to yield the corresponding poly(styrene-*b*-alkyl acrylate)s with a conversion of these acrylate monomers to polymers close to 15% (MA), 67% (EA) and 20% (*n*BA). This scission was suggested to be reversible, according to the fact that the radical polymerization of EA initiated by PS–O–N< did not proceed in the presence of the 3- equivalent of 4-methoxy-TEMPO.



Scheme 26.

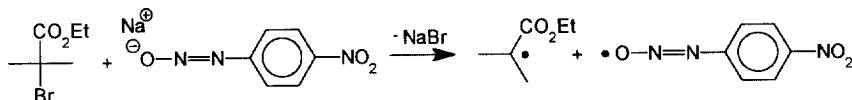
#### 4.2.2. Use of (aryloxy) radicals

Druliner reported and patented a variant of Solomon's chemistry<sup>204,205</sup>. He proposed a series of electron-transfer initiators which give rise to long-lived oxygen-centred radical species (radicals YO<sup>•</sup>), end-capping the propagating (meth)acrylate chain ends.

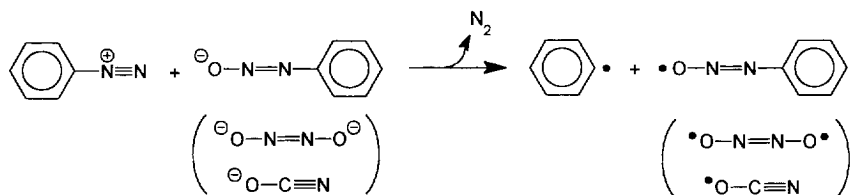
These (aryloxy) radicals are generated in two ways. The first method involves electron transfer between activated carbon-halogen compounds and arenediazoate anions (Scheme 27). This process gives rise to carbon-centred radicals which initiate monomer polymerization, and to (aryloxy) radicals which can recombine reversibly with the growing end of the chain. Quasi-living radical polymerization conditions were observed only when activated alkyl halides (e.g. those containing at least one electron-withdrawing group on the carbon atom paired to halogen) are used, even though radical polymerization of (meth)acrylates is possible with aliphatic alkyl halides. The second method involves a one-electron oxidation of arenediazoate, hyponitrite or cyanate anions by reaction with arenediazonium ions (Scheme 28). Aryl radicals then initiate polymerization of the monomer, and the corresponding stabilized oxy radical is associated with the growing end of the polymer (Scheme 29).

The long-lived nature of these chain-ends makes it possible, in some cases, to prepare block copolymers from sequential polymerization of MA, BA and MMA. Reactions are conveniently carried out over a temperature range of 25–40°C, in a variety of solvents, and are tolerant of aqueous media. The conversion is also high and the system is applicable to a wide range of monomers, including (meth)acrylates and chloroprene. The plot of the variation of the molar mass vs conversion in the radical polymerization of acrylate shows a linear growth in molar mass up to 40% conversion. The time/conversion plot for the same experiment suggests a slowing down of the rate at about 40% conversion, which may indicate the presence of termination reactions.

Kazmaier et al.<sup>163</sup> estimated by molecular orbital calculations (MOPAC) that the bond dissociation energy for Ph-N=N-O-PMMA homolysis was about 117–142 kJ mol<sup>-1</sup>. This bond dissociation enthalpy appeared slightly higher than those obtained with most of the ω-nitroxyl PMMA. However, this value is lower than that of iniferter homolysis and so is



Scheme 27.



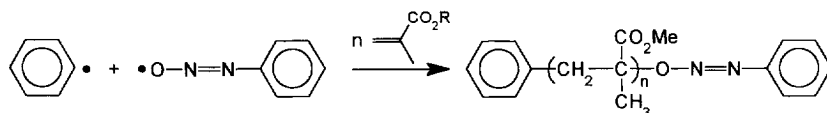
Scheme 28.

consistent with the 'livingness' of this system and the formation of block copolymers. Moreover, reaction enthalpies for the addition of (aryloxy) radicals to styrene were predicted to be fairly endothermic ( $-4$  to  $17 \text{ kJ mol}^{-1}$ ).

### 4.3. Atom transfer radical polymerization

Atom transfer radical addition is known as an efficient method for C–C bond formation in organic chemistry<sup>72,206</sup> and organometallic synthesis<sup>207</sup>. Wang and Matyjaszewski<sup>208</sup> reported that metal-catalysed atom transfer radical addition can be successfully applied to radical polymerization processes to control the growth of chains. For example, an alkyl chloride, 1-phenylethyl chloride, was proposed as an efficient initiator and a transition-metal halide, CuCl, complexed with 2,2'-dipyridyl ligands, was shown as an efficient chlorine atom transfer promoter. These systems yield, at  $130^\circ\text{C}$ , well-defined polymers with controlled molar masses and fair polydispersities ( $M_w/M_n = 1.3\text{--}1.45$ ). Block copolymers of styrene and (meth)acrylates were also produced.

Various other initiating systems based on a wide range of alkyl halide/transition metal species (viz. CuCl/coordination ligands) were also used for the controlled radical polymerization of vinyl monomers such as acrylics, styrenics and dienes<sup>209,210</sup>. The molar mass linearly increases with monomer conversion in these systems, which are different from typical redox radical telomerizations involving transition-metal species<sup>211</sup> (the molar mass does not increase with conversion in that case). In atom transfer radical polymerization (ATRP), the polymeric halides,  $\text{R}-(\text{M})_n\text{-X}$ , behave as *dormant* species and can be repeatedly activated by transition metal species,  $(\text{Met})^p$ , to give the growing radicals,  $\text{R}-(\text{M})_n\cdot$ . Oxidized transition metal species,  $(\text{Met})^{p+1}$ , can further react with  $\text{R}-(\text{M})_n\cdot$  to regenerate  $\text{R}-(\text{M})_n\text{-X}$  and  $(\text{Met})^p$ , i.e., a *reversible* transfer process.<sup>212</sup> In contrast to ATRP, the redox radical telomerization represents a degradative transfer process in which the resulting polymeric halides,  $\text{R}-(\text{M})_n\text{-X}$ , are *dead* chains.



Scheme 29.

#### 4.4. Polymerization via stable or persistent propagating radicals

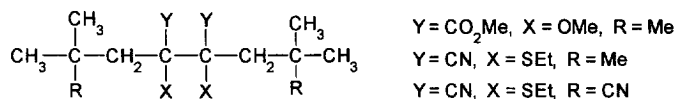
Obtaining living polymerization conditions by stabilization of a propagating radical is also possible by adding conjugated and bulky substituents to the radical centre moieties. Captodative substitution,  $\pi$ -conjugation and three-electron bonding of the radical end are typical examples of such stabilization. Arfaei et al.<sup>213,214</sup> reported a quasi-living radical copolymerization with stable radical monomers. A dinitroxyl radical, perfluoro-2,5-diazahexane-2,5-dioxy, which is stabilized by the formation of a three-electron bond, easily reacts with fluoro-olefins such as hexafluoropropylene to give an equimolar alternating copolymer with stable living nitroxyl ends and a molar mass of  $1.3\text{--}29 \times 10^3$  at room temperature. Introducing  $\text{SO}_2$  gas into the resulting copolymer gives a block terpolymer containing  $\text{SO}_2$  units. Iwatsuki et al.<sup>215</sup> observed living radicals in a similar system, viz. in spontaneous polymerization of 1-methylcycloheptene with  $\text{SO}_2$ . Similarly,  $\alpha,\alpha,\alpha',\alpha',2,5$ -hexachloro-*p*-xylylene also provides an alternating copolymer with styrene, where the radical end derived from the xylylene is stabilized by steric hindrance and  $\pi$ -conjugation.<sup>216</sup> These polymerizations proceed through a quasi-living radical mechanism. Therefore, the growing ends can be preferentially protected by thermodynamically stabilized nitroxyl and phenoxy radicals. That is, the propagation step giving these stable radical ends should be very fast in both polymerizations. Zutty et al.<sup>217,218</sup> studied the spontaneous copolymerization of bicyclo[221]-hept-2-ene and  $\text{SO}_2$  by ESR measurements and their results support the existence of 'living radicals'. Moreover, when the solution of this copolymerization mixture, in which both monomer components had been almost consumed during the reaction, was added to ethyl acrylate, polymerization continued, leading to terpolymer. The polymer chains contained long segments of alternating copolymerized bicycloheptane and  $\text{SO}_2$  and long segments of poly(ethyl acrylate).

#### 4.5. Polymerizations initiated by persistent radicals

There are some disadvantages to conventional azo and peroxy initiators, e.g. evolution of nitrogen gas, induced decomposition, and sensitivity to metals. Coupling dimers of persistent and/or stable radicals, however, provides unique initiators for radical polymerization. Since Gomberg's first discovery of a stable organic free radical, i.e. triphenylmethyl radical,<sup>219,220</sup> the synthesis, characterization and reaction studies of long-lived radicals have been investigated by many research groups. In order to find a system of living radical polymerization in homogeneous solution, one must try to form propagating polymer chain ends which may dissociate into a polymer with a radical chain end and a small counter-radical which must be stable enough not to initiate a new polymer chain. Such a radical polymerization would proceed via a living mechanism. As an extreme case, the polymerization can even proceed via a stepwise successive insertion of one monomer molecule into the weak bond by repeated cycles of slow dissociation, one fast monomer addition, and fast recombination. Several classes of initiators yielding polymer chains with weak bonds at their ends are described in the following sections.

##### 4.5.1. Use of coupling products of captodative substituted carbon radicals

Coupling products of captodative substituted carbon radicals dissociate at moderate

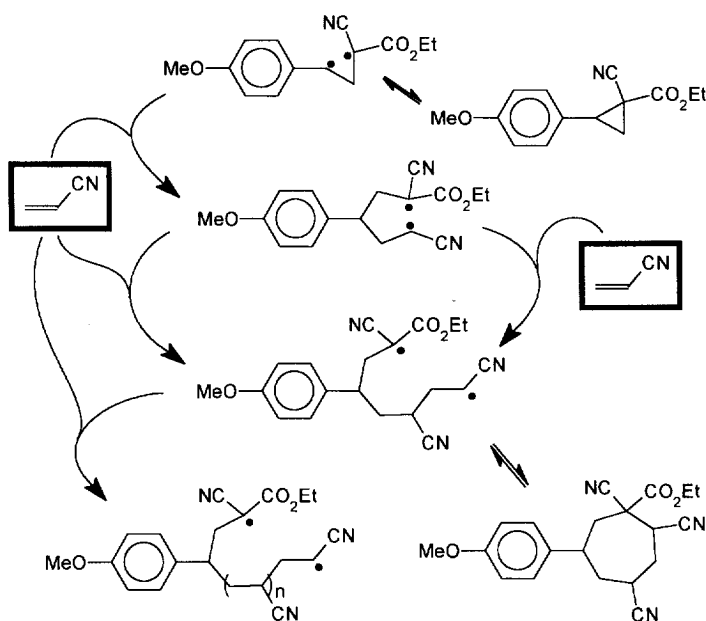


Scheme 30.

temperature (50–130°C) to initiate the radical polymerization of vinyl monomers (Scheme 30).<sup>221</sup> The bond dissociation energies of these dimers were expected to be 140–170 kJ mol<sup>-1</sup>, which is about one-half of the conventional hexaalkyl substituted C–C bond (ca. 340 kJ mol<sup>-1</sup>). The molar mass of the resulting polymers is in the range 25–40 × 10<sup>3</sup> g mol<sup>-1</sup>, suggesting no preferential primary radical termination. Even the polymerization of non-conjugated vinyl monomers such as vinyl acetate is possible with the present captodative substituted initiators, in contrast to the situation with tetraphenylethanes.

Hall et al.<sup>222</sup> demonstrated diradical propagation in the polymerization of AN by ethyl 1-cyano-2-(*p*-methoxyphenyl)cyclopropane carboxylate (ECMC) at temperatures above 80°C. The kinetic equation is  $R_p = [\text{AN}]^{1.5}[\text{ECMC}]^{0.5}$  and the apparent activation energy is very low (57 kJ mol<sup>-1</sup>). The molar mass of the polymer increases with time, and this tendency is more significant at lower initiator concentrations and at lower temperatures. Its mechanism is speculated in Scheme 31.

Diradicals generated by the addition of ECMC and AN are persistent, and some of them are further incorporated into propagation steps without giving a diamagnetic product by intramolecular coupling or disproportionation.



Scheme 31.

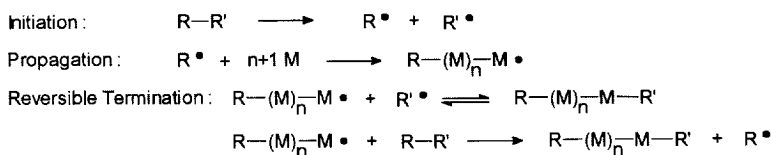


#### 4.5.2. Use of iniferters

A new class of compounds, called iniferters, was proposed in 1982 by Otsu and Yoshida.<sup>223</sup> These additives act as initiators, transfer agents and terminators. At least one of the two free radicals yielded on initiator decomposition is long lived (both radicals in the case of symmetrical compounds). Thus, the initiation of radical polymerization is very slow in most cases or even ineffectual for stable radicals. Long-lived radicals involve primary radical termination by recombination as the main reversible chain-stopping processes. Moreover, under further photochemical or thermal activations, these labile bonds are cleaved to regenerate the growing polymer chain and the counter-radical. Intermolecular homolytic substitutions on the iniferters may also temporarily terminate the polymer chain and transfer the radical activity to a new primary stable radical. The ideal polymerization mechanism is summarized in Scheme 32.<sup>224</sup>

Vinyl polymerization with iniferters is interesting as a living polymerization model in which a reversible combination of polymer radicals with stable primary radicals occurs continuously during the polymerization.<sup>223,225,226</sup> The resulting telechelic polymers initiate the polymerization of other monomers to give block copolymers in good yields.<sup>227-229</sup> Otsu and Matsumoto<sup>230</sup> proposed the use of initiators with very high reactivities for chain transfer for the insertion of monomer molecules into S-S or S-C weak bonds of the corresponding iniferters, leading to polymers with two initiator fragments.<sup>223,225,231,232</sup> Their weak bonds can be induced to dissociate thermally or photochemically, yielding radicals that further propagate the polymer chains. When the termination step in such secondary polymerizations also yields chain ends with weak bonds, reinitiation-termination cycles can repeat many times and the process has the characteristics and capabilities of living polymerization. A typical thermo-iniferter for MMA is triphenylmethylazobenzene<sup>233</sup> and typical photo-iniferters are dithiocarbamates.<sup>234</sup> In these polymerizations, the molar mass increases along with increasing conversion but the MWD is fairly broad (<2). In essence, all the chains are potentially active and so this technique can be used to produce controlled architectures. The polymerization behaviour is unique in the presence of iniferters: the iniferters are consumed at low monomer conversions, yielding oligomers that then grow into high molar mass polymers by undergoing reinitiation-termination cycles. This cycle repeats itself until the monomer is consumed. However, the usefulness of this system for the synthesis of narrow polydispersity polymers is limited by the slow rate of propagation,<sup>223,225,235</sup> the ability of the iniferter fragment to initiate new chains at any time during the course of the reaction and the loss of the iniferter fragment activity.<sup>236</sup>

Quasi-living radical polymerizations involving SFR end capping agents are mostly applicable to resonance-stabilized monomers such as styrene and methyl methacrylate, because the process requires that weak bonds be formed during termination. Ideally, the radical formed

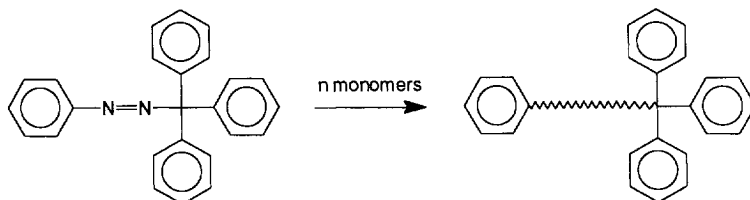


Scheme 32.

along with the propagating radical in the reinitiation step is stable and will not itself initiate polymerization. Also, termination by mutual reaction of propagating polymer chains should not occur. If these requirements are not met, the number of reinitiation–termination cycles that a polymer chain can undergo is limited, the living polymerization character of the process is diminished, and block copolymer synthesis is inefficient. The iniferter reaction has an inherent limitation for achieving all the features of the living reaction (e.g. no new chains have to be initiated by any of the intermediate species). Iniferter reagents are required both to initiate the polymerization and to reversibly capture the propagating radical to ensure the propagating species does not terminate prematurely. The reaction of dithiocarbamate radical derived from iniferter reagents with styrene is fairly exothermic and exhibits a non-negligible enthalpy of reaction ( $-46$  to  $33$   $\text{kJ mol}^{-1}$ , depending on the method of calculation),<sup>163</sup> consistent with undesirable continuous slow initiation reactions.

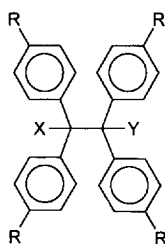
4.5.2.1. *Triphenylmethylazobenzene* — Otsu and Tazaki<sup>233</sup> examined the use of tritylazobenzene,  $\text{Ph}_3\text{C}-\text{N}=\text{N}-\text{Ph}$ , as an iniferter and reported also the use of  $\alpha$ -phenyl- $\omega$ -trityl oligomers as a monofunctional macro-iniferter in vinyl polymerization. The phenyl radical initiates polymerization and the triphenylmethyl radical acts as a radical trap. The trityl group attached to the polymer-end can further dissociate, being in equilibrium with a radical chain end, and a living radical polymerization may be performed via a monoradical mechanism. Otsu and Yoshida<sup>223</sup> showed that compounds of the phenylazotriphenylmethane type can act as a thermal initer in which the triphenylmethyl radical can act as a counter inactive radical, exhibiting a kind of living nature. One of the two polymer chain-ends is capped with the trityl group which undergoes reversible dissociation on heating (Scheme 33). The molar mass of the polymers obtained increased with conversion and this was claimed as evidence for the living nature. The use of such compounds suffers from the same disadvantages as that of the hexasubstituted ethanes (see Section 4.5.2.2), since trityl radical may slowly initiate polymerization<sup>237</sup> or undergo disproportionation with the propagating radical.

4.5.2.2. *Substituted tetraphenylethanes* — It is well known that sterically hindered C–C bonds such as those found in hexaphenylethane are easily thermally cleaved to produce trityl radicals.<sup>238</sup> But, in contrast to hexaphenylethane which is too stable to initiate vinyl polymerization,<sup>239</sup> tetraphenylethane derivatives can initiate conjugated vinyl monomer polymerization. Indeed, the  $\text{Ph}_2\text{CH}^{\bullet}$  radical was shown to participate in both initiation and termination by a kinetic study of vinyl polymerization initiated with



Scheme 33.

Table 1. Various types of tetraphenylethane derivatives



| R                                | X                              | Y                                  | Ref.    |
|----------------------------------|--------------------------------|------------------------------------|---------|
| H                                | CN                             | CN                                 | 258     |
| H                                | CN                             | CN                                 | 258     |
| H                                | C <sub>2</sub> H <sub>5</sub>  | C <sub>2</sub> H <sub>5</sub>      | 259     |
| H                                | C <sub>2</sub> H <sub>5</sub>  | C <sub>2</sub> H <sub>5</sub>      | 259     |
| H                                |                                | -(CH <sub>2</sub> ) <sub>3</sub> - | 259     |
| H                                |                                | -(CH <sub>2</sub> ) <sub>3</sub> - | 259     |
| H                                | OC <sub>6</sub> H <sub>5</sub> | OC <sub>6</sub> H <sub>5</sub>     | 260     |
| H                                | OC <sub>6</sub> H <sub>5</sub> | OC <sub>6</sub> H <sub>5</sub>     | 261     |
| H                                | OSiMe <sub>3</sub>             | OSiMe <sub>3</sub>                 | 261     |
|                                  | OSiMe <sub>3</sub>             | OSiMe <sub>3</sub>                 | 262,263 |
| OMe                              | CN                             | CN                                 | 258     |
| OMe                              | CN                             | CN                                 | 258     |
| Cl                               | CN                             | CN                                 | 264     |
| C(CH <sub>3</sub> ) <sub>3</sub> | CN                             | CN                                 | 264     |
| H                                | H                              | C <sub>6</sub> H <sub>5</sub>      | 258     |
| H                                | H                              | C <sub>6</sub> H <sub>5</sub>      | 258     |

2,2'-azobis(diphenylmethyl).<sup>240</sup> Braun et al. investigated a number of 1,2-disubstituted-1,1,2,2-tetraphenylethanes as reversible capping agents with regard to their initiation properties in free radical polymerization of vinylic and (meth)acrylic monomers, e.g. styrene and MMA, respectively.<sup>241-253</sup> Related systems were also examined by Otsu et al.<sup>254</sup> and Crivello et al.<sup>255</sup> Yamada et al.<sup>256</sup> also studied the initiation activity of oligomers terminated with stable free radicals such as 1,3,5-triphenylverdazyl or diphenylmethyl radical. Most of the polymers bearing the substituted diphenylmethyl moieties at the  $\alpha$ - and  $\omega$ -terminuses were shown to be particularly thermally unstable.<sup>241,257</sup> Several tetraphenylethane derivatives are reported in Table 1.

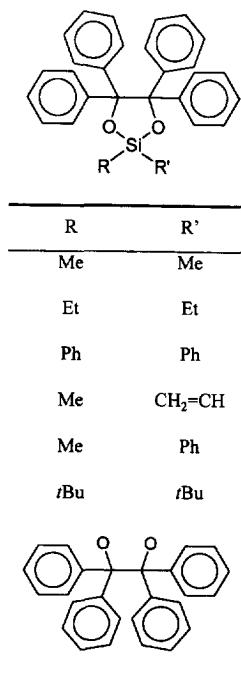
A stepwise polymerization process means that no 'dead end' polymerization characteristics are observed when using ethane initiators, in contrast to other thermolabile free radical polymerization initiators such as azo or peroxy compounds. In the initial phase of the polymerization reaction, a very high concentration of substituted diphenylmethyl primary radicals leads to the formation of short-chain telechelics with both end-groups originating from the initiator. The MMA telechelics are able to re-form radicals by the scission of thermolabile C-C bonds and by the release of initiator end groups, and so the MMA telechelics 'reinitiate' the free radical polymerization (which has been called 'resuscitatable free radical polymerization'). In St polymerization, the styrene telechelics formed in contrast to MMA telechelics are thermostable, and therefore no 'reinitiation' effect occurs. Indeed, measurements of the

thermolysis of isolated 2,2,5,5-tetraaryl-3-phenyladiponitriles exhibited no detectable thermal dissociation, even at temperatures up to 200°C.

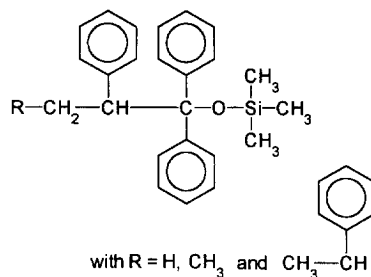
The stability of highly substituted C–C single bonds depends both on the sterical hindrance and the resonance stabilization caused by substituents. As an example, Braun et al.<sup>253</sup> estimated the thermal dissociation energy of tetraphenylsuccinonitriles to be about  $94 \pm 9 \text{ kJ mol}^{-1}$ . Therefore, quasi-living radical polymerization occurs in these systems according to the concept of iniferters. Loss of 'living' ends must occur as the diphenylalkyl radical produced from the macroinitiator also adds monomer. Otsu and Tazaki<sup>265</sup> have indicated that a further problem with these iniferters is loss of 'living' ends through primary radical termination by disproportionation. It is important in this polymerization that the end-capping radical should be persistent enough to take part preferentially in primary radical termination to form a weak covalent bond and should itself have low initiating ability toward polymerization.

The steric effects between the substituents on C–C bonds are considered as the major factors which affect the rate of homolysis of hexasubstituted ethanes<sup>266</sup> and the corresponding macroinitiators (end-capped oligomers bearing a hexasubstituted C–C bond on the end fragment). Thus, an efficient homolytic reversible equilibrium is obtained when these latter macro-iniferters are used in the radical polymerization of hindered 1,1-disubstituted monomers such as methyl methacrylate and  $\alpha$ -methylstyrene, leading to a continuous growth of the polymer chains.<sup>267</sup>

Iniferters based on cyclic silylated pinacol ethers were also investigated by Crivello et al.<sup>268</sup> Various cyclic compounds (Scheme 34), which undergo thermolysis to afford a diradical, offered a route to ABA block copolymers.



Scheme 34.

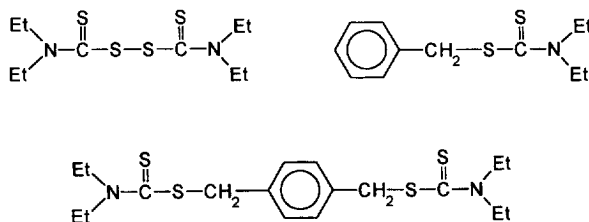


Scheme 35.

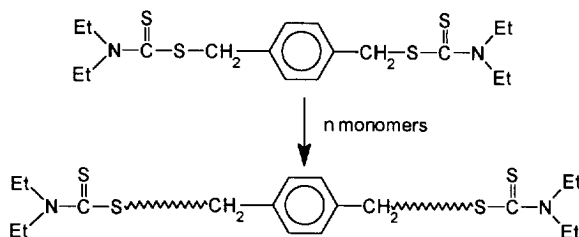
The use of small molecules to model the living chain end has shed significant light on the development of an understanding of polymerization processes. Recently, some authors<sup>262</sup> reported an investigation of the radical mechanism of styrene polymerization initiated by benzopinacolates based on the use of model compounds (Scheme 35) and showed that the process involved in such reactions cannot be called a 'living radical polymerization'.

4.5.2.3. *Disulphide derivatives* — Disulphides, including diaryl and dithiuram disulphides, were proposed by Otsu et al.<sup>269,270</sup> as photochemical iniferters. In this case, the termination of polymer chains may occur either by recombination with primary sulphur radicals or by chain transfer to the initiator itself, without any possibility of distinguishing the mechanism involved. Among organic disulphides, benzyl *N,N*-diethyldithiocarbamate, *p*-xylylene bis(*N,N*-diethyl dithiocarbamate) and tetraethylthiurame disulphide are particularly useful iniferters (Scheme 36).<sup>271-273</sup>

For the dithiocarbamates, studies on model compounds have shown that the end groups formed by addition to monomer (primary dithiocarbamates) are much less susceptible to photodissociation than benzyl or tertiary derivatives.<sup>274</sup> Therefore, the only *living* ends are those formed by primary radical termination or transfer to initiator. The disulphide iniferters suffer from the disadvantage that both of the radicals produced on decomposition of the initiator (or subsequent decomposition of the macroinitiator) may initiate polymerization. This reduces the steady-state concentration of the sulphur-centred radicals, and increases the likelihood that termination by the reaction of two propagating radicals will compete with primary radical termination. Consequently, there is a slow loss of 'living' ends. For instance, the yield of the polymerization and the molar mass of the polymer obtained increases with increasing reaction time in the photopolymerization of styrene by sulphides. In addition, the



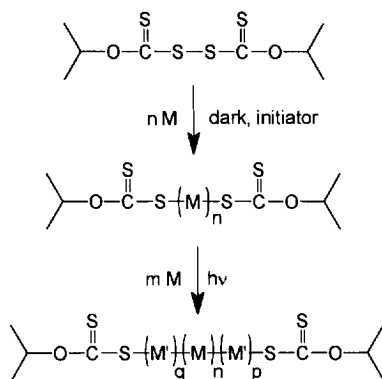
Scheme 36.



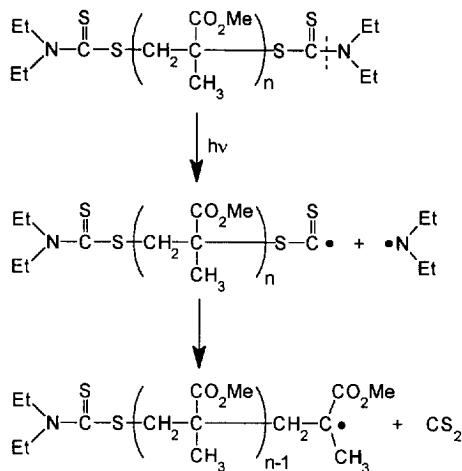
Scheme 37.

reaction of a second monomer and the isolated polymer, which is prepared by using iniferter, gives a block copolymer. However, control of the molar mass and its distribution in the resulting polymer is impossible at present, and the molar mass distribution increases with increasing conversion in this type of polymerization.

Benzyl and tertiary thiocarbamates may be used directly as photoiniters.<sup>274</sup> Photodissociation of the C–S bond affords a reactive alkyl radical (to initiate polymerization) and a less reactive sulphur-centred radical (to undergo primary radical termination). While initiation by the sulphur-centred radical cannot be completely avoided, the use of these compounds allows substantially better control of the polymerization process and greater scope for controlling polymer architecture. Otsu et al.<sup>274</sup> demonstrated the use of the mono-, di- and multifunctional initiators shown in Scheme 36. Polymers bearing dithiocarbamate end-groups were found to serve further as polymeric iniferters, i.e. macroiniferters, under irradiation of light to give AB and ABA block copolymers, star polymers<sup>270,275,276</sup> and graft polymers.<sup>277</sup> There are, however, indications that living requirements are not strictly met in the case of dithiocarbamate-initiated polymerizations. Thus, crosslinked products were obtained when styrene was polymerized using a tetrakis-(dithiocarbamate) photoinitiator,<sup>275</sup> and a statistical mixture of homopolymer and block copolymer was obtained when polystyrene with dithiocarbamate ends was used to initiate the polymerization of methyl methacrylate.<sup>283</sup> However, polymerizations initiated by mono-, di- and tetrakis-(dithiocarbamates) exhibit characteristics of living polymerizations and were used efficiently to prepare a variety



Scheme 38.



Scheme 39.

of block, multiblock, star and radical-block polymers.<sup>258,274–276,278</sup> Examples of initiating systems used for ‘quasi-living’ radical polymerization are illustrated in Scheme 37.

Niwa et al.<sup>279,280</sup> studied the use of bis(*isopropylxanthate*) disulphides for the preparation of oligomers and block copolymers of vinyl monomers with UV irradiation (Scheme 38).

Harwood et al.<sup>281,282</sup> prepared and studied the photochemical reactivity of polymers substituted with diethyldithiocarbamate, *isopropylxanthate* or mercapto-benzothiazole groups. Turner and Blevins<sup>236,283</sup> and Smets et al.<sup>284</sup> made block copolymers of styrene with MMA, using a dithiocarbamate iniferter. They reported a chain-killing reaction: irradiation of dithiocarbamate-terminated PMMA yields some CS<sub>2</sub> by homolysis of the dithiocarbamate group, thus deactivating the chain-end. They proposed a photochemical cleavage of the thiocarbamate nitrogen bond and subsequent elimination of CS<sub>2</sub> as the decomposition pathway (Scheme 39).

## 5. REPEATED REINITIATION OF POLYMER CHAINS

Another concept to access ‘controlled’ block copolymers in free radical polymerization is to consider that the termination step may be accepted as inevitable in radical processes and that compromise solutions can be found. Thus, instead of attempting to eliminate termination reactions as a means of achieving growth-controlled radical polymerization behaviour, polymer chains can be reinitiated repeatedly during the course of the reaction. Such processes have more easily achieved the desired results in polymerizations with the characteristics of those that occur without termination, but without the same precision of structure control. Three general methods for achieving repeated reinitiation are discussed in the following sections.

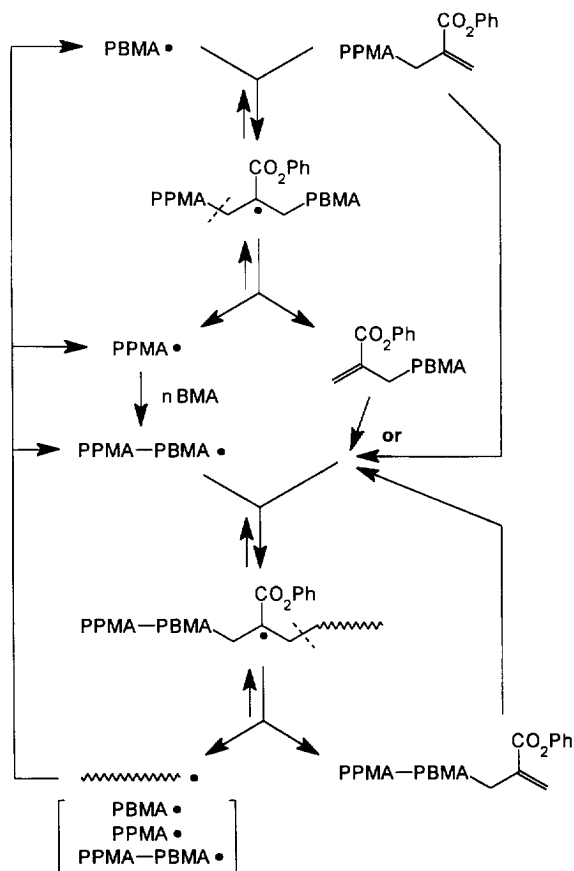
### 5.1. Polymerization in the presence of macromonomers

Vinyl macromonomers are available by a variety of methods<sup>30,285–288</sup> and were previously used both as precursors of block and graft copolymers<sup>286,289–291</sup> and as AFCTAs to

control polymer chain length.<sup>286,290</sup> Moad et al.<sup>292,293</sup> recently provided a high conversion method for producing narrow polydispersity homopolymers and block copolymers by free radical polymerization of monomers, involving an addition-fragmentation reaction on macromonomers<sup>294,295</sup> (Scheme 40).

Moad et al.<sup>292</sup> showed that, with appropriate control of both the macromonomer structural requirements and the reaction parameters, conditions can be found for producing high-purity narrow polydispersity block copolymers. Thus, AB diblock copolymers are formed in free radical polymerizations by significant insertion of monomer units (the B block) between the terminal  $\text{CH}_2=\text{C}(\text{Z})-\text{CH}_2$  unit and the  $-\text{C}(\text{X})(\text{Y})-\text{CH}_2$  segment (the A block) of the macromonomer ( $\text{X} = \text{H}, \text{CH}_3, \text{CO}_2\text{R}$ ;  $\text{Y}, \text{Z} = \text{Ph}, \text{CN}, \text{CO}_2\text{R}$ ).

The proposed mechanism for block formation is outlined in Scheme 40 for production of poly(BMA-*b*-PMA) from an  $\omega$ -(2-phenoxy-carbonyl-2-propenyl)PMA. When a PBMA<sup>\*</sup> macroradical reacts with the PPMA macromonomer, the diblock radical adduct that is formed can partition between reverting to starting materials or yielding a PBMA macromonomer and a new PPMA<sup>\*</sup> propagating species. This latter can further react with BMAs to produce



Scheme 40.



PPMA–PBMA diblock copolymer macroradicals. Further reaction of this species with a macromonomer (this may be one of the three possible in each case) produces a block copolymer macromonomer. The double bond is preserved in the whole process and the block copolymer macromonomer can undergo further reaction to extend the PBMA block length. The introduction of an additional monomer to form triblock or segmented copolymers appeared possible because all chains continue to grow throughout the polymerization; polydispersities are substantially less than those formed by conventional free radical polymerization with termination by chain transfer.<sup>296</sup> However, in block copolymer synthesis, chains formed from initiator-derived radicals can form by-products (homopolymer impurity) and classical chain termination by radical–radical reaction can occur. Chain transfer to macromonomer has to be the exclusive mechanism for the chain termination and initiation process to permit an accurate control of the growth of the polymer chain. For macromonomers based on methacrylic monomers, fragmentation of the adduct radicals always dominates over reaction with monomer, and graft copolymerization does not occur.<sup>286</sup>

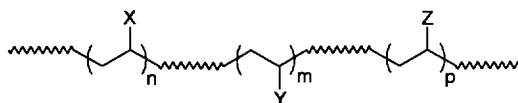
### 5.2. Polymerization in the presence of multifunctional initiators

Multifunctional initiators are either polycondensates containing peroxide or azo linkages, or organic molecules containing two or more peroxide or azo linkages or combinations of peroxide and azo linkages<sup>297–301</sup>. They have been used mostly for block copolymer syntheses. When a polymer bearing many sites capable of initiating polymerization is used in a radical reaction, many of the characteristics of a living polymerization process are realized if termination occurs exclusively by combination of radicals and if transfer reactions do not occur. Indeed, the average molar mass increases linearly with conversion, the molar mass distribution is narrow, high molar mass products are attainable and block or multiblock copolymer syntheses can be achieved. The structures that result when these sites initiate polymerization of three monomers are represented in Scheme 41.

The molar masses of the polymer segments generated from each radical (i.e.,  $A_n$  or  $B_n$ ) can be expected to conform to a most probable distribution (i.e.,  $M_w/M_n = 2.0$ ). The molar mass distribution of an aggregate of chains (linear, star or branched), each having a most probable distribution, is given by the following equation,<sup>3</sup> where  $n$  is the number of chain segments present in the aggregate:

$$M_w/M_n = 1 + 1/n$$

Thus, a polymer formed from a macroinitiator having 10 initiation sites ( $n = 20$ ) could have an  $M_w/M_n$  ratio as low as 1.05. Molar mass distribution broadening that would result from changes in monomer/initiator ratios, Trommsdorff effects, or other factors that broaden molar mass distributions are not taken into account for the calculation of polydispersity.<sup>3</sup>



Scheme 41.

### 5.3. Plasma-initiated induced polymerization

Ten years ago, considerable attention was paid to plasma-initiated polymerization of vinyl monomers, in which long-lived propagating radicals of ultra-high molar mass were found, even in homogeneous polymerization systems.<sup>302–304</sup> Bell et al., Osada et al. and Simionescu et al. claimed that a living radical polymerization behaviour was involved for polymerizations that occurred slowly at room temperature in the dark after monomers (mostly MMA) were exposed for brief periods (30–60 s) to microwave discharge.<sup>305–308</sup> Some block copolymers were prepared by using plasma-initiated polymerization. Conversion and molar mass increased steadily with time for periods up to 45 days, and molar masses as high as  $10^7$  were obtained. The conversions remained generally low ( $\sim 5\%$ ), except for polymers that precipitated during polymerization. A plasma-initiated polymerization process was used to prepare a variety of statistical and block copolymers, but little fundamental work was done. Bell et al.<sup>305,306</sup> isolated a highly branched and predominantly hydrocarbon oil from plasma-treated MMA that slowly initiated the polymerization of MMA and other monomers.<sup>306</sup> The capability of a plasma to initiate polymerization very slowly at room temperature may be responsible for some of the apparent living polymerization behaviour observed in plasma-initiated MMA polymerization, but it must also behave as a multifunctional initiator if the capability of plasma-initiated polymerizations to yield block copolymers is to be attributed to similar species.

## 6. RECENT ADVANCES

Very recently (since submitting this manuscript), a number of relevant papers have appeared in the literature, and these are mentioned here. Hawker published a short review (34 references) on architectural and structural control, focusing mainly on TEMPO-terminated polymers.<sup>309</sup> New advances were reported for the synthesis of end-functional polymers and allyl-type or vinyl acetate macromonomers,<sup>310</sup> gradient copolymers,<sup>311</sup> block and graft copolymers<sup>312,313</sup> and alternating copolymers.<sup>314</sup> A comparison of the three types of carbocationic and radical systems was also proposed.<sup>315</sup> Progress in the synthesis of very narrow distributed polymers was also proposed independently by Matyjaszewski et al.,<sup>316</sup> Percec et al.<sup>317</sup> and Sawamoto et al.,<sup>318</sup> using homogeneous atom transfer radical polymerization processes. These new approaches involve either a better solubilization of the Cu(bpy) complex by grafting alkyl substituents on the 2,2'-bipyridyl ligands or the use of some soluble metal catalysts based on other metal atoms.

Fundamental investigations of the characterization of the end-group composition, using UV-labelled initiators<sup>319</sup> or mass spectroscopy techniques,<sup>320</sup> have also been investigated in more detail. The influence of organic acids, such as CSA and excess nitroxide radical,<sup>321</sup> on the rate enhancement of TEMPO-mediated radical polymerization has been studied. Studies of the substituent effect on the phenyl ring of styrene<sup>322</sup> also showed that 3,4-chloromethylstyrene and 4-chlorostyrene, as previously observed in the case of the corresponding sulfonate,<sup>187</sup> polymerized faster than styrene itself.

Substituted nitronyl nitroxides<sup>323</sup> were investigated as new stable counter-radicals in the bulk-controlled radical polymerization of styrene, initiated by benzoyl peroxide or auto-initiation, at 120°C. Novel persistent borinate radicals,<sup>324</sup> generated from the in situ oxidation of alkyl-9-borabicyclononane with oxygen (or air) at ambient temperatures, were used in the

controlled radical polymerization of various alkyl methacrylates. High molar masses were achieved but dispersities were quite broad, close to 2.5. N-alkoxyphthalimides and succinimides were used as initiators by Druliner<sup>325</sup> in the radical polymerization of (meth)acrylates, styrene and vinyl acetate. THF was shown as the best solvent. Block copolymers, starting with PMA, PBA and PMMA, were also synthesized but always needed separation of homopolymers of the second monomer. Chernikova et al.<sup>326</sup> reinvestigated the radical polymerization of MMA in the presence of phenylazotriphenylmethane and showed that the mechanism proceeded in two stages, according to the difference in thermal stability of phenylazotriphenylmethane and the corresponding macroiniferter. Controlled radical polymerization of MMA was also developed in the presence of poly(urethane) iniferters<sup>327</sup> obtained from toluene diisocyanate and 1,1,2,2-tetraphenyl-1,2-ethanediol. Yang and Ráñdy<sup>328</sup> obtained surface grafted block copolymers by the surface grafting polymerization using 'living' radical polymerization techniques. Puts and Sogah<sup>329</sup> studied the use of asymmetric nitroxides and the implications for the controlled polymerization of styrene. The controlled radical polymerization of St, VAc and (meth)acrylates was also realized in the presence of TEMPO-type radicals attached to dendrimers of variable size.<sup>330</sup>

Müllen et al.<sup>331</sup> examined the effect of tetrathiafulvalene (TTF), a strong electron  $\pi$ -donor, on the radical polymerization of MMA and BA. TTF was shown to interact with the corresponding electrophilic growing macroradicals and minimize the occurrence of undesirable termination reactions. Both molar masses and polydispersities ( $<1.5$ ) of PMMAs were lower in the presence than in the absence of TTF. An analysis of the thermal behaviour of the PMMA obtained showed that radical disproportionation and recombination stayed limited. Similar results were obtained by Harwood et al.<sup>332</sup> in the polymerization on MMA in the presence of stilbene, used as solvent. Very narrow polydispersities ( $<1.1$ ) were claimed but no increase of molar mass during the polymerization time was reported. Harwood proposed a mechanism based on a *reversible addition-fragmentation* of macroradicals on stilbene, but it is still obscure.

Recent kinetic advances were reported by Veregin et al.,<sup>333</sup> Yan et al.<sup>334</sup> and Fukuda et al.<sup>335,336</sup> The former reported kinetics investigation of the slow equilibrium between growing and dormant chains, especially in the case of the nitroxyl-terminated chains. These results are similar to those previously reported by Müller et al.<sup>65</sup> (see Section 2.3). Yan et al.<sup>334</sup> investigated the kinetics of living radical polymerization by means of both the non-steady approach and the quasi-stationary state method. Fukuda and Terauchi<sup>335</sup> showed the independence of the rate of polymerization of St vs the concentration of nitroxyl radicals. They proposed an explanation based on the major production of radicals by thermal polymerization of the monomer, and estimated the equilibrium constant for the homolytic dissociation of the system PS-TEMPO to be close to  $1.2 \times 10^{-11}$  at 125°C.

Fukuda et al.<sup>337</sup> and Oulad Hammouch and Catala<sup>338</sup> continued to study the influence of the reaction parameters (i.e. dilution, active site concentration, temperature) on the polymerization of styrene mediated by TEMPO (at 125°C) or initiated by di-*tert*-butyl nitroxide, respectively. They confirmed that the rate of polymerization is independent of the nitroxide concentration. Matyjaszewski et al.<sup>339</sup> reported a similar analysis to Fukuda, connecting with comments on a paper of Catala et al.<sup>195</sup>

Matyjaszewski et al.<sup>340</sup> have tried to improve the controlled radical polymerization of St, VAc and (meth)acrylates by means of TEMPO-based stable radicals attached to dendrimers of variable size, without any success.

Puts and Sogah<sup>341</sup> studied the influence of asymmetric bulky nitroxides (i.e. 2,5-dimethyl-2,5-diphenylpyrrolidin-1-oxyl) in the free radical polymerization of styrene.

Hawker et al.<sup>342</sup> described the synthesis of a variety of new unimolecular initiators (e.g. alkylated TEMPO) and compared them with bimolecular systems involving a classic thermal initiator (BPO or AIBN) and TEMPO.

Schmidt-Naake and Butz<sup>343</sup> reported the free radical donor-acceptor copolymerization of St and N-cyclohexylmaleimide (CMI) in the presence of benzoyl peroxide (BPO) and TEMPO, as well as the synthesis of poly(St-co-CMI)-poly(St) block copolymers.

Wang et al.<sup>344</sup> synthesized a narrow polydispersed fullerene-end-capped poly(St) through a TEMPO-type mediated polymerization of St, and studied the photoconductivity of the polymer obtained so far.

Priddy et al.<sup>345</sup> reported results on the living radical polymerization of St, using 2,2,6,6-tetramethyl-1-(1-phenethyloxy)piperidine as initiator.

Boutevin et al.<sup>346,347</sup> and Yoshida<sup>348</sup> studied the controlled radical polymerization of *p*-chloromethylstyrene (CMS) and *p*-bromostyrene respectively, using BPO as initiator and TEMPO or 4-methoxyTEMPO as counter-radical respectively. Copolymers poly(CMS)-*b*-poly(St) and poly(styrene)-*b*-poly(*p*-bromostyrene) were also prepared by these authors.

Yoshida and Sugita<sup>349</sup> also proposed the synthesis of diblock copolymers by controlling the polymerization of styrene by reversible termination of the chain with a polymeric counter-stable radical (i.e. a poly(THF) bearing a TEMPO moiety at its chain end).

Odell et al.<sup>350</sup> and Scaiano et al.<sup>351</sup> studied the rate enhancement of reactions of polymer radicals and microradicals respectively, scavenging by TEMPO in the presence of acids (i.e. benzoic and camphorsulphonic acids) or organic acid salt (e.g. 2-fluoro-1-methylpyridinium *p*-toluenesulphonate) respectively. Odell et al. showed that this latter compound provides faster rates of 4-oxoTEMPO moderated polymerization than does camphorsulphonic acid. Scaiano et al. proposed that acids operate mainly on the recapping step, in a way reminiscent of the solvent effects, but an acceleration of thermal dissociation (i.e. the reverse reaction) is not excluded.

Tanaka et al.<sup>352</sup> have realized the controlled radical polymerization of St and MMA in the presence of a mono-captodatively substituted ethane-bearing nitrile and ethylsulphenyl groups on the same carbon atom. A reversible radical termination occurred only in the case of MMA, due to a favourable polar effect between the polymer chain radical and the  $\alpha$ -ethylsulphenylacrylonitrile-type radical.

Reetz et al.<sup>353</sup> proposed a specific controlled polymerization of MMA (i.e., acrylates or acrylonitrile are not polymerized) with dialkyl iodomethylmalonates in the presence of tetrabutylammonium iodide. The requirement for a tertiary carbon-iodide bond could be explained through a mechanism similar to an ATRP.

Tharanikkarasu and Radhakrishnan<sup>354</sup> have carried out controlled radical polymerization of acrylonitrile through the use of a poly(urethane) iniferter as reported previously in the case of polymerization of MMA.

Haddleton et al.<sup>355</sup> have used the AFCT polymerization technique to prepare  $\alpha,\omega$ -dihydroxy PMMA, using hydroxyethyl methacrylate dimer as an efficient CTA.

Zaremski et al.<sup>356</sup> and Wang and Råndy<sup>357</sup> studied the radical 'living' graft polymerization of St on the surface of silica gel (Silochrome C-120), and of (meth)acrylic acids or St on low density polyethylene films, respectively. Wang and Råndy employed benzophenone,

xanthone and 9-fluorenone as photoinitiators whereas Zaremski used a iniferter, e.g. S-benzyl-dithiocarbamate groups, similarly to the solid-phase block copolymer synthesis reported ten years ago by Otsu et al.<sup>358</sup>

Sebenik et al.<sup>359</sup> studied the structure of 'living' free-radical copolymers PVC-*g*-PMMA prepared by UV irradiation of the corresponding PVC-*n*-propyl xanthate macroinitiator in MMA.

'Living' radical polymerization involving reversible formation of Co-C bonds was studied by Wayland et al.<sup>360</sup> through the reaction of tetra(*p*-anisyl)porphyrinatocobalt(II) radicals with organic radicals of the form C(CH<sub>3</sub>)RCN in the presence of olefins, and determined thermodynamic parameters for Co-C bond homolysis. Gridnev and Ittel<sup>361</sup> studied the dependence of free radical propagation rate constants on the degree of polymerization of these radical polymerizations.

Sawamoto et al.<sup>362</sup> performed sequential living polymerizations of alkyl methacrylates (i.e. methyl, ethyl and *n*-butyl derivatives) using tertiary initiating systems (cf. Section 4.1.3.4 and ref.<sup>160</sup>).

Colombani et al.<sup>363,364</sup> investigated the controlled radical polymerization of MMA and St in the presence a new class of stable radical, i.e. 1,3,5,5-tetraphenyl- $\Delta^3$ -1,2,4-triazolin-2-yl radical. It was shown that the polymer chains are reversibly terminated by these radicals, and that the reinitiation of a second monomer was efficient in achieving AB block copolymers. The dependence of the molar mass vs conversion was demonstrated to be linear up to high conversion in the bulk polymerization of MMA and St (Figs 1 and 2). High molar mass PMMAs were achieved, in contrast to oligomers obtained by the use of nitroxides (Fig. 2). The molar mass distribution stays narrow at higher conversions.

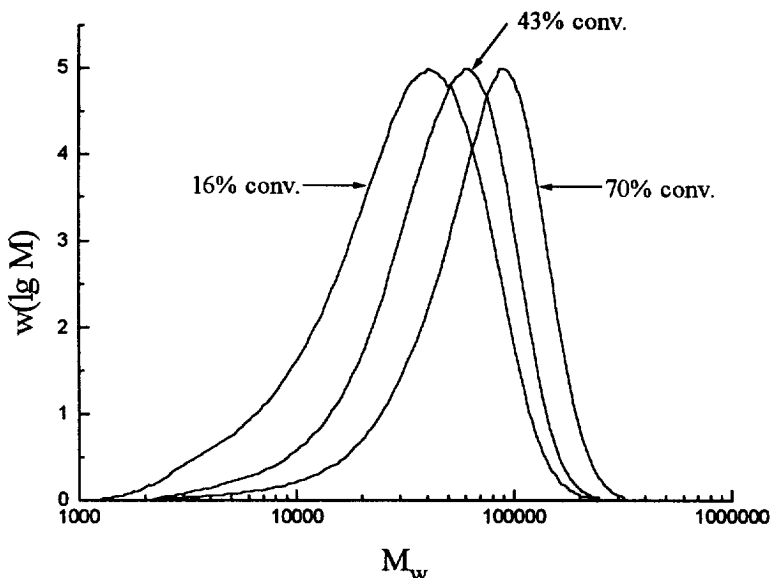


Fig. 1. GPC curves (THF, UV-detector) of PS, at different conversions.

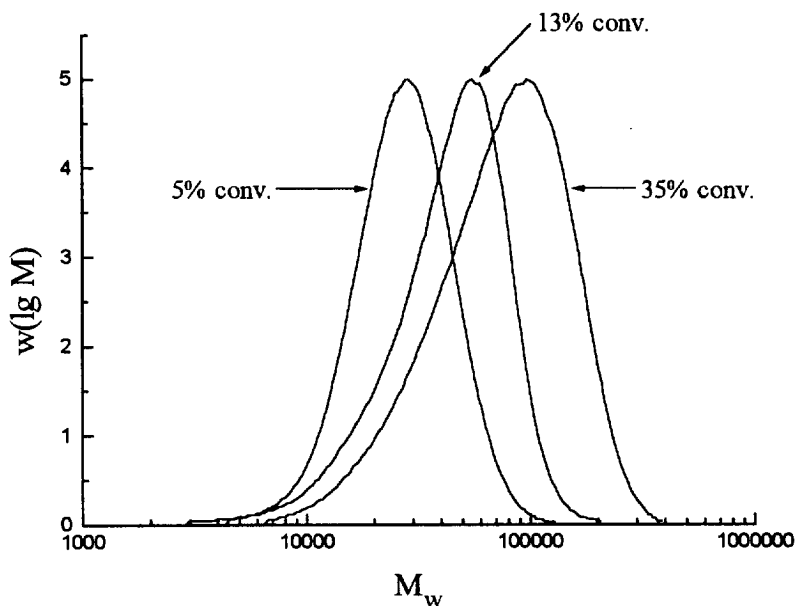


Fig. 2. GPC curves (THF, RI-detector) of PMMA, at different conversions.

## 7. CONCLUSIONS

The search for newer molecules and methodologies for the facile synthesis of functional polymers and block and graft copolymers by the free radical route is gaining importance in view of the increasing demand for these materials in various phases of modern technology. Indeed, the industrial synthesis of structurally well-defined, vinyl monomer-based block copolymers is presently largely underdeveloped and limited to styrene-butadiene, styrene-butadiene-styrene copolymers and some chemically modified derivatives thereof. The investigation of chain-growth-controlled radical polymers gives some thrust to this area and adds a new chapter to free radical polymerization chemistry.

Loss of termination between growing radicals is the most important factor in trying to achieve controlled polymerization conditions. Thus, the developed idea of end-capping the macroradical during polymerization provides one solution to the longstanding problem of control of the radical growth of the polymer chain. The radical 'living' polymers that have been developed have been reviewed. A large number of radical polymerization systems proceeding by different growth-controlled mechanisms have been developed over the past years, and the number of monomers amenable to use in these systems has been gradually increasing year by year. This shows that it is possible to design polymers more conveniently and, thus, to make a variety of speciality polymers in the future in which precise architectures are stipulated at the molecular level. Well-defined polymers can be produced by radical polymerization using three different approaches: degenerative transfer, reversible homolytic cleavage of covalent species, and reversible homolytic cleavage of persistent radicals. The first method requires high degenerative transfer coefficients but allows for slow initiation; the

other two methods require the equilibrium to be strongly shifted towards dormant species, and initiation to be fast.

All three approaches may provide controlled polymerizations, but not ideal living polymerizations, because chain-breaking reactions cannot be eliminated although their contribution can be strongly reduced. The polymerization should be carried out at a sufficiently low concentration of growing radicals and a sufficiently high concentration of dormant species. Some additional narrowing of the molar mass distribution may be achieved by adjusting the relative rates of propagation with those of initiation and/or transfer. Control of molar masses additionally requires fast initiation, which should be accomplished by the formation of the initiating species in situ or just prior to polymerization. Work at higher temperature is preferred due to the higher energy of activation of propagation in comparison with that of termination, which is the main, and most difficult to avoid, chain-breaking reaction in radical polymerization, provided that the contribution of transfer is low enough.

It is now time to consider from a technological viewpoint the practical uses and applications of such polymers prepared by means of living polymerizations. Indeed, quasi-living radical polymerization processes can be readily performed on a large scale for industrial applications, offering the potential to provide large amounts of polymeric materials with complex architectures (i.e., block, comb, star or dendrimeric architectures) with well-defined chain lengths and at low cost, and enabling the synthesis of materials that were previously the exclusive domain of traditional living polymerization processes such as ionic, cationic or group transfer polymerizations. Moreover, a particularly useful advantage of quasi-living radical polymerization systems involving SFR-terminated oligomers is the ability to isolate, purify and store the oligomers obtained. Thus, for the synthesis of AB blocks, a variety of B blocks can be added to the A block by changing the identity or amount of the monomer used for the B block.

The aim of this review was to attempt to outline some of the exciting advances being made in growth-controlled radical polymerization. The current renaissance in this area will lead to further rapid advances, and radical polymerization will thus maintain its importance both in industrial and in academic research.

## ACKNOWLEDGEMENTS

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