Controlled and Living Polymerizations

Methods and Materials

Edited by
Axel H.E. Müller
and Krzysztof Matyjaszewski

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Preface: Controlled and Living Polymerizations

The discovery of living anionic polymerization and subsequently other controlled/living polymerizations has had tremendous impact on polymer and materials science. It facilitated major developments not only in synthetic polymer chemistry but also in polymer physics as it opened an avenue to the preparation of well-defined polymers with precisely designed molecular architectures and nanostructured morphologies. As an example, block copolymers synthesized via sequential monomer addition by Szwarc *et al.* more than 50 years ago [1] have inspired a generation of polymer physicists due to their potential to self-organize in bulk or solution. They were successfully commercialized as thermoplastic elastomers, compatibilizers, surfactants, or components of medical and personal care products, to name just a few applications. Thermoplastic elastomers, first commercialized under the trade name Kraton®, are landmark materials made by living anionic polymerization and they are applied in many compounding applications, including footwear, pressure-sensitive adhesives, cables, soft-touch overmolding, cushions, lubricants, gels, coatings, or in flexographic printing and road marking. It is anticipated that materials made by other controlled/living processes will lead to more applications with even larger market impact. Many details on the current and potential future applications of polymers made by controlled/living polymerization can be found in all chapters of this book.

The term *living polymer* was coined by Michael Szwarc to describe the products of the anionic polymerization of styrene initiated by electron transfer in tetrahydrofuran [1, 2]. In this context, "living" denotes the ability of a polymer chain to further add monomer after the initial batch of monomer has been consumed, and this means that the polymer chains do not undergo irreversible chain breaking reactions, such as termination or chain transfer. The IUPAC Gold Book [3] defines "living polymerization" as *a chain polymerization from which chain transfer and chain termination are absent.* It adds (although this is not part of the definition) the following: *In many cases, the rate of chain initiation is fast compared with the rate of chain propagation, so that the number of kinetic-chain carriers is essentially constant throughout the polymerization.* Typically, such a process should lead to a very narrow (Poisson) molecular weight distribution

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(MWD). However, a slow initiation process can have a considerable impact on the molecular weights achieved and on the MWD.

It has been discussed how strict one should regard the absence of termination and transfer. For example, it is impossible to completely suppress termination in radical polymerization. Thus, Szwarc later modified his definition [4] saying that *a polymerization is living when the resulting polymer retains its integrity for a sufficiently long time to allow the operator to complete its task, whether a synthesis or any desired observation or measurement. Even in that time some decomposition or isomerization may occur, provided it is virtually undetectable and does not affect the results.*

The term *controlled polymerization* introduced by us in 1987 [5] can be defined as a synthetic method to prepare polymers, which are well-defined with respect to topology (e.g., linear, star-shaped, comb-shaped, dendritic, and cyclic), terminal functionality, composition, and arrangement of comonomers (e.g., statistical, periodic, block, graft, and gradient), and which have molecular weights predetermined by the ratio of concentrations of reacted monomer to introduced initiator, as well as a designed (not necessarily narrow) MWD.

Thus, a living polymerization is not always controlled and a controlled polymerization is not always strictly living, according to the definitions given above. In the ideal case, a living polymerization is also controlled; however, in some systems such as in a radical polymerization, termination can never be entirely avoided but its contribution can be sometimes significantly reduced.

The feature of livingness was discovered in carbanionic polymerization in 1956. Many efforts were made in other polymerization methodologies to achieve a level of control attainable in living carbanionic polymerization. However, it took nearly 20 years until living cationic ring-opening polymerization was developed (living anionic ring-opening polymerization was known already for some time). Group transfer polymerization (GTP; a process close to anionic polymerization) was reported in 1983 and the living carbocationic polymerization in 1984. Subsequently, living ring-opening metathesis polymerization (ROMP) was reported in 1986 and various controlled/living radical polymerization mechanisms were reported in the 1990s. Finally, even coordination polymerization of olefins was made living.

It is intriguing that almost all new controlled/living systems have one common feature, which is the coexistence of active and inactive (''dormant'') species, being in a dynamic equilibrium, either via *reversible deactivation* processes or via *reversible (degenerative) transfer.*

Reversible deactivation is a process where active species (ions, ion pairs, or radicals), P^*, are in a dynamic equilibrium with inactive (dormant), typically covalent species, P,

$$\sim\sim\sim\sim P\,(+C) \underset{k_{\mathrm{deact}}}{\overset{k_{\mathrm{act}}}{\rightleftharpoons}} \sim\sim\sim\sim P^*(+D)$$

Here, C is a catalyst (coinitiator/activator) and D is a deactivator or product of the activation process. As an example, in atom transfer radical polymerization (ATRP), P can be a bromine-terminated chain end, C can be a Cu(I) compound, P^* is the propagating radical, and D is a Cu(II) compound (Chapter 3). In GTP, P is a silylketene acetal, C can be a bifluoride anion, P^* can be an enolate, and D is a silyl fluoride (Chapter 1).

Reversible transfer is a bimolecular reaction between a dormant and an active polymer chain, which only differ in their degree of polymerization (degenerative transfer, i.e., equilibrium constant $K_{ex} = 1$), leading to a direct exchange of activity between two chain ends:

$$\sim\sim\sim\sim P_{\mathrm{n}} + \sim\sim\sim\sim P^*_{\mathrm{m}} \underset{k_{\mathrm{ex}}}{\overset{k_{\mathrm{ex}}}{\rightleftarrows}} \sim\sim\sim\sim P^*_{\mathrm{n}} + \sim\sim\sim\sim P_{\mathrm{m}}$$

A typical example is the exchange reaction between an iodine-terminated chain end and a propagating radical. Reversible addition–fragmentation chain transfer (RAFT) polymerization is also closely related to such a process (Chapter 3).

As a consequence of these processes, the MWD may be considerably broader than the Poisson distribution, where the polydispersity index, PDI $= M_{\mathrm{w}}/M_{\mathrm{n}}$, is close to unity. The PDI depends on the ratio of the rate constants of propagation to deactivation (or exchange) and decreases with monomer conversion [6]. If deactivation/exchange is slow relative to propagation, broad MWDs are observed. Many such systems have been called nonliving, because broad MWDs were assumed to originate in chain breaking reactions.

The first four chapters in this book present the mechanisms and the most recent advances in controlled/living polymerization of vinyl monomers. The first chapter summarizes anionic polymerization using classic systems and also recent developments employing equilibria between active and dormant species that enabled reduction of the rate of polymerization of styrene and also controlled polymerization of (meth)acrylates. The second chapter is devoted to carbocationic polymerization and illustrates examples of equilibria between carbocations and various dormant species and their applications to synthesis of well-defined (co)polymers. The third chapter describes a state of the art in controlled radical polymerizations, predominantly in stable free radical polymerization, atom transfer radical polymerization, and degenerative systems such as RAFT, and also presents how controlled molecular architecture can lead to new applications. The fourth chapter is focused on controlled/living coordination polymerization of olefins and presents some new materials prepared by this technique.

The next two chapters are focused on ring-opening polymerization. Chapter 5 presents recent advances in both anionic and cationic polymerization of heterocyclics together with examples of well-defined (co)polymers and their applications. Chapter 6 is focused on ROMP of cycloolefins and a variety of resulting new materials prepared by ROMP.

Chapters 7 and 8 illustrate how various controlled/living polymerizations can be employed to precisely control various elements of macromolecular architecture, such as chain composition and microstructure, chain topology and functionality, including block and graft copolymers. Chapter 9 presents how segmented copolymers self-organize in bulk, thin films, and solution into various nanostructured morphologies and how precise synthesis and processing can generate new materials with exciting properties.

Finally, the last chapter provides not only a state-of-the-art summary of current and forthcoming applications of Kraton, a large-volume block copolymer prepared by anionic vinyl polymerization, but also (co)polymers prepared by other controlled/living techniques.

We are confident that this book provides an excellent overview of various controlled/living polymerization techniques and hope that it will stimulate new discoveries and will facilitate developments of new polymeric materials for many exciting applications.

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1
Anionic Vinyl Polymerization

Durairaj Baskaran and Axel H.E. Müller

1.1
Introduction

1.1.1
The Discovery of Living Anionic Polymerization

The concept of anionic polymerization was first developed by Ziegler and Schlenk in early 1910. Their pioneering work on the polymerization of diene initiated with sodium metal set the stage for the use of alkali metal containing aromatic hydrocarbon complexes as initiators for various α-olefins. In 1939, Scott and coworkers used for the first time the alkali metal complexes of aromatic hydrocarbon as initiators for the polymerization of styrene and diene. However, in 1956, it was Michael Szwarc who demonstrated unambiguously the mechanism of anionic polymerization of styrene, which drew significant and unprecedented attention to the field of anionic polymerization of vinyl monomers [1, 2]. Michael Szwarc used sodium naphthalenide as an initiator for the polymerization of styrene in tetrahydrofuran (THF). Upon contact with styrene, the green color of the radical anions immediately turned into red indicating formation of styryl anions. He suggested that the initiation occurs via electron transfer from the sodium naphthalenide radical anion to styrene monomer. The styryl radical anion forms upon addition of an electron from the sodium naphthalenide and dimerizes to form a dianion (Scheme 1.1).

After the incorporation of all the monomer, the red color of the reaction mixture persists, indicating that the chain ends remain intact and active for further propagation. This was demonstrated by the resumption of propagation with a fresh addition of another portion of styrene. After determining the relative viscosity of the first polymerized solution at its full conversion, another portion of styrene monomer was added and polymerization was continued. Thus, Szwarc characterized this behavior of the polymerization as *living polymerization* and called the polymers as *living polymers* [2]. Here, the term *living* refers to the ability of the chain ends of these polymers retaining

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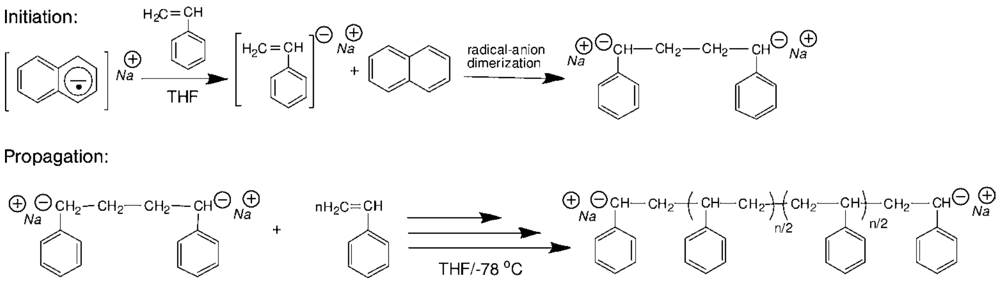
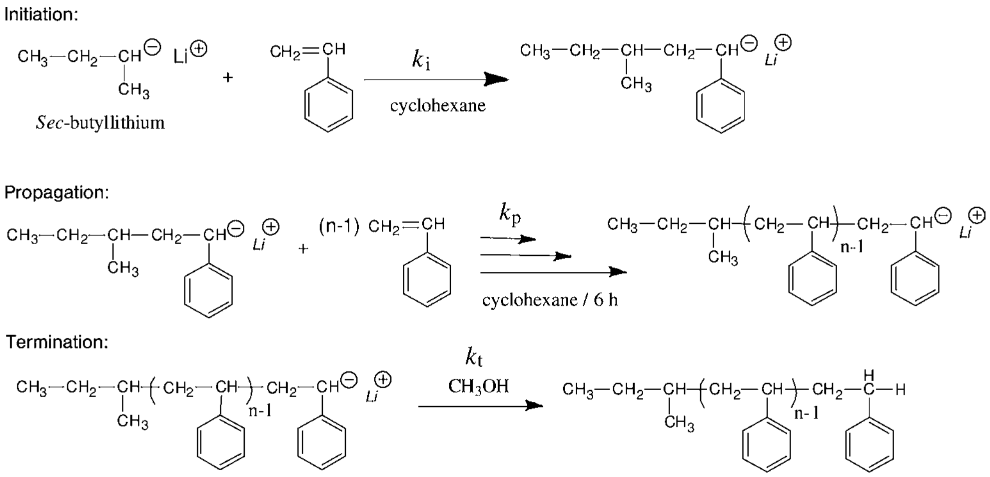


Scheme 1.1 Anionic polymerization of styrene using sodium naphthalene as initiator in THF.



Scheme 1.2 Anionic polymerization of styrene using *sec*-butyllithium as initiator.

their reactivity for a sufficient time enabling continued propagation without termination and transfer reactions.

Szwarc's first report of living anionic polymerization of styrene free from termination and transfer reactions in THF marks the beginning of lively research activities in this field [1–5]. Subsequent work on the anionic polymerization of styrene and dienes in hydrocarbons using alkyllithium initiators stimulated interest in this field [6–8]. Scheme 1.2 shows the anionic polymerization of styrene initiated by *sec*-butyllithium.

1.1.2
Consequences of Termination- and Transfer-Free Polymerization

Detailed kinetic measurements confirm that the polymerization of styrene in fact is free from termination and transfer reactions [1, 2]. Assuming a fast

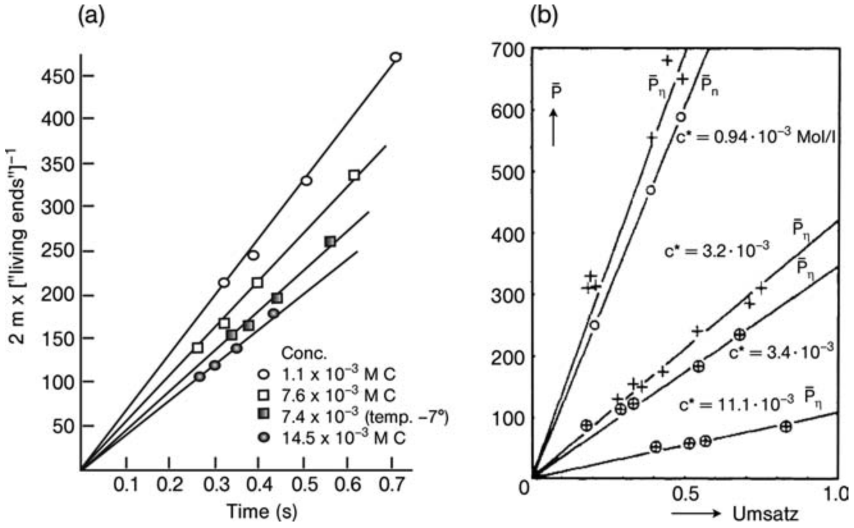


Figure 1.1 (a) Rate of polymerization of polystyrene in THF at 25 °C ('m' corresponds to $[M]_0/[M]_t$) [9]. (b) Number- and viscosity-average degrees of polymerization of polystyrene vs. conversion at various chain-end concentrations, c^* [10]. (Reprinted with permission from Wiley-VCH.)

initiation step, the rate of polymerization is given by

$$R_p = -\frac{d[M]}{dt} = k_p \cdot [P^*] \cdot [M] \tag{1.1}$$

where $[M]$ is the monomer concentration, k_p is the rate constant of propagation, and $[P^*]$ is the concentration of active chain ends. In the absence of termination, $[P^*]$ is constant, and the product $k_\mathrm{p}[P^*] = k_\mathrm{app}$ can be regarded as an apparent first-order rate constant. Introducing monomer conversion, $x_\mathrm{p} = ([M]_0 - [M]_t)/[M]_0$, integration of Eq. (1.1) leads to

$$\ln\frac{[M]_0}{[M]_t} = -\ln(1 - x_\mathrm{p}) = k_\mathrm{p} \cdot [P^*] \cdot t = k_\mathrm{app}t \tag{1.2}$$

Figure 1.1a shows a historic plot of such a first-order time-conversion relation. The linearity indicates that the active center concentration remains constant throughout the polymerization. In case of termination, $[P^*]$ depletes and thus the slope of the first-order plot decreases. It must be noted that this plot does not give evidence for the absence of transfer, since in this case the concentration of active chain ends remains constant.

The absence of transfer can be demonstrated by the linearity of a plot of the number-average degree of polymerization, DP_n, vs. conversion:

$$\overline{\mathrm{DP}}_n = \frac{\text{concentration of consumed monomers}}{\text{concentration of chains}}$$

$$= \frac{[M]_0 - [M]_t}{[P]} = \frac{[M]_0}{[P]} \cdot x_p \tag{1.3}$$

where $[P]$ denotes the *total* number of chains, active and inactive ones, which are generated in the transfer process. In an ideal polymerization $[P] = [P^*] = f[I]_0$, where $[I]_0$ is the initial initiator concentration and f the initiator efficiency. In case of transfer, $[P]$ increases and the slope of the plot decreases. Figure 1.1b shows a historical plot from Schulz *et al.* [10]. This indicated that the propagating anions are free from transfer and the molecular weight of the chains correspond to theoretical molecular weight depending on the monomer conversion [11].

The absence of termination and transfer reactions has two important consequences: (i) the number-average molecular weight, M_n, of the resulting polymer is determined by the amount of consumed monomer and the initiator used for the polymerization[12] and (ii) all the chains at any time, t, propagate at the same rate and acquire the same length after a subsequent time interval, $t + \Delta t$. This leads to a linear growth of polymer chains with respect to the monomer consumption, leading to a narrow distribution of chain lengths characterized by a *Poisson* distribution; the polydispersity index is given by

$$\mathrm{PDI} = \frac{\overline{M}_w}{\overline{M}_n} \approx 1 + \frac{1}{\overline{\mathrm{DP}}_n} \tag{1.4}$$

This distribution had already been derived by Flory in 1940 for the ring-opening polymerization of ethylene oxide [13]. This was experimentally confirmed by Schulz and coworkers who determined the polydispersity index, M_w/M_n, of Szwarc's samples and found that they were in the range of 1.06–1.12 [14].

Monomer resumption experiment is another way to show the absence of termination. Here, a second batch of monomer is added after a certain period has elapsed after full monomer conversion. In case of termination, one will find a bimodal distribution, one peak from the terminated chains and another from the active chains that participated in chain extension with the second batch of monomer.

It is important to note that not all living polymerizations lead to narrow molecular weight distributions (MWDs). First, a *Poisson* distribution is obtained only if the rate of initiation is much faster than that of propagation. Second, as is discussed later, many chain ends in anionic polymerizations (and also in other types of living polymerizations) can exist in various states, e.g., covalent species, aggregates, various types of ion pairs, or free anions, which propagate at different rates or are inactive ("dormant"). Different types of chain ends in anionic polymerization exist in equilibrium with each other and a chain end can change its state depending on the reaction condition such as the polarity of solvent and the temperature. If the rate of exchange between these species is slow compared to the rate of propagation, this can lead to a significant broadening of the MWD.

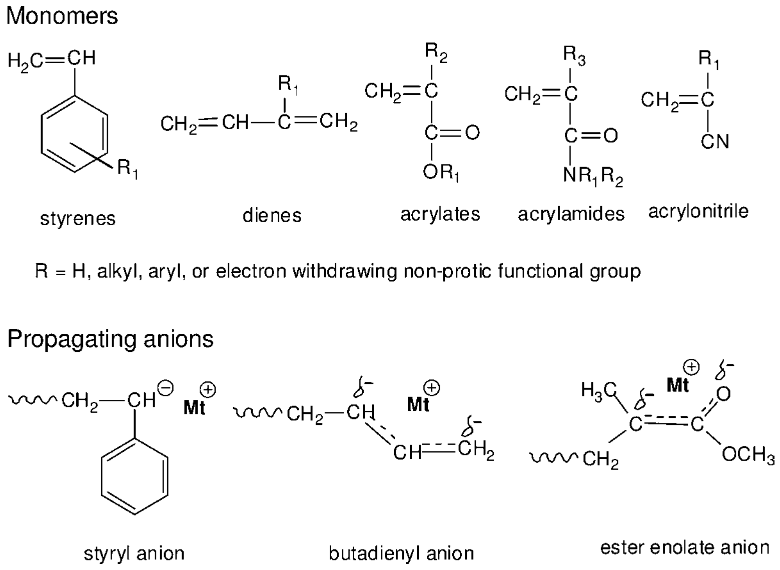


Figure 1.2 Major class of vinyl monomers and their corresponding propagating anions.

1.1.3
Suitable Monomers

A variety of α-olefins substituted with an electron withdrawing group have been subjected to anionic polymerization [15, 16]. Several substituted α-olefin monomers can be polymerized via anionic polymerization except the ones with functional groups bearing acidic protons (or other electrophiles) for the obvious reason that electrophiles react with carbanions and thus either quench the initiator or terminate anionic propagation. However, after appropriate protection, those monomers can be polymerized [17–19]. Hydrocarbon monomers such as dienes and styrene, polar vinyl monomers such as vinyl pyridines, (meth)acrylates, vinyl ketones, acrylonitriles, and cyclic monomers containing oxirane, lactones, carbonates, and siloxanes have been polymerized using anionic initiators [16]. The anionic polymerization of heterocyclic monomers is discussed in Chapter 5. A list of major classes of substituted α-olefin monomers with their corresponding propagating anions is given in Figure 1.2. The reactivity of these propagating anions and their nature of ion pairs are dependent on reaction conditions. The substitution (R_1, R_2, R_3) in the olefin monomers can vary from H, alkyl, aryl, and protected silyl group, leading to numerous monomers that are amenable for anionic polymerization [20, 21]. Various other monomers that are anionically polymerizable with limited control over the polymerization include ethylene, phenyl acetylene, vinyl ketones, and vinyl sulfones and α-olefins with other electron withdrawing group such as $-CN$ and $-NO_2$. A detailed list of monomers for anionic polymerization is given in various books and reviews [21, 22].

In the following, we first discuss characteristics of carbanions and their ion pairs in different conditions and their function as initiators and chain ends in the anionic polymerization of vinyl monomers. As our intention is to cover the fundamental aspects related to the mechanism of anionic vinyl polymerization in this chapter, the architectural controls using active chain-end manipulations and copolymerization have not been included; they will be covered in other chapters of this book. The existence of different forms of ion pairs in polar and nonpolar solvents and their dynamic equilibrium will be described. Subsequently, the detailed mechanism of anionic polymerization of styrene, dienes, and acrylic monomers in polar and nonpolar solvents will be discussed. Finally, we present some examples of industrial and scientific applications of anionic polymerization.

1.2
Structure of Carbanions

The rate of anionic polymerization of styrene using alkyllithium as initiator strongly depends on the solvent. It is very fast in polar solvents like THF. It is much slower in aromatic hydrocarbons such as benzene and even slower in aliphatic hydrocarbons such as cyclohexane. This is due to the different states of solvation and aggregation of carbanions in these solvents [23, 24]. Therefore, the mechanism of anionic polymerization is complicated due to the contribution of different forms of ion pairs. Thus, we will first examine the various forms of carbanions used in polar and nonpolar solvents before analyzing the mechanisms of initiation and polymerization.

Various factors affect the reactivity of carbanions, and it is important to understand the properties of carbanions that assume different structures depending on the environment. The polarity of the solvent in which anion is prepared and used, the intermolecular ionic interactions, and the size of metallic counterion all dictate the characteristics of a particular carbanion. The stabilization of anions through intermolecular interaction leads to the formation of different associated states called *aggregates*. The nature of anion aggregation is governed by various factors such as the charge density of anion, interionic distances, the dielectric constant, and the donating properties of the solvent [25]. Thus, the aggregated anions always exist in dynamic equilibrium with nonaggregated ones.

Fuoss [26, 27] and Winstein *et al.* [28] independently proposed the existence of two different forms of ion pairs based on the interionic distance. Accordingly, the anion present in solution may be tightly associated with counterion or loosely with solvated counterion. They named a tightly associated anion with cation as contact ion pair and a loosely associated anion with solvent-coordinated cation as solvent-separated ion pair. The different forms of ion pairs that are in equilibrium with each other are shown in Scheme 1.3. Depending on the concentration, the solvent-separated ion pairs can dissociate