

Feature article

Recent progress in the use of photoirradiation in living radical polymerization

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ABSTRACT

The effects of photoirradiation in controlled and living radical polymerization (LRP), namely nitroxide-mediated radical polymerization (NMP), atom-transfer radical polymerization (ATRP), cobalt-mediated radical polymerization (CMRP), reversible addition-fragmentation chain transfer polymerization (RAFT), organoiodine-mediated radical polymerization (IRP), and organotellurium-mediated radical polymerization (TERP), are summarized. As in the conventional radical polymerization, photoirradiation has been used for generating radicals under mild conditions in LRP methods. In addition to this use, photoirradiation is also used to overcome the difficulties characteristic to each method, such as activation of catalysis, generation of controlling agents, and increasing the polymer-end structure. The most-recent developments in the use of photochemistry in LRP are summarized in this review.

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1. Introduction

Radical polymerization is one of the most important industrial polymerization technologies, and 40–45% of all synthetic polymers are estimated to be produced by this method [1]. This is primarily because of the robustness of this method, which originates from the neutral and highly reactive character of radicals. Polymerization proceeds with a variety of monomer families and is compatible with various polar functional groups and solvents, including water [2–6]. These conditions are in sharp contrast to other vinyl polymerization methods, namely, anionic, cationic, and coordination polymerizations, which require stringent reaction conditions to avoid the occurrence of undesirable side reactions involving protic solvents, oxygen, and/or polar functional groups.

The disadvantage of conventional radical polymerization, however, is insufficient control of the macromolecular structure, resulting in macromolecules that are polydisperse with a broad molecular weight distribution (MWD). Controlled and living radical polymerization (LRP) methods have been developed primarily to overcome this difficulty in controlling molecular weights and MWDs. In addition, LRP also creates the new possibility of controlling the monomer sequence through block copolymer

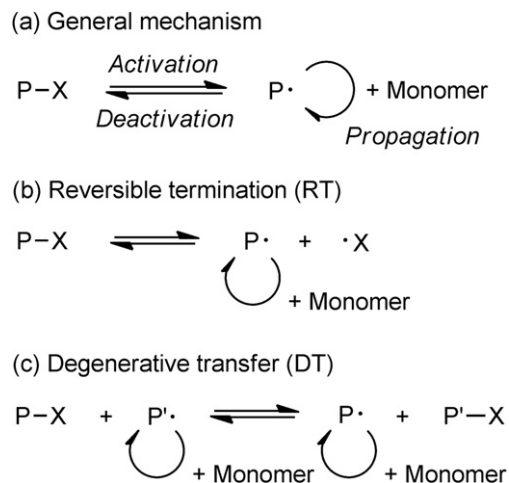
synthesis and synthesizing end-functional polymers by selective transformation of the living polymer-ends. Therefore, LRP is now widely used on the bench scale for the synthesis of new polymeric materials with improved and/or new properties and functions, and its industrial applications have been rapidly progressing [7].

LRPs that have been widely used include nitroxide-mediated radical polymerization (NMP) [8,9], atom-transfer radical polymerization (ATRP) [10–15], and reversible addition-fragmentation chain transfer radical polymerization (RAFT) [16–19]. Organotellurium- [20–22], organostibine- [23–25], and organobismuthine-mediated LRP [26,27] (SBRP, BIRP, and TERP, respectively) [28–32] are relatively new methods developed by the author's research group. New variants of LRP have also emerged, such as cobalt-mediated polymerization [33–36], titanium-catalyzed polymerization [37], and single-electron transfer LRP [38,39]. Organoiodine-mediated LRP (IRP), which is one of the oldest LRP [40–42], has been also used in many instances.

LRP relied on reversible generation of the polymer-end radical $P\cdot$ from a dormant species $P-X$, which possesses appropriate functional group X at the polymer-end for radical generation (Scheme 1) [14,43]. This pseudo deactivation of the polymer-end radical to the dormant species decreases the concentration of the radical species in solution and minimizes undesirable side reactions leading to dead polymers. Therefore, the activity of polymer-end radical species is preserved throughout the polymerization period as a form of dormant species. Furthermore, the rapid deactivation makes it possible to elongate all of the polymer chains

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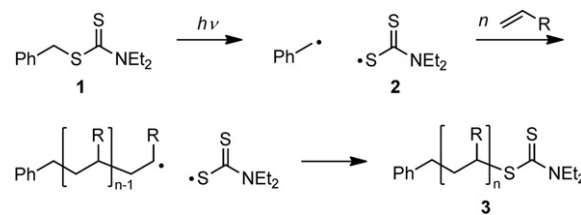
Scheme 1. Activation and deactivation mechanism of dormant ($P-X$ and $P'-X$) and polymer-end radical species ($P\cdot$ and $P'\cdot$), respectively, in living radical polymerization.

with similar chain lengths giving structurally well-controlled polymers with narrow MWD. The term “living” will be used throughout this manuscript when these criteria are fulfilled, despite the IUPAC recommends use of “reversible-deactivation radical polymerization” for this type of polymerization because the termination reaction of polymer-end radicals cannot be completely inhibited [44].

There are two activation/deactivation mechanisms of the dormant/radical species. One is reversible termination (RT) shown in Scheme 1b, in which homolytic cleavage of the $P-X$ bond in the dormant species generates polymer-end radical $P\cdot$ (P denotes polymer here) and persistent radical $\cdot X$. The selective recombination of $P\cdot$ and $\cdot X$ radicals is controlled by the persistent radical effect [45]. The other mechanism is degenerative chain transfer (DT) shown in Scheme 1c, in which polymer-end radical $P'\cdot$ (P' denotes polymer having either same or different chain length with P) undergoes a homolytic substitution reaction with dormant species $P-X$, generating new radical $P\cdot$ and new dormant species $P'-X$.

The chemical structure of X and the activation/deactivation mechanisms of the dormant/radical species make each LRP method unique, both mechanistically and synthetically. NMP and ATRP exclusively proceed by the RT mechanism, and RAFT proceeds by the DT mechanism. TERP, SBRP, BIRP, and IRP predominantly proceed via the DT mechanism, but RT also contributes to a small extent. CMRP also proceeds by both RT and DT depending on the conditions, but RT plays a more important role than DT for the MWD control.

Various physical and chemical stimuli, such as heat, metal catalysts, and free-radical initiators, have been used to realize efficient activation/deactivation and control of the molecular weight and MWD. Photochemical stimuli have been widely employed in conventional radical polymerization as a key technique in various applications, such as coatings, adhesives, microelectronics, and so forth [46,47], and the use of photochemistry in the control of radical polymerization has also emerged since the pioneering work on the invention of photoiniferter (initiator-transfer agent-termination) [48–50]. Otsu and coworkers reported photopolymerization in the presence of dithiocarbamate, such as **1**, showing living character, including a linear increase in molecular weight upon monomer conversion and successful synthesis of block copolymers. The mechanism of iniferter is identical to the RT mechanism shown in Scheme 1b, in which homolytic C–S bond cleavage of **1** by photoirradiation generates a transient benzyl radical and dithiocarbamyl



Scheme 2. Controlled polymerization using “photoiniferter”.

radical **2** (Scheme 2). After propagation with the monomer, the polymer-end radical reacts with **2** giving dormant species **3** having a dithiocarbamate group at the polymer-end. However, this method is not a living system and gives polymers with a broad MWD. This is because dithiocarbamates are poor chain transfer agents (CTAs) and because **2** is not a persistent radical and initiates a new polymer chain. Kwon and coworkers utilized diphenyl diselenide and organoselenium compounds as photoiniferters, but sufficient control could not be attained for the same reason as that mentioned above with respect to dithiocarbamate [51–53].

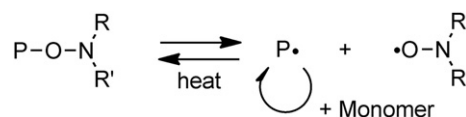
This review focuses on the use of photoirradiation in LRP [54,55]. The major motivation to utilize photochemistry is to enable LRP to proceed under mild thermal conditions by activating the dormant species at low temperature. In addition, photochemistry has been utilized to overcome the difficulties particular to each LRP method. Therefore, photoirradiation is used not only for generating initiating radical species as in conventional photopolymerization, but also for other purposes, such as activation of catalysis, generation of controlling agents, and increasing the polymer-end structure. The most-recent developments in the use of photochemistry in LRP are summarized in this review.

2. Photo-induced LRP

2.1. Photo-induced NMP

The conventional NMP relies on the thermal homolysis of an alkoxyamine dormant species, generating a polymer-end radical and a persistent nitroxyl radical (Scheme 3). The major drawback is the high temperature required for the activation of dormant species. This condition is unattractive for monomers having low thermal stability and low ceiling temperature. Furthermore, since the activation of dormant species having strong oxygen-carbon bonds, such as polyacrylate polymer-ends, is difficult, polymerizable monomer families are quite limited. This problem has been partly solved by the invention of bulky nitroxides, such as TIPNO [56], DEPN [57], and hydroxyl- and siloxy-substituted TEMPO derivatives [58], enabling acrylate polymerization in a controlled manner. However, the polymerization still requires a high temperature, such as heating at 90 °C. Photochemical activation of the dormant species would enable polymerization at a lower temperature.

The first work towards the photochemical NMP was reported by Scaiano and coworkers in 1997 [59]. They found that TEMPO-derived alkoxyamines were activated by photosensitization from either the triplet excited state of xanthone or the singlet excited state



Scheme 3. Activation/deactivation mechanism in NMP.

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