Mechanistic Transformations Involving Radical and Cationic Polymerizations

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Abstract Mechanistic transformation approach has been widely applied in polymer synthesis due to its unique feature combining structurally different polymers prepared by different polymerization mechanisms. Reported methods for the formation of block and graft copolymers through mechanistic transformation involve almost all polymerizations modes. However, certain polymerization processes require extensive purification processes, which can be time-consuming and problematic. Recent developments on controlled/living polymerizations involving radical and cationic mechanisms with the ability to control molecular weight and functionality led to new pathways for mechanistic transformations. In this mini-review, we systematically discussed relevant advances in the field through three main titles namely (i) from radical to cationic mechanism, (ii) from cationic to radical mechanism, and (iii) application of specific catalyst systems for both radical and cationic polymerizations.

Keywords Transformation; Radical polymerization; Cationic polymerization; Controlled/living polymerization; Photopolymerization

INTRODUCTION

Synthesis of complex polymeric structures has been a key challenge in the last decade. Introduction of various controlled/living polymerization methods and their combinations allow the synthesis of polymers with various compositions and topologies.[1–7] Both living radical and cationic polymerizations have been employed and their mechanisms have been investigated in detail. Specifically, atom transfer radical polymerization (ATRP), reversible addition-fragmentation-chain transfer (RAFT) polymerization, and nitroxide mediated radical polymerization (NMRP) have opened new possibilities for macromolecular syntheses as polymers with controlled molecular weight and functionality can be formed. There are also promising advances in cationic polymerization systems, which allow the polymerization of monomers that cannot be performed by radical methods.[8–10] More recent developments on highly efficient coupling reactions further expanded research to much higher levels as specific polymer types can be ligated with almost quantitative efficiency.[11,12]

Mechanistic transformation is a powerful polymerization technique that allows the formation of a variety of copolymers by combining different polymerization techniques that otherwise could not be synthesized by a single polymeriza-

tion mechanism.[13] The concept of mechanistic transformation was originally proposed by Burgess *et al*.[14,15] more than four decades ago and applied to almost all modes of the polymerization processes to form block copolymers with diverse structures and properties. In this article, we do not intend to review all published work on transformation reactions, but focus to illustrate broad versatility of the transformations involving radical and cationic polymerizations with a special emphasis on the work reported from the authors laboratory.

Typically, two different mechanistic transformation strategies are available, namely direct and indirect transformation reactions. Direct transformation considers the transformation of a propagating active center to another active center with different polarity. Generally, an electron transfer reaction is responsible for such transformation as typically demonstrated below in Scheme 1.

The shortcoming associated with the direct transformation is the short lifetime of propagating sites, particularly radicals. The active center must have a lifetime sufficient to permit transformation. Furthermore, a thermodynamic limitation for a successful redox process may result from unsuitable redox potentials of the propagating species and oxidant and reductant.

On the other hand, indirect transformation technique is more attractive by the practical point of view due to easier handling and applicability to a variety of polymerization modes. Therefore, the following sections will essentially concentrate on indirect transformations. As illustrated in Scheme 2, indirect transformation usually requires multistep

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Scheme 1 Direct mechanistic transformation.

**Scheme 2** Indirect mechanistic transformation pathways.
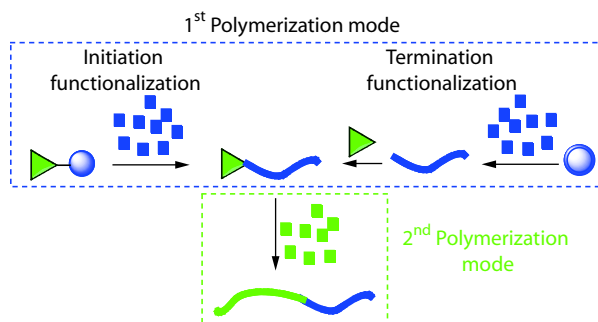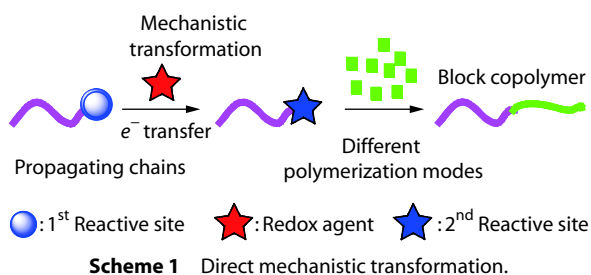
reactions. The stable but potentially reactive functional group for the second polymerization mode is introduced at the chain ends, either in the initiation or in the termination steps of the polymerization of the first monomer. The polymer is isolated and purified, and finally the functional groups are converted to another species.

Mechanistic transformations can be performed between all kinds of addition polymerizations, namely radical, cationic, and anionic polymerizations. In this particular mini review, we would like to focus on transformations comprising radical and cationic strategies. Such transformations are considered in three main titles: (i) from radical to cationic mechanisms, (ii) from cationic to radical mechanisms, and (iii) application of specific catalyst systems for both polymerizations.

MECHANISTIC TRANSFORMATION ROUTES

Mechanistic Transformations from Radical to Cationic Mechanisms

Especially after the development of controlled/living radical polymerizations, the transformation approach became a more attractive tool for the synthesis of block and graft copolymers possessing segments polymerizable with different mechanisms. The control over chain-end functional groups makes it easier for further modifications and thus more suitable for mechanistic transformations.
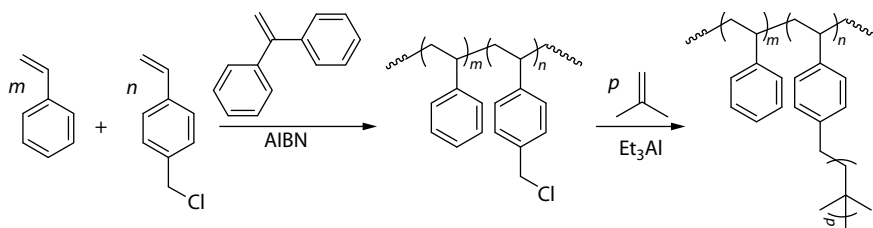
Earlier examples of such transformations include the use of iniferter processes using diphenylethylene as the transfer agent. To exemplify, Nuyken and co-workers demonstrated the possibility of synthesizing graft copolymers by combining iniferter and cationic polymerizations.[16] For this purpose, first poly(methyl methacrylate)-*b*-poly(styrene-*co*-chloromethylstyrene) was synthesized by diphenylethylene mediated iniferter polymerization, which was then used as the precursor for cationic polymerization. Eventually, polyisobutylene was grafted from the main chain and the final graft copolymer was prepared (Scheme 3).

An alternative way of this concept was accomplished by incorporating initer functionality to the polymer chain ends at the ATRP stage using trityl halide as the initiator.[17] In a previous study, Kamigaito and co-workers have presented a novel strategy for the synthesis of block copolymers by *in situ* transformation from radical RAFT polymerization to cationic polymerization.[18] For this purpose, (meth)acrylates were polymerized together with vinyl ether monomers using an azoinitiator and trithiocarbonate type RAFT agents. The RAFT functional polymers were then treated with several Lewis acids simultaneously to generate cationic species at the chain ends, which act as initiating sites only for cationic polymerization in the presence of monomers capable of undergoing cationic polymerization. Thus, the polymerization mode was altered concurrently to give block copolymers in an efficient manner. The simple representation of the strategy is shown below on the example of methyl methacrylate and isobutyl vinylether as monomers and $EtAlCl_2$ as the Lewis acid catalyst (Scheme 4).

Other examples of radical to cationic transformations are mostly based on the use of ATRP. In a previous study, we have shown that ATRP could be combined with $Mn_2(CO)_{10}$ assisted photoinitiated radical polymerization to form block copolymers.[19] As the second mode involves photoinduced conventional radical polymerization, it may be classified as a kind of transformation involving the same mode with different activation mechanisms. It was further shown that the radical produced at the chain end could be oxidized and cationic polymerization of appropriate monomers could be initiated from the carbocations thus formed to yield block copolymer (Scheme 5).

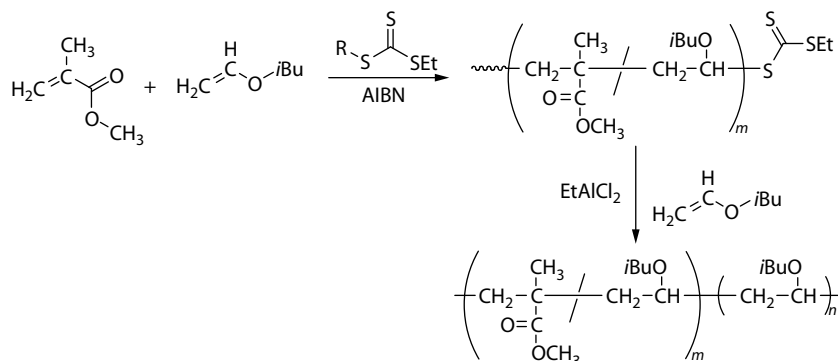### Mechanistic Transformations from Cationic to Radical Mechanisms

Mechanistic transformations can also be performed from cationic to radical polymerization modes. One of the first examples of such transformation was demonstrated by Yagci, which considers the use of a dual initiator consisting of acyl chloride and diazo units responsible for cationic and radical

Scheme 3 Mechanistic transformation from iniferter to cationic polymerization.

polymerizations, respectively.[20] After the activation of acyl chloride functions by silver salts, first the cationic polymerization of THF was realized. Once the PTHF segments were formed, thus formed macroinitiators were heated in the presence of appropriate monomers and eventually the block copolymers were formed (Scheme 6). Block copolymers with crystalline and side-chain liquid-crystalline segments can be prepared through this transformation.[21] The reverse mode of the transformation using the same catalysts is also possible.[22]

Another example on transformation from cationic polymerization to free radical polymerization considers the synthesis of macroinitiators, by taking advantage of the co-initiators

bearing chromophore groups.[23] In a previous work, epichloro-hydrin was polymerized by activated monomer mechanism using a photoactive group. The resulting polyepichloro-hydrine (PECH) chains bearing photoactive end groups were then employed as the initiator for photopolymerization.[24] The overall mechanism is shown in Scheme 7.

Conceptually same approach was also applied to living cationic polymerization of poly(tetrahydrofuran) (PTHF). Ter-mination of growing PTHF with sodium salt of benzoin gives a photoactive PTHF, which can be used for block copolymer synthesis. Depending on the type of initiator used in the cationic step, either α and α,ω-terminated PTHFs can be syn-
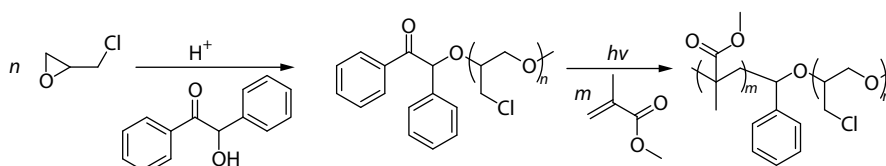

Scheme 4   Mechanistic transformation from RAFT polymerization to cationic polymerization.
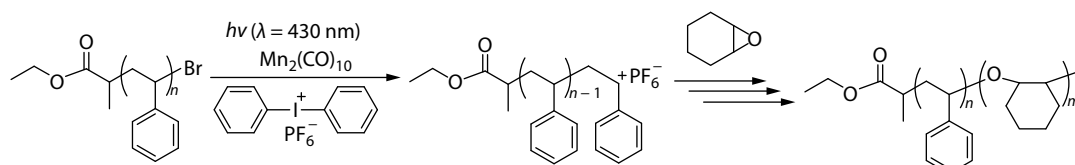
Scheme 5   Mechanistic transformation from ATRP to photoinduced cationic polymerization.
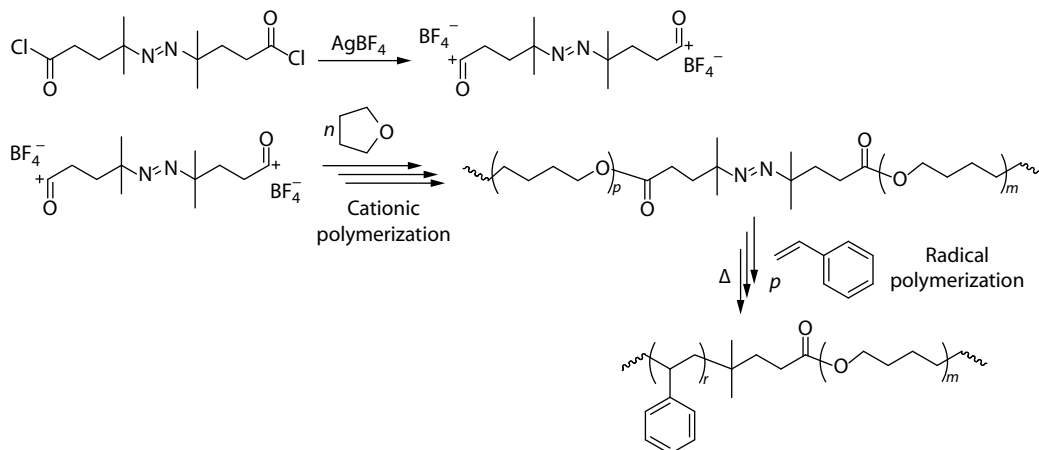
Scheme 6   Mechanistic transformation from cationic to free radical polymerization using dual initiator based on diazo-benzoyl structure.

Scheme 7   Mechanistic transformation from cationic polymerization to photoinduced radical polymerization.

thesized leading to the formation of AB and/or ABA type block copolymers, respectively (Scheme 8).[25]

Similar termination strategy to obtain polymers with photoactive end groups can be realized by using pyridinium *N*-oxides as nucleophiles (Scheme 9).[26] Photoinduced *α*-cleavage of the end groups in the presence of a second monomer gives block copolymers through mechanistic transformation from living cationic polymerization to photoinduced radical polymerization.

Such transformations have also been applied to all well-known living radical polymerizations.[27−32] One example of transformation from cationic polymerization to NMRP was demonstrated by Yoshida *et al.*[33] For this purpose, PTHF chains were quenched with sodium 4-oxy TEMPO to afford

TEMPO end-functionalized PTHF. Afterwards, it was used as the macroinitiator for NMRP of styrene to afford PTHF-*b*-PS (Scheme 10).

The TEMPO moieties can also be attached to the chain ends by photochemical means.[34] Matyjaszewski reported an interesting variation of dual initiator approach using 2-bromopropionyl bromide.[35] The acyl bromide site was activated by silver triflate for the cationic polymerization of THF. Once the PTHF segment was prepared, the secondary bromide functionality could be activated by low oxidation state copper complexes for the ATRP of vinylic segments. By this way, block copolymers with the corresponding diverse segments were readily prepared as depicted below (Scheme 11).
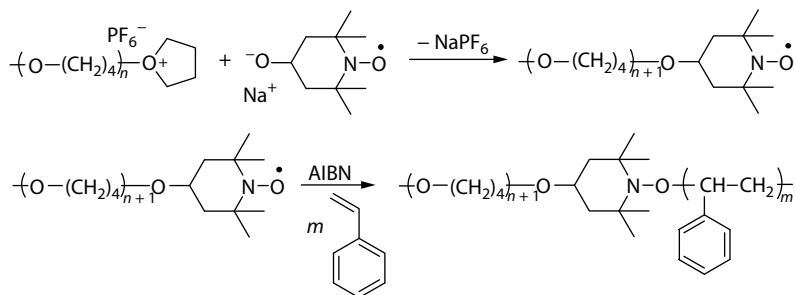
We have recently presented a novel synthetic strategy for
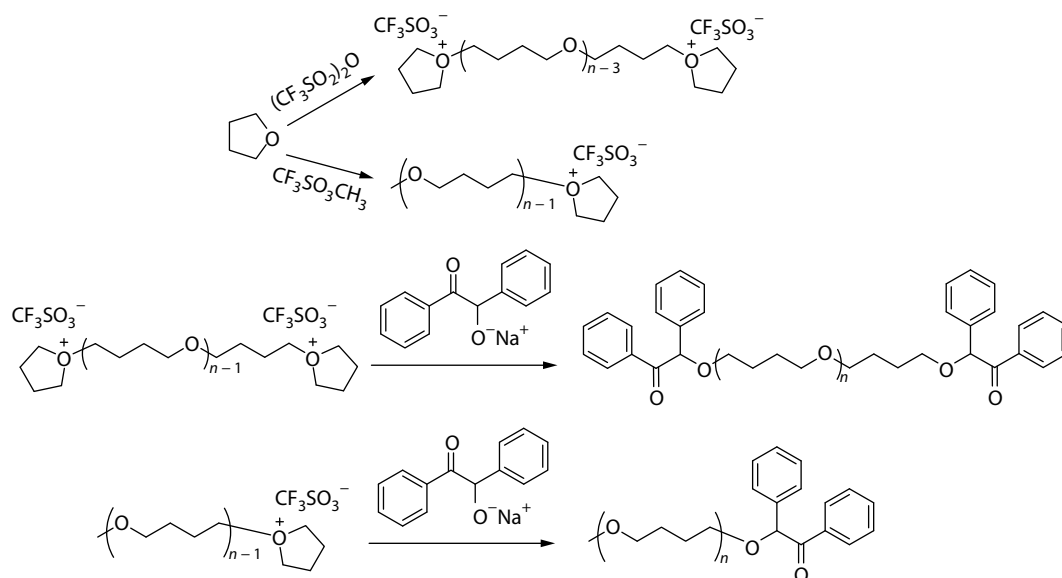
Scheme 8　Synthesis of PTHF macroinitiators bearing benzoin as photoactive groups at the chain ends.
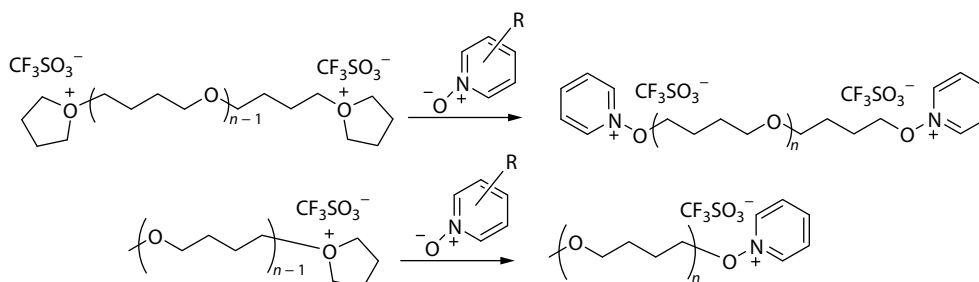
Scheme 9　Synthesis of PTHF photoinitiators bearing pyridinium oxides as photoactive groups at the chain ends.

Scheme 10　Example on the mechanistic transformation from cationic polymerization to NMRP.
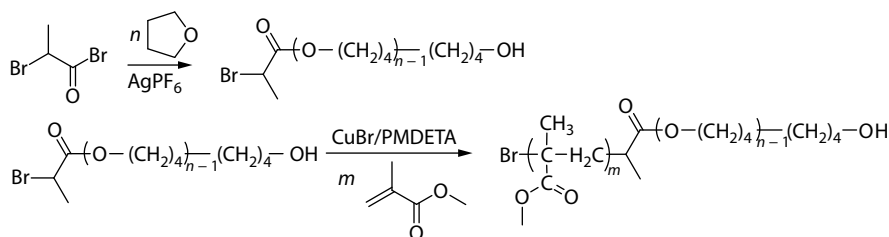
Scheme 11   Mechanistic transformation from cationic polymerization to ATRP.

the synthesis of block copolymers based on mechanistic transformation from photoinitiated cationic polymerization to RAFT polymerization.[36] By terminating the living cationic polymerization of PTHF using a carboxylic acid functional RAFT agent, PTHF possessing end groups capable of mediating RAFT process was obtained. Afterwards, this polymer was used as a precursor for the production of PTHF containing block copolymers as a shown in Scheme 12.

Similar transformation from living cationic to RAFT polymerizations has also been demonstrated by Kamigaito and co-workers where they functionalized growing cationic chains with RAFT agents to prepare precursors for RAFT polymerization. Then these precursors were used as macroinitiators for block copolymer synthesis.[37]

Very recently, a novel initiating system consisting of manganese decacarbonyl/diphenyl iodonium couple ($Mn_2(CO)_{10}$/$Ph_2I^+PF_6^-$) was shown to initiate polymerization of vinyl ethers in the presence of alkyl halides in a controlled/living fashion under visible light irradiation. This process follows a photoinduced radical oxidation/addition/deactivation (PROAD) mechanism and allows the preparation of monodisperse polyvinyl ethers.[38] In a more recent study, trityl bromide was used as the halide source and $Mn_2(CO)_{10}$/$Ph_2I^+PF_6^-$ was used as initiating system for the production of poly(isobutyl vinyl ether) (PIBVE) with trityl end group. Upon heating, this

macroiniferter agent was employed for the copolymerization of methyl methacrylate (MMA), which eventually yielded P(IBVE-*b*-MMA) (Scheme 13).[39]

A typical strategy was also applied by Li *et al*. which focuses on the formation of polyvinyl ether blocks by PROAD system, followed by the formation of the acrylic second block either by ATRP or RAFT polymerization for the synthesis of block copolymers.[40]

Application of Specific Catalyst Systems for Both Radical and Cationic Polymerizations

Depending on the reaction conditions and monomer type, some specific catalyst systems can initiate both cationic and radical polymerizations. An early example was reported by Kamigaito and co-workers, who showed the applicability of $FeCl_3$ for the catalytic initiation of both polymerizations.[41] In the presence of a benzylic halide, $FeCl_3$ catalyzed the polymerization of styrene by heterolytic abstraction of the halide functionality from the initiator. After certain polymerization time, triphenylphosphine was added to the polymerization media, which regulated the dissociation behavior of the halide end group. The polymerization mode concurrently shifted to a free radical path, as reflected by the polymerization of methyl methacrylate, which is not polymerizable cationically (Scheme 14).
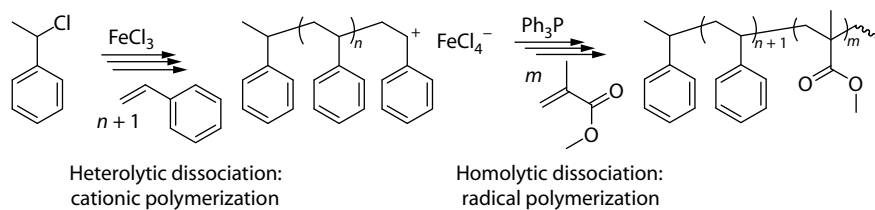
Another simultaneous utilization of both polymerization
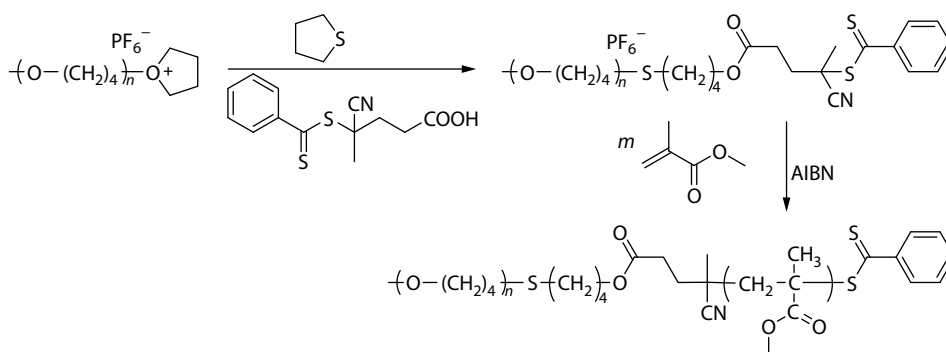
Scheme 12   Mechanistic transformation from cationic polymerization to RAFT polymerization.
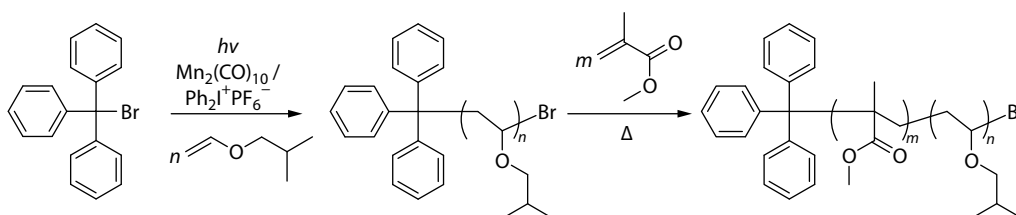
Scheme 13   Synthesis of PIBVE-*b*-PMMA copolymers by the combination of PROAD and iniferter processes.

Scheme 14 *In situ* application of cationic and radical polymerizations *via* FeCl₃-based catalyst system for block copolymer synthesis.

modes was shown on the example of specific RAFT agents, which provides the synthesis of various comonomer sequence distributions in a controlled manner. Using appropriate monomer compositions and RAFT agents, statistical multiblock and kinetic diblock copolymers can be prepared easily by adjusting the reaction conditions through a controlled/living fashion as shown in Scheme 15.[42]

Notably, a similar approach was shown by Fors and coworkers, which considers the use of RAFT agents for the polymerization of vinyl ethers and acrylates through switchable radical and cationic polymerizations on demand.[43]

Analogous approach was also applied for the synthesis of core-cross-linked star copolymers.[44] For this purpose, first the arms of the star polymers were prepared by cationic RAFT polymerization, which was then subjected to radical RAFT or both radical and cationic crosslinking to construct the core
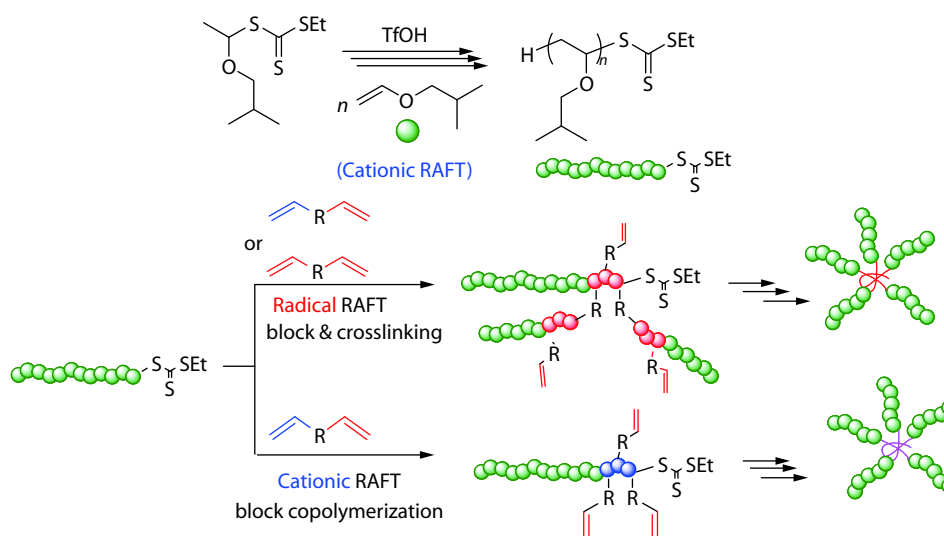
(Scheme 16).

Similarly, specially designed RAFT agents were also employed in cationic and radical polymerizations to form block copolymers possessing poly(vinyl fluoride) segments that cannot be simply synthesized by conventional methodologies (Scheme 17).[45]

Kamigaito group designed and used special RAFT agents for the radical alternating copolymerization of vinyl ether/chlorotrifluoroethylene monomer system and sequential cationic polymerization of the vinyl ether units under specified reaction conditions. It was also shown that this target block copolymer can also be obtained by applying polymerization modes in a reverse mode as shown below (Scheme 18).[46]
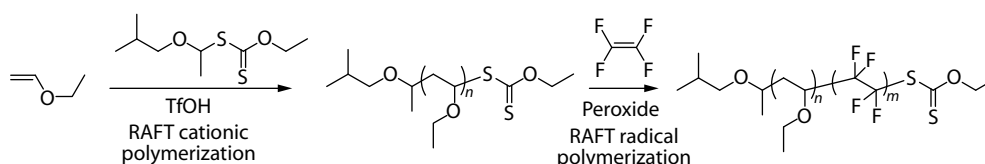
The preparation of multiblock copolymers composed of vinyl ether and acrylic monomers can be accomplished by such dual activity.[47]
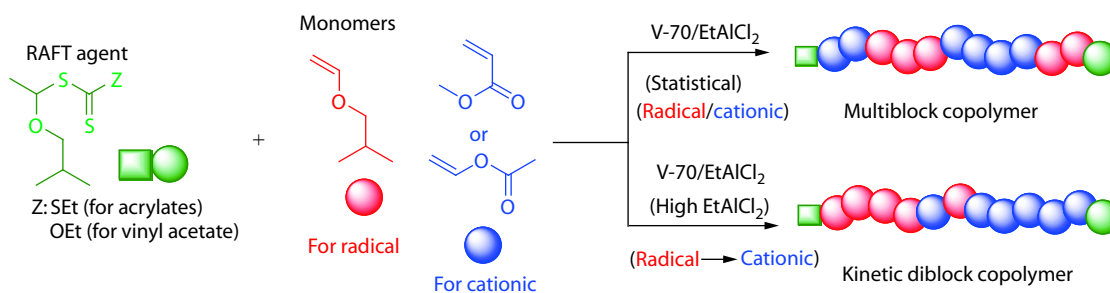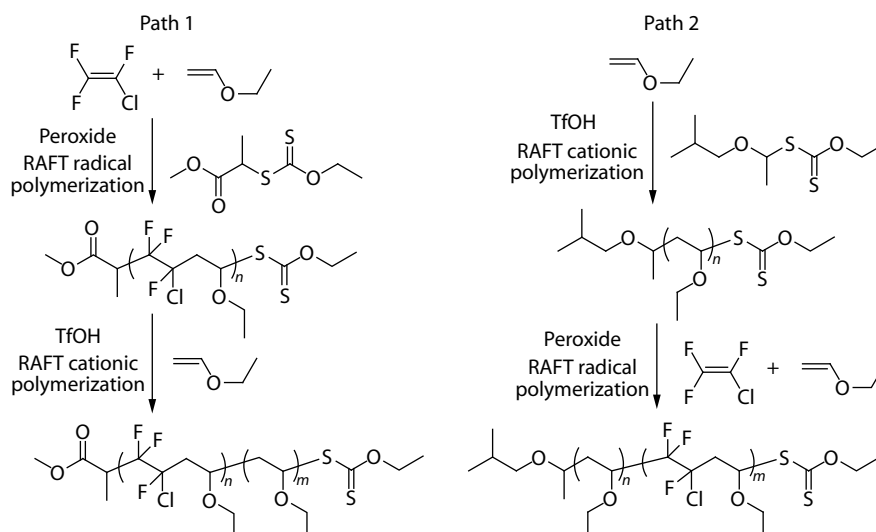

Scheme 15 One-shot radical and cationic RAFT copolymerization to generate comonomer sequence distributions.

Scheme 16 Star polymers *via* a cationic and radical RAFT cross-linking reaction.

Scheme 17   Preparation of poly(vinyl fluoride) containing block copolymers by the combination of RAFT radical and cationic polymerizations.

Scheme 18   Combination of RAFT radical and cationic polymerizations for block copolymer synthesis.

CONCLUSIONS

In conclusion, the research field of mechanistic transformation has a very bright future due to the ease of use combined with the range of possible combinations. Once the desired initiating functionalities are successfully incorporated to the polymer chains, the mechanistic transformation approach would offer scientist new tools to fabricate complex macromolecular structures with desired properties. From the practical point of view, among the various methods applied, direct transformation appears to be more suitable which eliminates disadvantage of being multistep syntheses. In principle, such transformations are not limited to block and graft copolymers, but can be extended to the polymers with more complex topologies such as star and hyperbranched copolymers and co-networks providing that appropriate initiators and monomers are designed and synthesized. Free radical and cationic processes appear to be particularly important as new metal free methodologies have recently been developed providing compatibility between the modes and could be used to fabricate sophisticated biomaterials. Future research is expected to focus on the simplification of transformation reactions with the development of new initiating sytems that have the potential to achieve materials with desired structures and properties.

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