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Overview of Tacticity Control in Radical Polymerization

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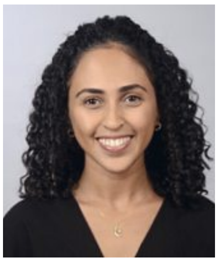
Abstract: The stereoregularity of a polymer plays a key role in determining its properties. While stereocontrol can easily be achieved in coordination and ionic polymerization, it remains a challenge with radical polymerization. Considering the ubiquity and versatility of radical polymerization, significant efforts have been made over the past 50 years to address this issue. In this mini review, we highlight some of the strategies that have been developed to enable stereospecific radical polymerization, from the use of Lewis acid additives to the application of high electric fields. We hope that this review will provide the reader with a comprehensive overview of the current state of the art and equip them with the foundational knowledge needed to explore new avenues in this domain.

Keywords: Stereospecific radical polymerization · Tacticity



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1. Introduction

The invention of synthetic polymers has revolutionized and shaped humanity. Although initially envisioned to just be a replacement for natural materials,[1] synthetic polymers have since become indispensable to our daily lives, being used from food packaging[2] to airplane components.[3] Their sheer versatility stems from our ability to tailor polymer material properties *via* precise control over their composition and microstructure.

Microstructure control is particularly important as the microstructure of the polymer plays a significant role in dictating its physical form and properties[4] – polymers with the same chemical composition but with slightly different molecular weights,[5] degrees of crystallinity,[6] crosslink densities,[7] or chain architectures,[8] can exhibit drastically different properties. For example, small changes in the crosslink density of a polymer can lead to large changes in its solubility, stiffness, and ductility.

A key aspect of polymer microstructure is its tacticity, which is the relative stereochemical configuration between adjacent chiral centers in the polymer backbone. Simply put, tacticity, as defined by the IUPAC, is "*the orderliness of the succession of configurational repeating units in the main chain (backbone) of a regular macromolecule*".[9] With that in mind, the three most basic types of tacticity are: isotactic, where the repeating units have the same spatial orientation; syndiotactic, where the repeating units have alternating spatial orientations; and atactic, where the orientations are random. The tacticity of a polymer is important because the spatial orientation of the repeating unit (and thus the 3D arrangement of the pendant groups along the polymer backbone) impacts its ability to pack together and crystallize, which in turn, affects its properties (Fig. 1). This interplay between tacticity, crystallinity, and property is best exemplified by polypropylene: isotactic polypropylene is semi-crystalline, and is thus stiff and strong,[10] whereas atactic polypropylene is amorphous, which makes it compliant and weak.[11] Given the impact that the degree of crystallinity has on the optical, mechanical, thermal, and chemical properties of the polymer,[12] significant efforts have been made over the past decades to understand how to control polymer tacticity during synthesis.[13]

Today, tacticity control can easily be achieved with coordination[14–18] and ionic polymerization[19–23] but still remains a challenge with radical polymerization. This is due to the fact that the terminal carbon of a propagating radical has an sp^2 planar-like structure that is not stereochemically defined, resulting in non-stereoselective chain propagation (Fig. 1).[24] The difficulty with tacticity control in radical polymerization is unfortunate given the numerous advantages that it has over its ionic and coordination counterparts, from improved functional group tolerance to its relative insensitivity to impurities. These advantages have led to the ubiquitous use of radical polymerization in both industry and academia, accounting for the synthesis of nearly half of all commodity polymers.[25]

As such, considering the importance of radical polymerization and tacticity control, this review article seeks to briefly outline the current strategies available to achieve stereocontrol during radical polymerization, both in controlled radical polymerization and free radical polymerization.

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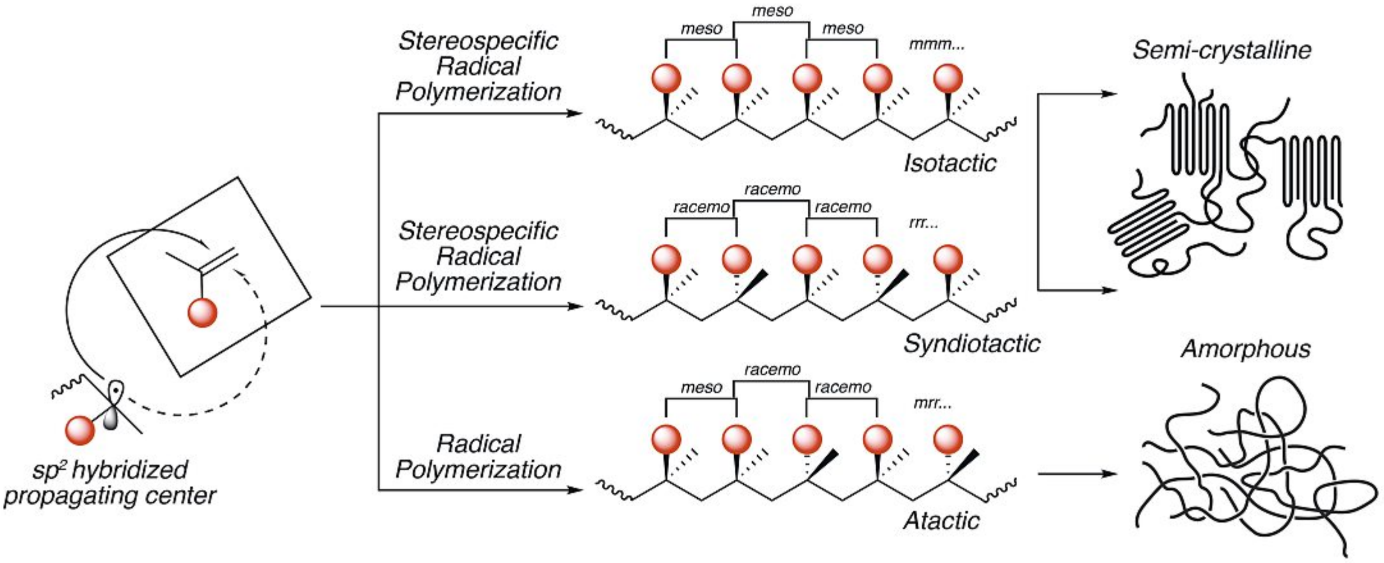

Fig. 1. Stereocontrol during radical polymerization enables the synthesis of semi-crystalline tactic polymers.

2. Stereospecific Radical Polymerization

2.1 *Confinement*

Stereospecific radical polymerization can be achieved *via* the use of confined environments that limit the ability of the propagating radical and monomer to rotate and diffuse during polymerization. One common approach to achieve confinement is to polymerize within inclusion canals.[26–30] For example, Zou *et al.* showed that the radical-induced inclusion polymerization of acrylonitrile within urea canals resulted in completely isotactic polyacrylonitile (*mm* >99%).[31] Using a similar concept, Zhao *et al*. showed that nanoconfinement of liquid methyl methacrylate within porous glasses drove changes in polymer tacticity, with the percentage of isotactic triads increasing from 12% in bulk to 52% with nanoconfinement.[32] More recently, radical polymerization within confined metal organic frameworks (MOFs) have similarly been shown to improve the stereoregularity of the resulting polymer.[33–36] Hwang *et al*. reported that both the free radical polymerization and reversible addition fragmentation chain transfer (RAFT) polymerization of vinyl propionate within a MOF increased the *meso* diad fraction by 14% as compared to in the bulk without the MOF.[34] Confinement can also be realized *via* solid state[37–39] and template polymerization,[40–42] and exploited to obtain stereoregular polymers. It is important to note that, while effective, confinement methods are complicated by the need to: a) introduce the monomers into the host; b) remove any unconfined monomers; and c) remove the host after polymerization to isolate the polymer. In addition, since confinement of the radical species suppresses termination reactions, the use of confinement methods also impacts the molecular weight of the polymers.[24]

2.2 *Monomer Design*

Although stereocontrol can be achieved in confined environments, it is considerably more difficult in solution since the monomers and propagating chains can move much more freely. One strategy to circumvent this is to use monomers with structures that bias the formation of stereoregular polymers. For example, monomers with bulky side groups can interact with each other *via* steric effects to influence the tacticity of the resulting polymer (Fig. 2).[43–50] Ishitake *et al*. reported a series of silyl methacrylates with varying substituent bulkiness that enabled the synthesis of polymers with tacticities ranging from syndiotactic-rich to isotactic-rich.[51] More recently, Yoshinaga and Yoshida synthesized a methacrylic monomer bearing a bulky oxazolidone structure and used it to modulate the stereoregularity of copolymers made with it.[52] Stereospecific polymerization can also be achieved using monomers that contain chiral auxiliaries.[53–55] In one of the earliest and most successful examples of this, Porter *et al.* showed that chiral oxazolidine acrylamides could undergo stereospecific polymerization to yield 92% isotactic polymers.[56] Tanaka *et al.* recently demonstrated that chiral lactic acid-based acrylates enabled the controlled radical polymerization of polymers with tunable tacticities (*mm*: 28 – 100%).[57] Although successful in achieving stereospecific polymerization, the key challenge with the monomer design approach is that it is inherently limited in monomer scope.

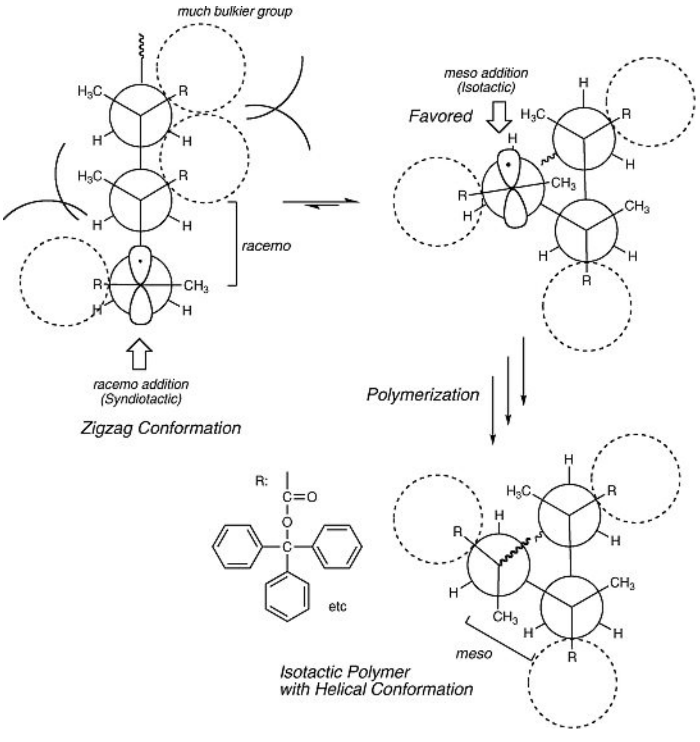

Fig. 2. Schematic showing how bulky side groups can bias the formation of isotactic polymers. Adapted with permission from ref. [24]. Copyright 2009 American Chemical Society.

2.3 *Solvent Effects*

A more general approach is to utilize solvents and additives (*vide infra*) that can interact with the monomer and the propagating chain to create stereospecific environments.[13,24] Fluoroalcohols, in particular, have been found to be one of the most effective solvents in inducing stereospecific polymerization. While the exact stereospecificity mechanism is monomer dependent, it is largely due to hydrogen bonding and/or the steric interactions between the fluoroalcohols and the monomer/polymer (Fig. 3).[58–64] For example, Nagara *et al.* showed that the free radical polymerization of vinyl acetate in nonafluoro-*tert*-butyl alcohol resulted in a largely syndiotactic polymer (r = 72%).[65] Taking it a step further, Li *et al.* reported the synthesis of stereoblock polymers by using temperature to regulate the interactions between the fluoroalcohols and the growing chain during RAFT.[66] The main disadvantage of the fluoroalcohol approach is that cold temperatures (< 0˚C) and low monomer concentrations are often required to achieve substantial changes in the tacticity of the polymer; this can negatively impact the polymerization kinetics and the molecular weight of the resulting polymer. Although not as heavily explored, it is worth noting that the use of alkyl alcohols,[67,68] silyl alcohols,[69] and liquid crystalline solvents[70] during polymerization have also been found to result in polymers with increased stereoregularity.

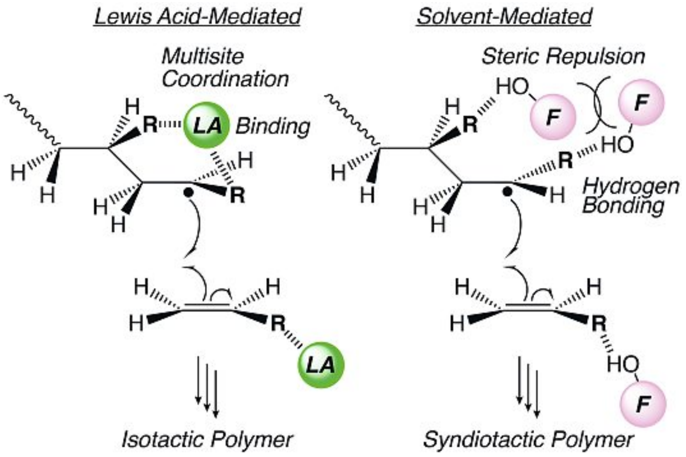

Fig. 3. Schematic showing how stereospecific radical polymerization is achieved with fluoroalcohols (right) and Lewis acids (left). Redrawn and adapted with permission from ref. [74]. Copyright 2008 American Chemical Society.

2.4 *Lewis Acids Additives*

The use of Lewis acids additives during polymerization is the most employed method today to achieve stereospecific radical polymerization.[71–74] The Lewis acid is believed to form a chelate between the terminal and penultimate side groups of the polymer terminus, which results in an energetic bias towards subsequent *meso* propagation (Fig. 3).[75]

For example, early work from Isobe *et al*. demonstrated that the use of catalytic amounts of ytterbium (III) triflate during the free radical polymerization of methacrylamides resulted in highly isotactic polymers (up to 80% m).[76] Lewis acids can also be used with controlled radical polymerization techniques to obtain stereoregular polymers.[77–84] Imamura *et al*. recently reported the synthesis of isotactic homopolymers and stereoblock copolymers *via* organotellurium-mediated radical polymerization in the presence of Lewis acids.[85] Shanmugam and Boyer showed that stereogradient polymers could be achieved by slowly deactivating their Lewis acid with a Lewis base during PET-RAFT.[86] Since the Lewis acids are added as additives during polymerization, they can be synergistically combined with some of the other strategies described above to enhance stereocontrol: Pan and Ouchi obtained isotactic-rich polymers by polymerizing bulky acrylamide monomers in the presence of a Lewis acid;[87] Schaubach *et al.* used both Lewis acids and fluoroalcohols with atom transfer radical polymerization (ATRP) to synthesize highly isotactic polymers (mm = 69%);[88] Fujita and Yamago showed that the Lewis acid catalyzed polymerization of acrylimides containing chiral oxazolidinones gave polymers with up to >99% *meso* tetrads.[89] Despite their utility, the Lewis acid approach is hampered by the need for high Lewis acid loadings, typically upwards of 10 mol%, which can negatively impact polymerization. To address this, Zhong and colleagues developed a Lewis acid-tethered cobalt(III)-porphyrin bimetallic complex that enabled the stereocontrolled radical polymerization of acrylamides. Since the tethered Lewis acid is always in close proximity to the growing chain end, only low concentrations of the Lewis acid are needed; using this bimetallic catalyst, polymers with >90% m could be achieved with only 2.5 mol% of the Lewis acid.[90]

2.5 *Hydrogen Bonding Additives*

Additives that can form multiple hydrogen bonds to the monomer/propagating chain can also induce stereocontrol during radical polymerization, although they have not been as explored recently.[91–96] Murayama *et al*. reported that hydrogen bonding between thiourea derivates and acrylamides during RAFT resulted in isotactic-rich polyacrylamides.[97] Tao *et al*. synthesized an acrylamide monomer with a specific proton donor-acceptor-donor sequence and showed that the use of a thymine-derivative that contained the complementary proton acceptor-donor-acceptor sequence during RAFT enabled the synthesis of highly syndiotactic polymers.[98] Along those lines, Saito and Saito demonstrated that hydrogen bonding between catechol and methacrylic acid could be exploited during free radical polymerization to give syndiotactic-rich polymers (r = 91%).[99] While similar in mechanism to the fluoroalcohol approach, an advantage of using these additives that can form multiple hydrogen bonds is that the hydrogen bonded complexes can be more thermally stable, which allows for stereospecific radical polymerization to occur at higher temperatures.

2.6 *Emerging Approaches*

It is worth noting that most recent work on stereospecific radical polymerization are still primarily based on the stereocontrol strategies listed above; improvements in stereocontrol have largely been due to creative variations and/or combinations of the previously established tried-and-true approaches. Some notable exceptions include the recent work by Adrjanowicz and coworkers on the use of an external high electric field to induce stereospecific radical polymerization.[100,101] In 2022, they showed that isotactic-rich poly(methyl methacrylate) (PMMA, mm = 57.3%) could be synthesized in the presence of a 154 kV/cm electric field; when no DC field was applied, the synthesized PMMA was syndiotactic with an mm value of 11.5% (Fig. 4).[100] They were able to achieve such high electric fields by using two parallel plate electrodes that were spaced 19.5 µm apart and applying high voltages up to ± 500V to them.

Building on that work, Tu *et al.* reported that the electric-field assisted radical polymerization of isobornyl acrylate (a bulky monomer) resulted in an increase of mm from ~16% at 0 kV/cm to 36% at 140 kV/cm.[101] Although the exact stereocontrol mechanism of this electric-field assisted method has yet to be precisely determined, it represents a significant advancement in the state of the art and is a valuable addition to our toolbox of stereospecific radical polymerization. It is worth noting that electric-field controlled transformations can also be found in other areas of the chemical sciences.[102]

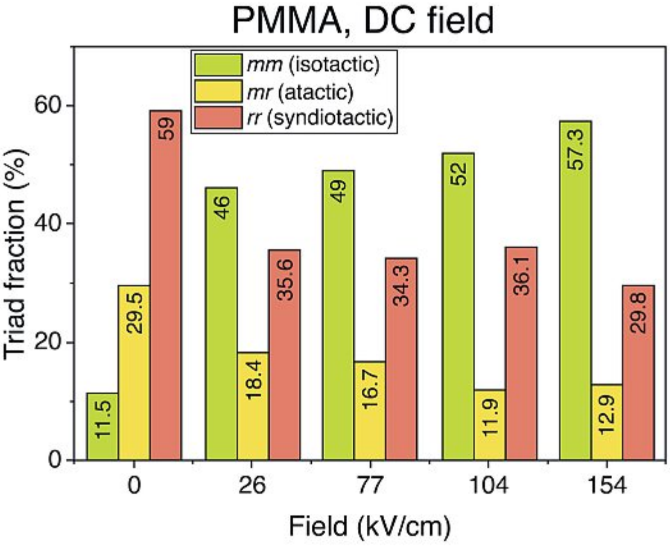

Fig. 4. Triad fraction of α-CH_3 in PMMA as a function of applied electric-field during radical polymerization. Redrawn and adapted from ref. [100] with permission from the Royal Society of Chemistry.

3. Conclusions

The nature of radical polymerization inherently makes stereocontrol challenging, but we hope that this mini-review highlights that it is not impossible. Indeed, many strategies exist to achieve stereospecific radical polymerization. Although these methods do not yet afford the same level of stereocontrol seen in coordination or ionic polymerization, they are still of significant utility as they enable the use of tacticity as a design handle in radical polymerization. Looking forward, the emergence of electric-field assisted polymerization as a radical new method to induce stereocontrol suggests that there is still significant room for innovation in this field. We expect that understanding the stereocontrol mechanism of the electric-field approach will unlock new opportunities and directions in the field, which will hopefully spur the development of novel chemistries and methods for stereospecific radical polymerization.

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