

# Recent Developments on Cationic Polymerization of Vinyl Ethers

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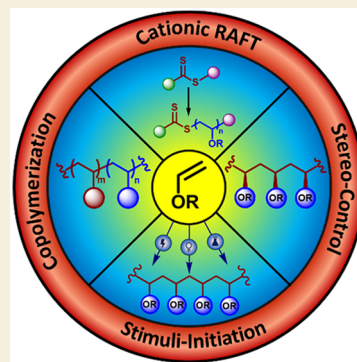
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**ABSTRACT:** In recent times, the evolution of cationic polymerization has taken a multidirectional approach, with the development of cationic reversible addition–fragmentation chain transfer (RAFT) polymerization. In contrast to the conventional cationic polymerization methods, which were typically carried out under inert atmospheres and low temperatures, various novel polymerization techniques have been developed where the reactions are carried out in open air, operate at room temperature, are cost-effective, and are environmentally friendly. Besides, several external stimuli, such as heat, light, chemicals, electrical potential, etc. have been employed to activate and control the polymerization process. It also enables the combination of cationic polymerization with other polymerization methods in a single reaction vessel, eliminating the necessity for isolation and purification during intermediate steps. In addition, significant advancements have been made through various modifications in catalyst systems, resulting in polymers with an exceptionally high level of stereoregularity. This review article comprehensively analyses the recent developments in cationic polymerization, encompassing their applications and offering insights into future perspectives.

**KEYWORDS:** Cationic Polymerization, Cationic RAFT Polymerization, Copolymerization, Vinyl Ether, Lewis Acid, External Stimuli, Photocatalyst, Organocatalyst, Stereoregularity



## INTRODUCTION

Depending on the structure and chemical properties of the monomers, polymers may be synthesized using a variety of processes, such as condensation,<sup>1</sup> ring opening,<sup>2</sup> free radical,<sup>3</sup> cationic,<sup>4</sup> and anionic<sup>5,6</sup> polymerization. Among these techniques, cationic polymerization of vinyl monomers is applicable to a relatively smaller number of monomers, but is important in both academia and industry.<sup>7</sup> It offers a versatile platform to produce polymers having tailored properties, which makes them valuable for a wide range of applications. It is a chain growth polymerization that involves the initiation through the formation of a carbocationic active center. A cationic initiator, typically a Lewis acid or a protonic acid compound, transfers charge to a monomer, leading to the formation of carbenium ions which are then attacked by other monomers. Polymer chain growth continues as new monomers join the chain via successive carbocation formation and propagation steps.<sup>8</sup> Termination occurs through proton transfer or chain transfer to counterion, polymer, monomer, or solvent (Figure 1A). In this process, the choice of monomers is very crucial, as it involves carbocationic intermediates. The monomers having electron donating groups are preferred as they stabilize the positive charge on the growing cationic chain, which facilitates propagation. Therefore, this polymerization is applicable for monomers that have electron-rich double bonds, such as isobutylene (IB),<sup>9</sup> vinyl

ethers (VEs),<sup>10,11</sup> styrene,<sup>12,13</sup> *N*-vinylcarbazole,<sup>14,15</sup> etc. (Figure 1B). Here, the overall polymerization rates are higher compared to radical polymerization, and there are several cationic polymerizations where the polymerization rates at low temperatures are faster.<sup>16</sup>

Since the early studies in the 20<sup>th</sup> century, researchers have explored cationic polymerization reactions involving diverse monomers, employing a variety of initiators and catalysts. However, controlling cationic polymerization has always been a challenge due to the high reactivity of the active cationic species. Living polymerization technique stands as an appealing method to synthesize well-defined polymers having controlled molecular weight, narrow dispersity ( $\mathcal{D}$ ), and predetermined chain end functionalities.<sup>17,18</sup> In 1984, Miyamoto and co-workers reported the first living cationic polymerization (LCP) utilizing alkyl vinyl ethers.<sup>19</sup> Later in 1986, Kennedy and Faust also used LCP to obtain a narrow molecular weight distribution ( $\mathcal{D}$ ) of polyisobutylenes.<sup>20</sup> Since then, numerous innovations have been made in living cationic polymerization

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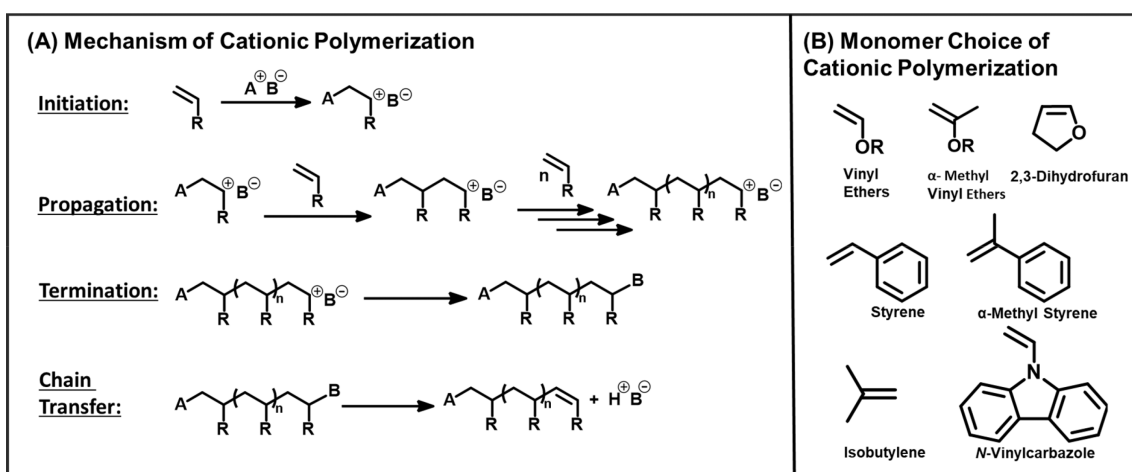


Figure 1. (A) Mechanism of cationic polymerization. (B) Monomer choice of cationic polymerization.

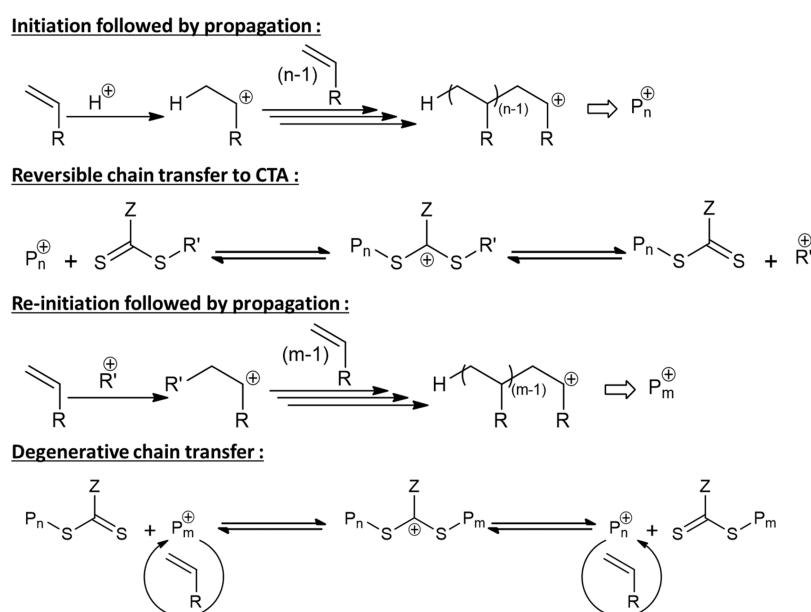


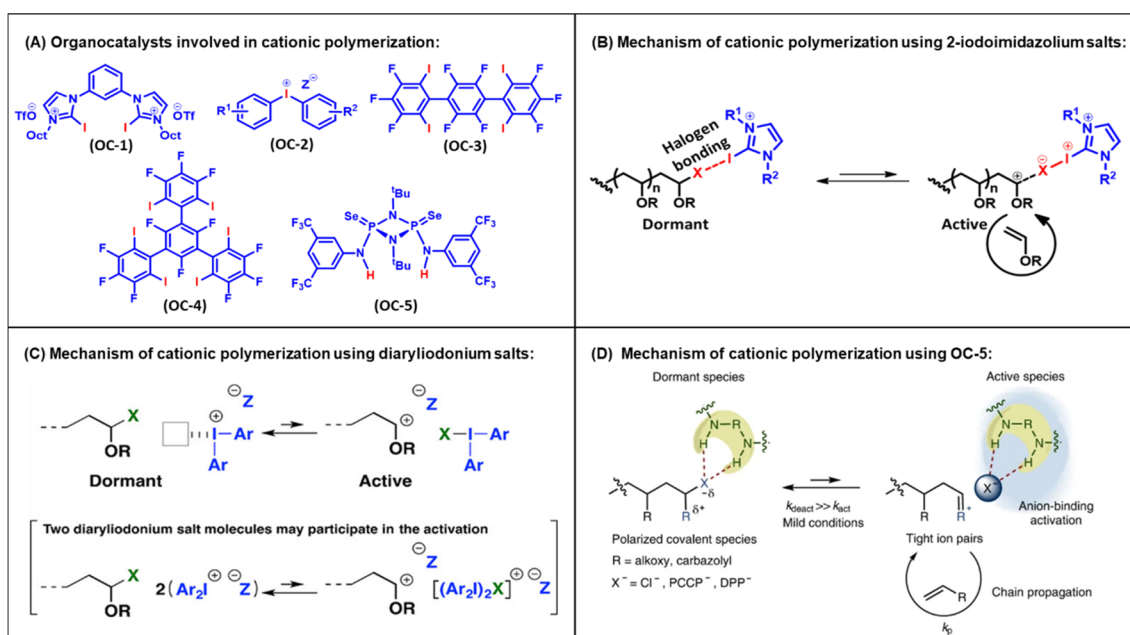
Figure 2. Mechanism of cationic RAFT polymerization. Adapted with permission from ref 25. Copyright 2021 Elsevier.

in terms of monomers, initiators, and catalysts.<sup>21</sup> Nonetheless, the combination of cationic polymerization and reversible addition–fragmentation chain transfer (RAFT) polymerization has opened a new frontier in the realm of living polymerization.<sup>22</sup> RAFT polymerization has emerged as a transformative technique that offers unparalleled control over polymer architecture, molecular weight, and dispersity.<sup>23,24</sup> The dynamic equilibrium between the dormant and active forms of the radicals enables controlled chain growth, yielding precise polymer structures with controlled functionality and molecular weights. Although this RAFT technique was initially confined to radical chemistry, it became evident that both cationic and RAFT polymerization could coexist, giving rise to the concept of cationic RAFT polymerization, which was developed by Kamigaito and co-workers in 2015.<sup>22</sup> This method involves a similar degenerative chain transfer mechanism involving a cationic active center generated by a protonic initiator (Figure 2).

Unlike the radical RAFT polymerizations, cationic RAFT polymerization is not restricted solely to thiocarbonylthio-based RAFT agents. This approach can be successfully

employed with various chain transfer agents (CTAs),<sup>25</sup> encompassing carbamates, thioethers, selenoethers, phosphates, and sulfonates. The molecular weights can be regulated by varying the feed ratio of monomer and CTA. Cationic RAFT can effectively be applied to produce precisely controlled polymers with structured characteristics, including end-functionalized, block, and star polymers. Moreover, this approach facilitates the creation of block copolymers comprising both radically and cationically polymerizable monomers.<sup>26</sup>

While significant progress has been made in controlling factors like molecular weight, dispersity, and composition, achieving precise stereocontrol in these processes remains exceptionally difficult. Attaining a high degree of stereoregularity in polymer synthesis has become one of the most significant and appealing objects in polymer science. In the past, numerous efforts have been made to obtain stereocontrol in the cationic polymerization of vinyl ethers. In the late 1940s, Schildknecht and co-workers documented the initial instance of stereoregular synthetic polymerization,<sup>27,28</sup> where the strong Lewis acid  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  as a catalyst for VE polymerization at a



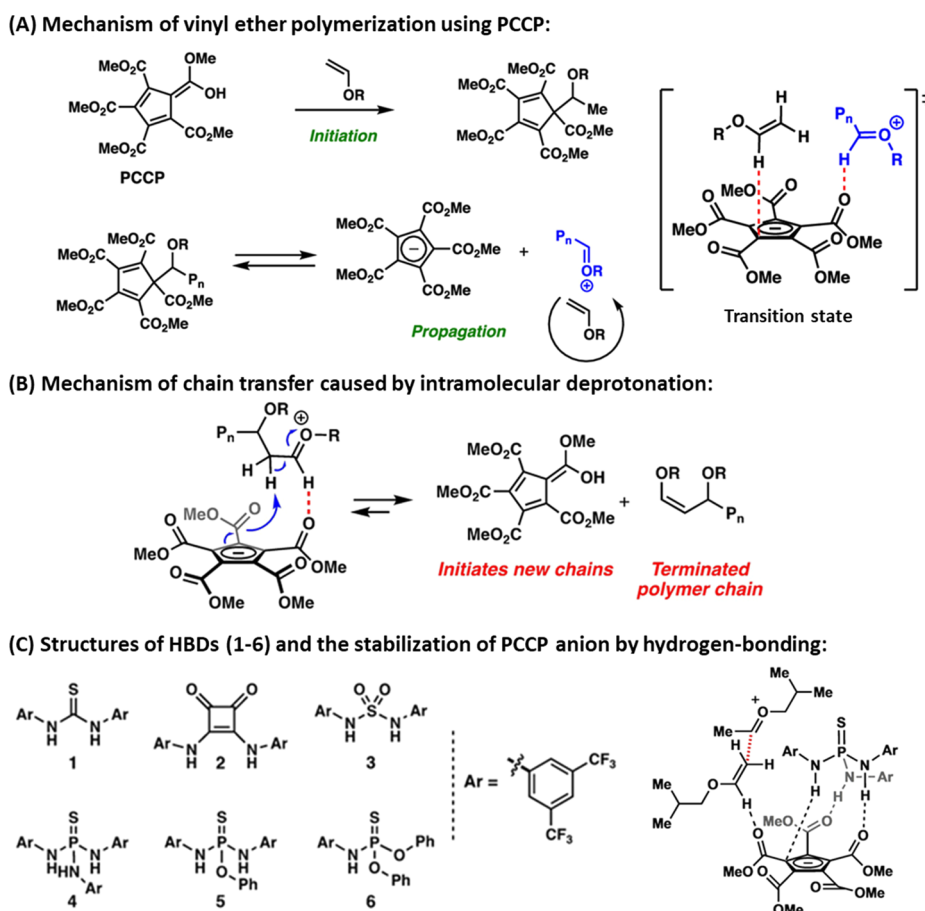
**Figure 3.** (A) Various organocatalysts used in cationic polymerization. (B) Mechanism of cationic polymerization using 2-iodoimidazolium salts. Adapted with permission from ref 44. Copyright 2017 John Wiley & Sons. (C) Mechanism of cationic polymerization using diaryliodonium salts. Reproduced with permission from ref 45. Copyright 2020 American Chemical Society. (D) Mechanism of cationic polymerization using OC-5. Reproduced with permission from ref 49. Copyright 2022 Springer Nature.

low temperature ( $-78\text{ }^{\circ}\text{C}$ ) resulted in the formation of semicrystalline materials with significantly greater hardness and toughness compared. In 1969, Yuki et al. obtained highly isotactic poly(benzyl vinyl ether) using  $\text{BF}_3\cdot\text{OEt}_2$  as a catalyst at  $-78\text{ }^{\circ}\text{C}$ .<sup>29</sup> The polymer's isotacticity remained unaffected by catalyst concentration while decreasing initial monomer concentration led to an increase in isotacticity. Also, isotacticity reduction occurred with increased reaction temperatures. Sawamoto and co-workers obtained highly isotactic polymers of isobutyl vinyl ether (iBVE) using titanium-based Lewis acid catalysts with bulky aryloxy substituents with iBVE-HCl adduct as an initiator at  $-78\text{ }^{\circ}\text{C}$  temperature in hexane.<sup>30,31</sup> Subsequently, they discovered that a combination of  $\text{SnCl}_4$  Lewis acid and a bulky phosphoric acid ligand was also effective.<sup>32</sup> Sudhakar and co-workers reported triamine-based bulky complexes in combination with methylaluminumoxane (MAO) and borate to obtain stereoregular poly(vinyl ether)s having narrow dispersity and high molecular weight at ambient temperatures.<sup>33</sup> The selected catalysts in the study served both as initiators and stereoregulating agents. After that, their group modified the ligand structures to manipulate the steric hindrance and the electronic nature of the metal complexes to control stereoregularity in *n*-butyl vinyl ether (nBVE) polymerizations. The obtained polymers at or around ambient temperature were highly stereoregular.<sup>34,35</sup> In recent years, various endeavors have been undertaken to regulate tacticity in cationic polymerization, resulting in the successful production of stereoregular polymers.

There have been numerous notable developments in cationic polymerization of vinyl ethers in recent years with the establishment of cationic RAFT polymerization. Several organic catalyst systems have emerged as viable alternatives to the metal-based Lewis acid catalysts. Moreover, various external stimuli have been effectively utilized to trigger and regulate the polymerization process. This capability also facilitates the integration of cationic polymerization with

other polymerization mechanisms for the synthesis of novel copolymers. Besides, several significant advancements have been achieved to manage the tacticity of polymers. Numerous chiral catalyst systems have been discovered that are capable of producing extremely stereoregular polymers. When these catalyst systems are used in conjunction with cationic RAFT polymerization, it is possible to create highly isotactic polymers with controlled molecular weight. Additionally, a few stereo-block copolymers have been reported by combining these approaches, in which these stereoregular cationic polymers have been linked with other polymerization techniques to generate block copolymers.

Indeed, there are already several review articles reported that concentrate on various recent advancements in cationic polymerization. In a previous review article from our group, Dey and co-workers focused on the development of block copolymer synthesis combining cationic polymerization along with other polymerization methodologies.<sup>26</sup> Chen and co-workers have also published a review article focusing on recent advancements of LCP in terms of initiators and controlling systems.<sup>36</sup> Likewise, the Kamigaito group presented a concise discussion on the progression of cationic RAFT polymerization.<sup>25</sup> The Leibfarth group has also discussed the progress of stereoregular polymerization in their recent article.<sup>37</sup> Feng and co-workers have summarized the latest advancements in visible-light-induced cationic polymerization.<sup>38</sup> In a recent review article, Wu and co-workers highlighted the latest developments in the control of cationic polymerization, which included chemically recyclable/degradable polymers, stereo-selective polymerization, and temporally controlled polymerization (using light or electricity).<sup>39</sup> This article offers a thorough analysis of the recent advancements in the cationic polymerization of vinyl ether monomers, encompassing their applications and potential future prospects.



**Figure 4.** (A) Mechanism of vinyl ether polymerization using PCCP as organocatalyst. Reproduced with permission from ref 51. Copyright 2019 American Chemical Society. (B) Mechanism of chain transfer caused by intramolecular deprotonation. (C) Structures of HBDs (1–6) and the stabilization of PCCP anion by hydrogen bonding. (B) and (C) are reproduced with permission from ref 52. Copyright 2020 John Wiley & Sons.

### Cationic Polymerization Using Metal-Free Organocatalysts

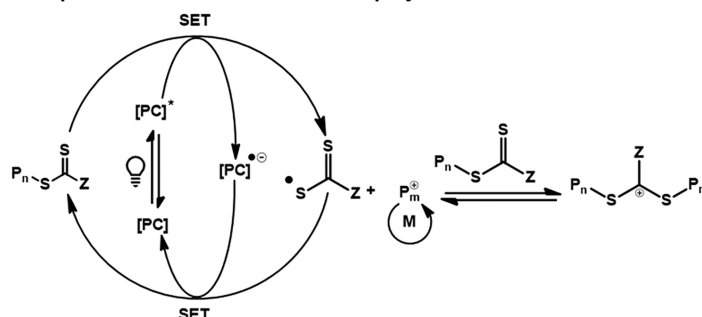
In a traditional cationic polymerization process, the cationic initiator species is often generated through the action of Lewis acid–based metal catalyst systems. While these catalyst systems have been widely used and have contributed significantly to the development of various polymers, they exhibit several disadvantages. They generally require high catalyst loading and due to the presence of metal residues, the obtained polymers are not compatible to be used in metal-sensitive fields.<sup>40,41</sup> Therefore, metal-free organic catalysts are gaining much more attention compared to other transition metal catalysts in various catalytic cycles,<sup>42</sup> including polymerization reactions.<sup>43</sup> However, these organocatalytic systems generally demonstrate lower reactivity than the metal-catalyzed systems, and their reaction scopes are also limited. Nevertheless, the utilization of such systems for vinyl ether polymerization holds great significance. Furthermore, in most circumstances, these organic catalysts neither require any inert atmosphere nor any rigorous purification of monomers, solvents, and other reagents, making them more relevant and viable.

In 2017, Takagi and co-workers used 2-iodoimidazolium derivatives (OC-1) (Figure 3A) as halogen bonding organocatalysts for living cationic polymerization of iBVE.<sup>44</sup> Here, the iodine atoms abstract halides from carbon–halogen bonds resulting in the formation of the propagating carbocations (Figure 3B). Later, in 2020, Aoshima and co-workers used

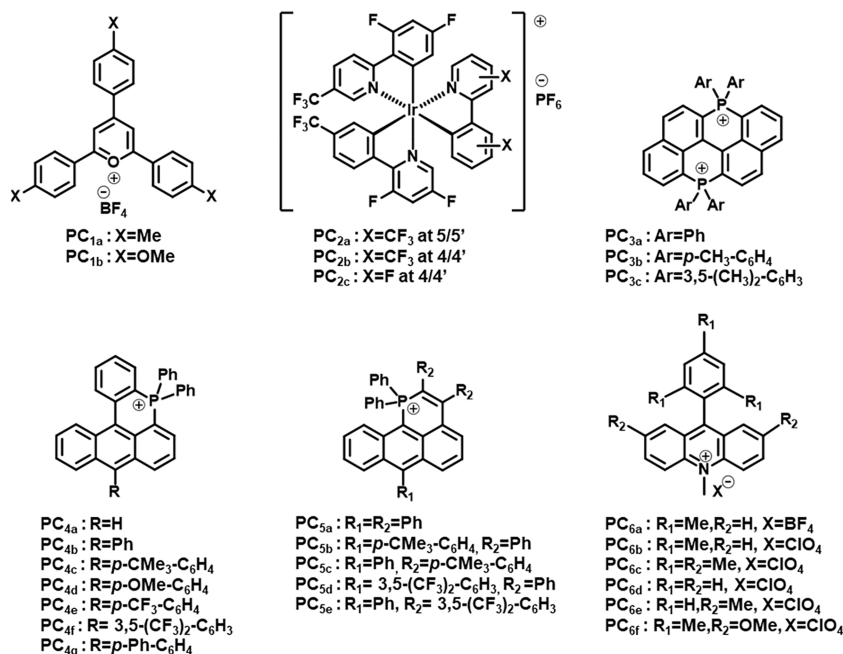
several diaryliodonium salts (OC-2) as Lewis acid catalysts (which were typically used as photoinitiators) to polymerize several VEs and styrene derivatives (Figure 3C).<sup>45</sup> Here, the incorporation of an electron-withdrawing group as a substituent increased the Lewis acidity of the catalyst, consequently leading to an enhancement in the polymerization rate. In the same year, the Takagi group explored these polymerizations utilizing nonionic halogen bonding catalysts (OC-3,4) (Figure 3A)<sup>46</sup> to address issues related to solubility and dissociation that were encountered with the ionic catalysts. Later on, the Takagi group<sup>47</sup> and the Wu group<sup>48</sup> have used chalcogen bonding organocatalysts for cationic polymerization of *p*-methoxystyrene (pMOS). Alternatively, the Tao group employed the hydrogen bond donor selenocyclodiphosph(V)-azane complex OC-5 (Figure 3A) as an anion-binding catalyst to extract the halide anion from the carbon–halogen bond of the dormant species (Figure 3D), leading to the formation of a carbocationic active center to undergo living cationic polymerization.<sup>49,50</sup>

The Fors group accomplished a noteworthy feat in cationic vinyl ether polymerization through the utilization of the organic acid 1,2,3,4,5-pentacarbomethoxycyclopentadiene (PCCP) as catalysts.<sup>51</sup> In this process, initiation occurs as the PCCP acid protonates the VE monomers, leading to the formation of an adduct which then equilibrates between the propagating unit and the cyclopentadienyl anion (Figure 4A). The hydrogen bonding interaction between the cyclo-

## (A) Mechanism of photo-controlled cationic RAFT polymerization:



## (B) Various photocatalysts to undergo cationic RAFT polymerization:



**Figure 5.** (A) Mechanism of photocontrolled cationic RAFT polymerization. Adapted with permission from ref 67. Copyright 2016 American Chemical Society (B) Various photocatalysts to perform cationic RAFT polymerization.

pentadienyl anion and the propagating carbocationic chain end inhibits the chain-transfer events, allowing for a polymerization process with living characteristics. Through the implementation of this method, various VE monomers including iBVE, nBVE, ethyl vinyl ether (EVE), 2,3-dihydrofuran (DHF), cyclohexyl vinyl ether (CyVE), and *tert*-butyl vinyl ether (tBVE) were polymerized at room temperature under ambient conditions, without the need for any extensive purification. While the polymers exhibited controlled molecular weight and lower dispersity at relatively lower degrees of polymerization (DP), the precision in control was compromised when aiming for higher molecular weight polymers (DP > 100). Here, termination takes place as the PCCP anion deprotonates the propagating chain end in the polymerization process (Figure 4B). For this reason, to stabilize the PCCP anions, several hydrogen bond donors (HBD 1–6) were employed as cocatalysts in the system (Figure 4C).<sup>52</sup> Among these compounds, HBD-4 displayed higher outcomes in controlling the polymerization due to its ability to form three hydrogen bonds that can engage with several methyl esters of the PCCP anion (Figure 4C). In 2022, the same research team utilized this PCCP-HBD combination to synthesize high molecular weight poly(2,3-dihydrofuran) under ambient conditions at room temperature.<sup>53</sup> The resulting polymers displayed a

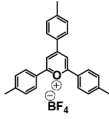
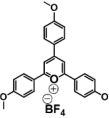
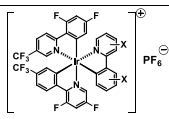



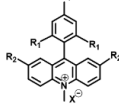

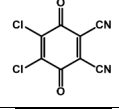

molecular weight of up to 256 kg/mol. Moreover, the efficacy of this combination was also found beneficial in cationic RAFT polymerization.<sup>54,55</sup>

### Various External Stimuli to Initiate and Control Cationic Polymerization

The use of external stimuli to initiate polymerization allows for precise control over the polymerization process, including the rate of polymerization, molecular weight, and polymer structure. It also provides opportunities for designing and tailoring polymers with specific properties for various applications in materials science, coatings, adhesives, and more.<sup>56</sup> In recent years, several major developments have been made to undergo different types of polymerizations using external stimuli, including heat,<sup>57</sup> chemicals,<sup>58</sup> light,<sup>59,60</sup> electronic,<sup>61,62</sup> and sound waves.<sup>63,64</sup> When these initiating systems are combined with RAFT polymerization, polymers with controlled molecular weight and narrow *D* are obtained.

The utilization of visible light has become a focal point of research in the field of polymerization due to its simplicity, environmental friendliness, and affordability. Visible lights can be involved in cationic polymerization in two different ways: one is photoinitiated and the other one is in a photocontrolled mechanism.<sup>65</sup> In the case of photoinitiated polymerization, the

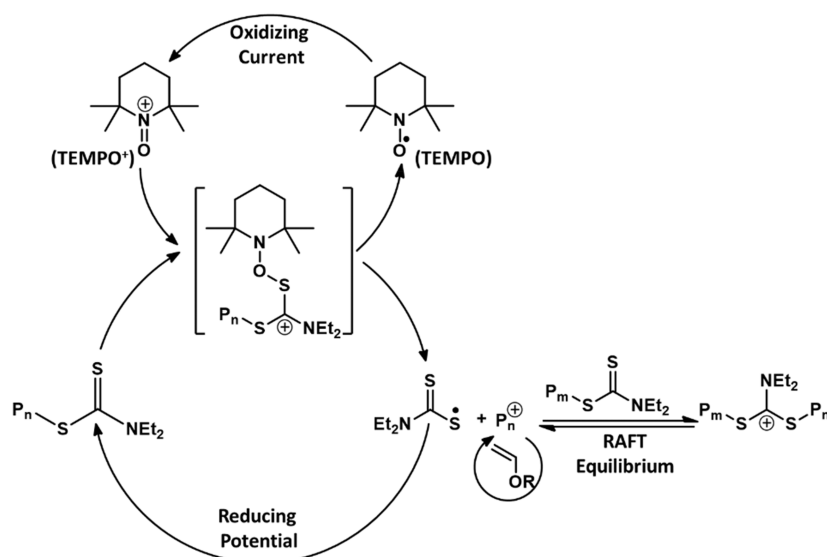
Table 1. Different Catalysts, Their Stimuli, and Choice of Monomers to Undergo Cationic Polymerization

Entry	Catalyst	Stimuli	Monomer	Reference
1		Light	pMOS	66
2		Light	iBVE, EVE, nPVE, nBVE, Cl-EVE	67
3		Light	iBVE	68
4		Light	iBVE, EVE, nPVE, nBVE, DHF, Cl-EVE, CyVE	69
5		Light	iBVE, nPVE, nBVE, tBVE, CyVE, DHF, Cl-EVE	70
6		Light	iBVE, EVE, nPVE, DHF, Cl-EVE	71
7		Light	iBVE, EVE, Cl-EVE, iPVE	72
8		Electrical	nBVE, nPVE, EVE, Cl-EVE, pMOS	73
9		Electrical	iBVE, EVE, nPVE, nBVE, Cl-EVE, pMOS, pHS	74
10		Chemical	iBVE	75

photoinitiating system reaches the excited state by absorbing visible lights and then it undergoes an electron transfer reaction to produce cationic active centers. Nonetheless, when the irradiation process begins, there is no control over the expansion of the chain growth reaction. In the case of photocontrolled polymerization, CTAs are involved which act as carbocation donors. They are oxidized using an appropriate photocatalyst, and following mesolytic cleavage, a carbocation is generated that takes part in the RAFT process (Figure 5A). Following this, the CTA undergoes reduction, reverting to a dormant state. To reactivate the CTA, light irradiation is once again necessary. This establishes a catalytic cycle. In this way, by switching the light on and off, one can precisely regulate the creation of cationic active or dormant species, which in turn controls the polymerization procedure. This allows for the temporal control of polymerization by the regulation of the polymer's molecular weight, molecular weight distribution, and monomer conversion.

In 2015, Perkowski and co-workers reported the first use of a photoredox catalyst to undergo cationic RAFT polymerization.<sup>66</sup> They have excited the 2,4,6-triarylpyrylium tetrafluoroborate salt PC<sub>1a</sub> (Figure 5B) using a blue LED (450 nm)

in the presence of methanol and dichloromethane (DCM) to polymerize pMOS (Table 1, entry 1). Similar to the role of bisulfide in RAFT polymerization, methanol here serves as a reversible CTA in the system. The Fors group employed the methoxy-modified pyrylium salt PC<sub>1b</sub> (Figure 5B) as a photocatalyst for cationic RAFT polymerization.<sup>67</sup> With this approach, they effectively polymerized compounds like iBVE, nBVE, EVE, 2-chloroethyl vinyl ether (Cl-EVE), and *n*-propyl vinyl ether (nPVE) (Table 1, entry 2). These complexes exhibited a remarkable temporal control by light over chain propagation for the first time. However, the control was lost at high monomer conversion in the dark. Later on, their group used polypyridyl iridium complexes (PC<sub>2a</sub>, PC<sub>2b</sub>, PC<sub>2c</sub>) (Figure 5B) as photocatalysts (Table 1, entry 3).<sup>68</sup> These complexes had redox potential values comparable to those of the previously reported pyrylium catalysts but upon polymerization, they obtained a much better temporal control. Although strong temporal control was seen, the expensive and heavy catalyst loading restricted its usefulness. Later in 2021, the Liao group discovered that P<sup>+</sup>-doped anthranthrenes (PC<sub>3a</sub>, PC<sub>3b</sub>, PC<sub>3c</sub>) (Figure 5B), a family of bisphosphonium salts (BPS), can effectively catalyze the cationic RAFT



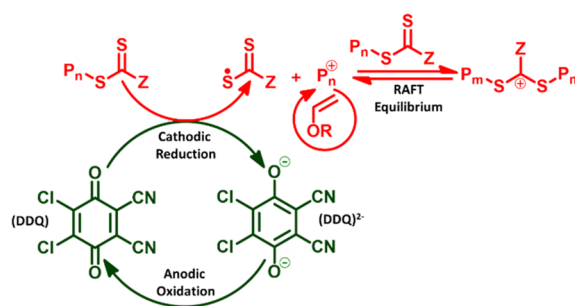
**Figure 6.** Cationic RAFT polymerization using TEMPO as an electroredox catalyst. Adapted with permission from ref 73. Copyright 2018 American Chemical Society.

polymerization of VEs (Table 1, entry 4).<sup>69</sup> These organic photocatalysts are more stable, exhibit a strongly reducing radical state, a highly oxidizing excited state, and absorb a significant amount of visible light. This allowed for a firm temporal control over chain expansion. However, the poor yields in the synthesis of BPS impeded a systematic tuning of the redox potentials. Additionally, these catalysts have a narrow redox potential and a lack of structural diversity. As a result, they sought novel phosphonium photocatalysts with a distinctive structure, different framework, and great tunability. By doping  $P^+$  to naphtho-anthracene, they discovered a class of monophosphonium photocatalysts (MPS) ( $PC_{4a}$ – $PC_{4g}$ ) (Figure 5B) that could open an adjustable redox window by changing the  $-R$  group linked with the aromatic ring of the catalyst (Table 1, entry 5).<sup>70</sup> However, compared to the previously reported BPS, these MPS were substantially less active. Following that, their group developed  $P^+$ -doped benzo-anthranthrenes salts  $PC_{5a}$ – $PC_{5e}$  (Figure 5B), a new type of MPS having a different framework (Table 1, entry 6).<sup>71</sup> These compounds have two variable sites ( $-R_1$  and  $-R_2$ ) which can be modified by electron-donating and withdrawing groups so that a range of redox potentials become accessible. With a ppm level loading of these novel photocatalysts, they were able to produce extremely effective and tightly regulated cationic polymerizations of vinyl ethers under visible light, which is more efficient than the previously reported MPS. However, the Kamigaito group has used several acridinium salts with different substituents ( $PC_{6a}$ – $PC_{6f}$ ) (Figure 5B) as photocatalysts to undergo polymerization.<sup>72</sup> Upon irradiation with blue, green, and white LEDs, these catalysts facilitated cationic RAFT polymerization of various vinyl ethers, including iBVE, EVE, Cl-EVE, and isopropyl vinyl ether (iPVE) (Table 1, entry 7). Moreover, the study investigated temporal control using light, and explored the synthesis of block copolymers.

Similar to this, a RAFT CTA molecule may also be oxidized into a radical cation upon the application of an electrical potential instead of using light. By mesolytic cleavage, the radical cation creates a cation that goes through RAFT equilibrium. An appropriate electroredox catalyst is needed in this case to enable reversible electron transfer, which is

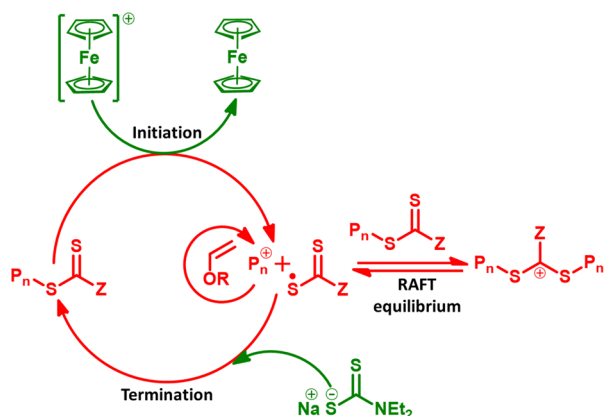
necessary to control the cationic polymerization. This allows polymerization to be turned “on” and “off” in the presence and absence of the oxidizing current, resulting in excellent temporal control. In 2018, the Fors group reported the first cationic RAFT polymerization using an electroredox catalyst.<sup>73</sup> In the presence of dithiocarbamate CTA, they have employed 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) as an electroredox catalyst and tetrabutylammonium perchlorate ( $n\text{-Bu}_4\text{NClO}_4$ ) as an electrolyte (Figure 6). When an oxidizing current was applied at the anode, TEMPO was oxidized into the TEMPO<sup>+</sup> cation, which then oxidized the CTA to produce the carbocation and dithiocarbamate radical by mesolytic cleavage of the C–S bond. Different VE monomers (Table 1, entry 8) underwent controlled polymerization in the presence of an oxidizing current to produce poly(VE)s with low dispersity ( $\mathcal{D} < 1.20$ ), great temporal control, and good agreement between theoretical and actual molecular weight.

In the same year 2018, Sang and co-workers achieved electro-controlled cationic RAFT polymerization using the organocatalyst 2,3-dichloro-5,6-dicyanoquinone (DDQ).<sup>74</sup> In the presence of oxidizing potential, the dianion  $DDQ^{2-}$  was oxidized to DDQ which then further oxidized the CTA to form the carbocation (Figure 7). Using this catalyst, they have successfully polymerized a wide variety of vinyl ethers, pMOS and *p*-hydroxylstyrene (pHS) monomers (Table 1, entry 9).



**Figure 7.** Cationic RAFT polymerization using DDQ as an electroredox catalyst. Adapted with permission from ref 74. Copyright 2018 John Wiley & Sons.

Similar to this, a chemical redox catalyst can also initiate and regulate cationic polymerization. In 2018, the Fors group used ferrocenium tetrafluoroborate ( $\text{FcBF}_4$ ) as an initiator for cationic RAFT polymerization of iBVE (Table 1, entry 10).<sup>75</sup>  $\text{FcBF}_4$  could successfully oxidize dithiocarbamate and trithiocarbamate CTAs itself being reduced to ferrocene (Fc). The chain termination was achieved by the addition of a dithiocarbamate anion (Figure 8). This method was further combined with photocontrolled radical polymerization to obtain block polymers.



**Figure 8.** Cationic RAFT polymerization using the chemical redox catalyst  $\text{FcBF}_4$ .

### Combination of Cationic Polymerization with Other Polymerization Techniques

Polymerization of two or more monomers together gives copolymers with unique tailor-made properties. By this method, the desired properties of different monomers can be combined into a single polymer. In particular, block polymers, which are composed of two or more segments with distinct monomer compositions and complex arrangements, hold significance in the progress of developing new technologies.<sup>76,77</sup> Depending on the monomer selection, length of individual blocks, and number of polymer blocks, multiblock copolymers can exhibit a range of unique characteristics.<sup>78,79</sup>

The homopolymers of acrylates provide adhesion and chemical resistance,<sup>80</sup> whereas, poly(vinyl ether)s have flexibility, impact resistance, and low-temperature performance.<sup>81</sup> When they are copolymerized, the resulting polymers have the balance of these properties. However, the necessity of well-tuned reactivity for successfully controlled polymer synthesis often comes with the price of limited monomer substrate scope. The electron-deficient acrylates are compatible with free radical<sup>82</sup> or anionic<sup>83</sup> polymerization, whereas the electron-rich VEs are mostly polymerized by cationic polymerization.<sup>11</sup> Thus, achieving a precisely controlled synthesis of block copolymers involving acrylates and vinyl ethers requires the implementation of efficient and versatile mechanistic transformation reactions that can convert radical polymerizations into cationic polymerizations, and vice versa.

In 1987, Yagci and co-workers reported the first block copolymer synthesis using the combination of radical and cationic polymerization.<sup>84</sup> At first, they polymerized styrene by radical polymerization and then the reaction was transformed into cationic polymerization of nBVE. They have used diphenyliodonium hexafluorophosphate ( $\text{Ph}_2\text{I}^+ \text{PF}_6^-$ ) or silver tetrafluoroborate ( $\text{AgBF}_4$ ) to oxidize the radicals into cations.

Yet, the polymers obtained using this method exhibited a very minute fraction of block copolymer structure with the dominance being attributed to the cationic polymerization of nBVE. Similar radical and radical-promoted cationic block copolymerization was reported using methyl methacrylate (MMA) and nBVE.<sup>85</sup>

However, in these approaches for copolymerization, different types of polymerization mechanisms require different reaction conditions. Achieving the copolymerization of distinct monomer types within a single reaction vessel, without the need for extra polymer separation and purification during intermediate processes, is fascinating as well as challenging. In 2014, the Kamigaito group successfully accomplished the interchange between radical polymerizations of acrylate monomers and living cationic polymerizations of vinyl ethers within a single reaction vessel.<sup>86</sup> They employed a single dormant group that could be activated by two distinct activators, leading to both cationic and radical polymerization. Through this innovative approach, they effectively created copolymers by the combination of vinyl ethers and acrylates. In 2017, the same research group carried out a one-shot copolymerization procedure that included radical polymerizable acrylates and vinyl esters, as well as cationic polymerizable vinyl ethers (Figure 9).<sup>87</sup> In this study, a sole RAFT agent was utilized, triggered by an aluminum-based Lewis acid for cationic polymerization and an azo-initiator, 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) for radical polymerization. In this way, different arrangements of monomers were attained in the copolymer chains, encompassing statistical, alternating, block, and multiblock copolymers. The ability to integrate two polymerization processes in one reaction vessel and modify monomer selectivity by applying an external stimulus offers a promising avenue for precisely controlling polymer sequence and structure. As discussed earlier, several external stimuli can initiate and control different kinds of polymerization. Here the key challenge is to find a suitable condition for one set of polymerizations while the other one remains intact in that state, and vice versa.

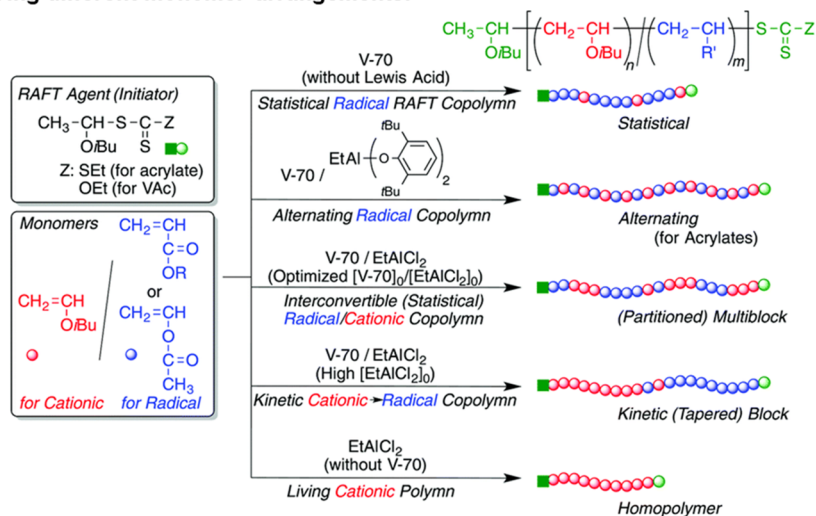
In 2017, Kottisch and co-workers used light as an external stimulus for switching the polymerization mechanism between radical and cationic polymerization.<sup>88</sup> They have taken 2,4,6-tris(*p*-methoxyphenyl) pyrylium tetrafluoroborate as an oxidizing photocatalyst for the selective polymerization of iBVE and tris[2-phenylpyridinato- $\text{C}^2, \text{N}$ ]iridium(III), i.e.,  $\text{Ir}(\text{ppy})_3$  as a reducing photocatalyst for the radical polymerization of methyl acrylate (MA). Hence, two polymerization mechanisms were interchanged by just changing the wavelength of light (Figure 10). In this way, under identical conditions, they discriminatorily synthesized homo, diblock, and multiblock copolymers.

In the dual catalysis system, selective promotion of the radical mechanism could not be achieved due to the overlapping absorption spectra of the two catalysts. For this reason, two different orthogonal stimuli were introduced where the ferrocenium salt  $\text{FcBF}_4$  was employed as an initiator to polymerize iBVE, and this controlled cationic polymerization was combined with a previously established photocontrolled radical polymerization of MA to create block copolymers.<sup>75</sup> This enabled complete orthogonal switching of the polymerization mechanism at a single chain-end in situ (Figure 11).

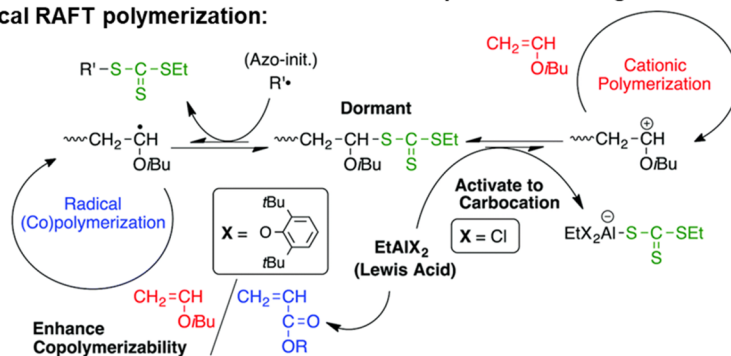
Zhu and co-workers reported the first electrochemically interconvertible living radical and cationic polymerization. They have taken a combination of electrocatalysts: the dianion



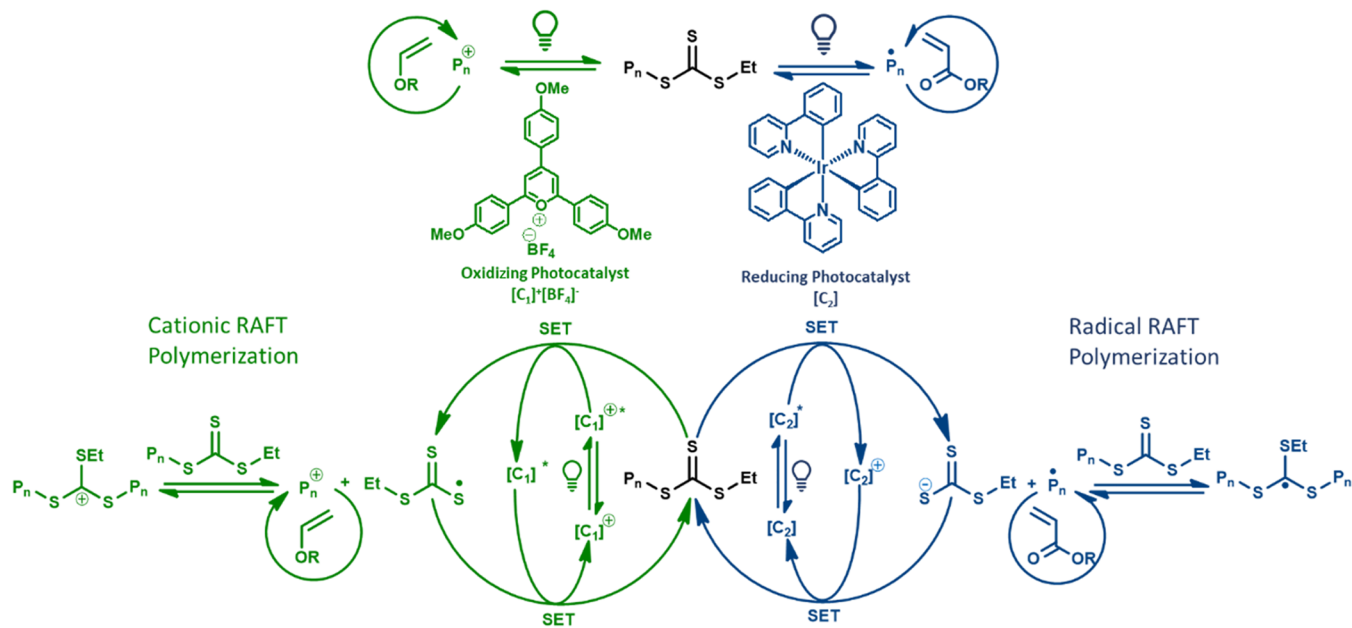
**(A) One shot cationic and radical polymerization to synthesize copolymers having different monomer arrangements:**



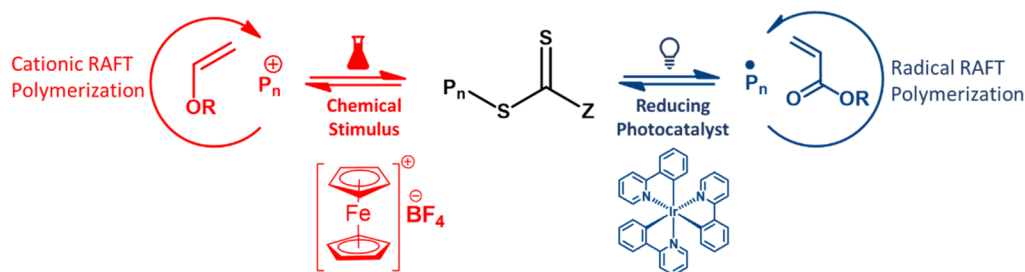
**(B) Mechanism of activation of the dormant species to undergo cationic and radical RAFT polymerization:**



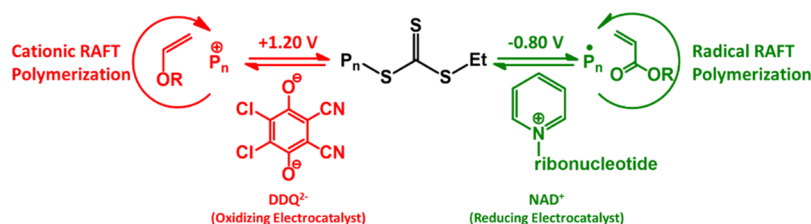
**Figure 9.** (A) One shot cationic and radical polymerization to synthesize copolymers having different monomer arrangements. (B) Mechanism of activation of the dormant species to undergo cationic and radical RAFT polymerization. Reproduced with permission from ref 87. Copyright 2017 Royal Society of Chemistry.



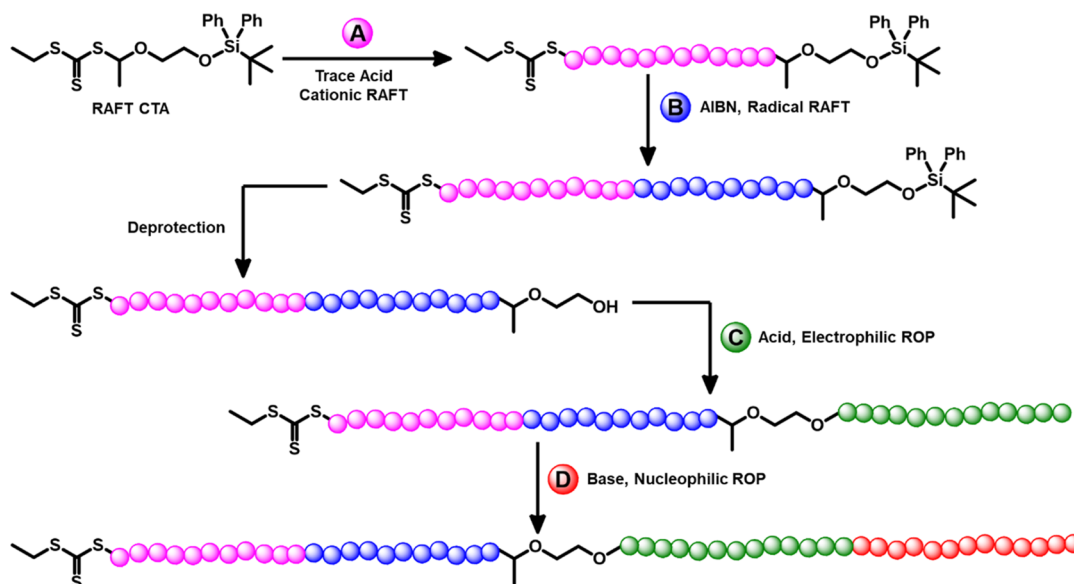
**Figure 10.** Photocontrolled interconversion between cationic and radical RAFT polymerization.



**Figure 11.** Interconversion between cationic and radical polymerization using two orthogonal stimuli.



**Figure 12.** Electroselective interconversion between cationic and radical RAFT polymerization. Adapted with permission from ref 89. Copyright 2019 Springer Nature.



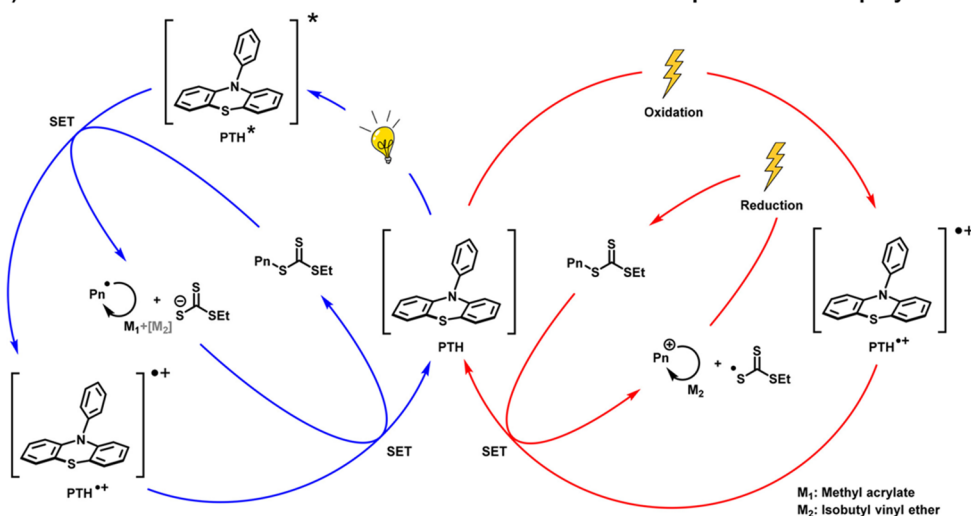
**Figure 13.** Proposed polymerization mechanism switching strategy to prepare ABCD type tetrablock copolymers in one pot. Adapted with permission from ref 91. Copyright 2021 Royal Society of Chemistry.

of 2,3-dichloro-5,6-dicyanoquinone ( $\text{DDQ}^{2-}$ ) as an oxidant and the cation of nicotinamide adenine dinucleotide ( $\text{NAD}^+$ ) as a reductant (Figure 12). Equimolar mixtures of iBVE and MA were mixed with  $\text{DDQ}^{2-}$  and  $\text{NAD}^+$ . The polymerizations were performed by altering the potentials of +1.20 V,  $\text{DDQ}^{2-}$  was selectively activated, and the cationic polymerization of iBVE turned on while the radical polymerization of MA was prohibited due to the deactivation of  $\text{NAD}^+$ . The reverse selectivity was observed when the reaction mixture was switched to a reducing state of  $-0.80$  V. In this way, they successfully synthesized block copolymers with different combinations.<sup>89</sup>

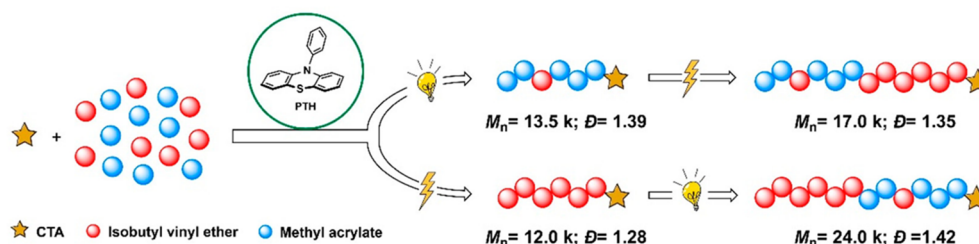
The Fors group has combined electrically controlled cationic RAFT polymerization with photochemically controlled radical polymerization.<sup>90</sup> They have taken Fc as an efficient electrochemical mediator for cationic RAFT polymerization. Electro-

chemical oxidation of Fc to ferrocenium ion oxidized the dithiocarbonyl CTA to initiate the cationic polymerization of iBVE. They applied a cathodic current to reduce the disulfide to the dithiocarbonyl anion, which capped the propagating polymer chain ends and reversibly terminated the cationic polymerization. For the radical polymerization of MA, they have chosen  $\text{Ir}(\text{ppy})_3$  as a photocatalyst. In this way, a variety of well-defined multiblock copolymers were synthesized where the final structure was dictated by the order and duration of the applied stimuli. Later in 2021, Zhu et al. created ABCD-type tetrablock copolymers by combining cationic and radical RAFT polymerizations with electrophilic and nucleophilic ring opening polymerizations (ROP).<sup>91</sup> A bifunctional RAFT agent that is suitable for both radical and cationic polymerization was developed. A hydroxyl group was then added to start ROPs, and it was protected by a silyl group as the free  $-\text{OH}$  group is incompatible with cationic polymerization. A trace of acidic

## (A) PTH controlled interconversion between electrochemical and photochemical polymerization:



## (B) Synthesis of block copolymers of different compositions:



**Figure 14.** (A) PTH controlled interconversion between electrochemical and photochemical polymerization. (B) Synthesis of block copolymers of different compositions. Reproduced with permission from ref 92. Copyright 2021 American Chemical Society.

catalyst was utilized to initiate the cationic RAFT polymerization (A) and then, free radical initiators were added to initiate the radical RAFT polymerization (B). Tetrabutylammonium fluoride (TBAF) was then utilized to generate the  $-OH$  group, after which some acidic catalysts were used to quench the remaining TBAF and regulate the ring-opening polymerizations of lactones (C). Finally, basic catalysts were added to regulate the ROPs of lactides (D) via an “acid/base” switch (Figure 13).

In the above-mentioned ABCD type tetrablock copolymer synthesis in one pot, different initiators and/or catalysts are required for different polymerization mechanisms. Here, the major challenge is to balance the reactivity and selectivity of a particular catalyst while the other one must remain intact in that condition. Nikolaev and co-workers have used 10-phenylphenothiazine (PTH) as the dual-responsive catalyst which selectively mediated monomer addition in cationic and radical polymerization (Figure 14).<sup>92</sup> This single catalyst could successfully initiate radical polymerization of MA upon irradiation of light along with the cationic polymerization of iBVE upon the exposure of anodic potential. This enabled the synthesis of copolymer chains consisting of iBVE and MA where the length of each block was controlled by the duration of the stimulus exposure.

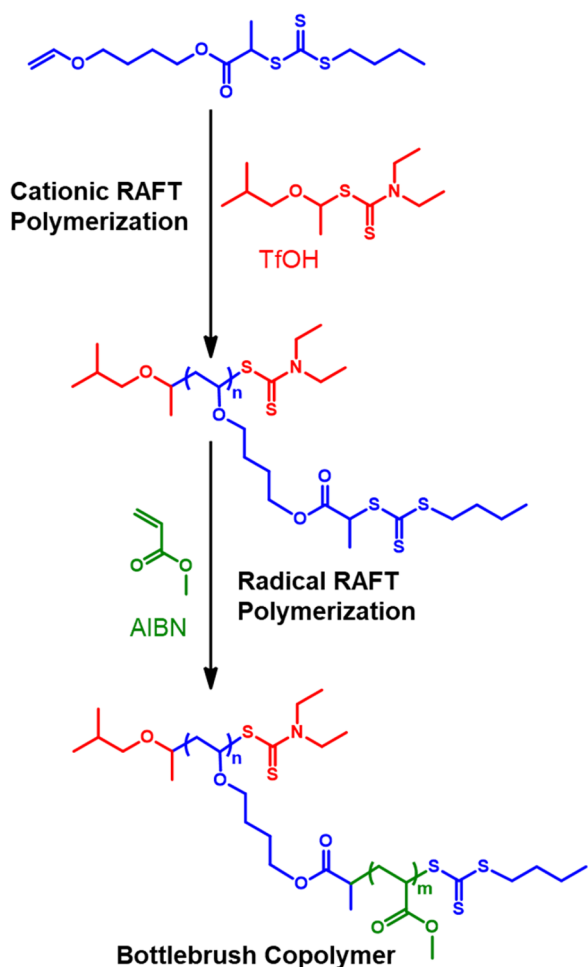
Tanaka and co-workers have designed a novel selective RAFT process to obtain orthogonal polymerizations which were independent of any other external stimuli.<sup>93</sup> They have taken a RAFT agent with the ability to control the cationic polymerization of a VE monomer, which itself had another RAFT agent within its structure. This second RAFT agent remained inactive during the cationic chain transfer process

and after that, it facilitated the consecutive radical-centered RAFT polymerization of a different monomer, resulting in the creation of precisely structured bottlebrush polymers (Figure 15).

## Control over Stereoregularity

Tacticity plays a crucial role in determining key physical properties of polymeric materials, such as crystalline melting temperature ( $T_m$ ) and glass transition temperature ( $T_g$ ), solubility, mechanical properties, chemical reactivity, morphology, etc. The ability to control tacticity is a powerful tool to dictate the physical and mechanical properties of polymers for specific industrial applications.<sup>94,95</sup> For example, the atactic polypropylene is amorphous and fluid, while its isotactic form is crystalline and rigid. Whereas, syndiotactic polypropylene exhibits much higher impact strength and optical clarity.<sup>96,97</sup> Likewise, the tacticity of vinyl ether polymers plays a crucial role in determining their properties. For example, commercially available poly(iBVE) products exhibit as a liquid at room temperature due to their lower tacticity, whereas, highly isotactic poly(iBVE) has a semicrystalline nature.<sup>98</sup>

However, obtaining the desired stereoregularity during polymerization requires precise control of the spatial arrangement between the active site and the incoming monomers. So, it is not an easy task to control the tacticity in cationic polymerization because of the planar carbocationic propagating unit and very fast reaction rate. Therefore, a steric bias is required to achieve a particular orientation during the polymerization. In conventional polymerization methods, stereoregularity has been achieved by chain-end control where the stereochemistry of the last added monomer



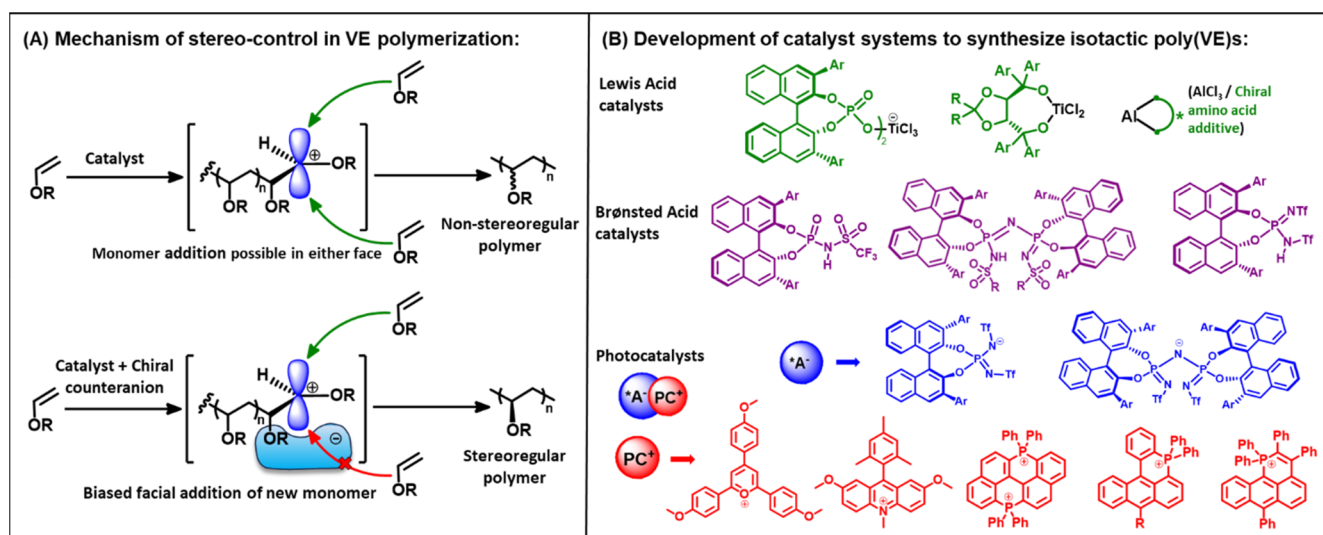
**Figure 15.** Bottlebrush copolymer synthesis by the orthogonal combination of cationic and radical RAFT polymerization. Adapted with permission from ref 93. Copyright 2020 John Wiley & Sons.

determines the orientation of facial addition of the next monomer. Nevertheless, the widespread use of this method is limited because the achieved stereoselectivity is inherently tied to the specific steric requirements of each substrate. The most

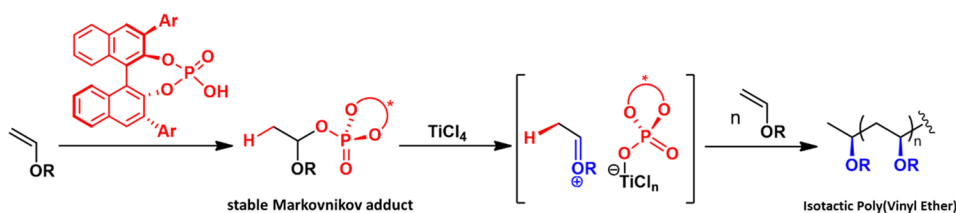
effective strategy entails incorporating a steric bias within the catalyst system.<sup>99</sup> An organometallic catalyst can be designed in such a way that the bulky and chiral ligand environment influences the selective addition of the incoming monomers to the growing polymer chain end. However, this coordination–insertion mechanism is limited to polypropylene and other poly- $\alpha$ -olefins only. This method is incompatible with polar monomers because of catalyst poisoning. The most effective approach involves the design of chiral counterions to the catalysts that systematically influence reactivity and control the stereochemical environment of chain ends during polymerization (Figure 16A). In recent times, several attempts have been made to develop catalysts for stereospecific cationic polymerization (Figure 16B).

In 2019, Leibfarth and co-workers used several 1,1'-bi-2-naphthol (BINOL)-based chiral phosphoric acids (CPA) to undergo stereoselective cationic polymerization of VEs.<sup>98</sup> However, these CPAs alone were not enough active to initiate cationic polymerization. At first, these CPAs formed chiral adducts with monomers, and later on these adducts were exposed to  $\text{TiCl}_4$  which produced highly isotactic poly(VE)s having more than 90% *meso* diads (% *m*) (Figure 17).

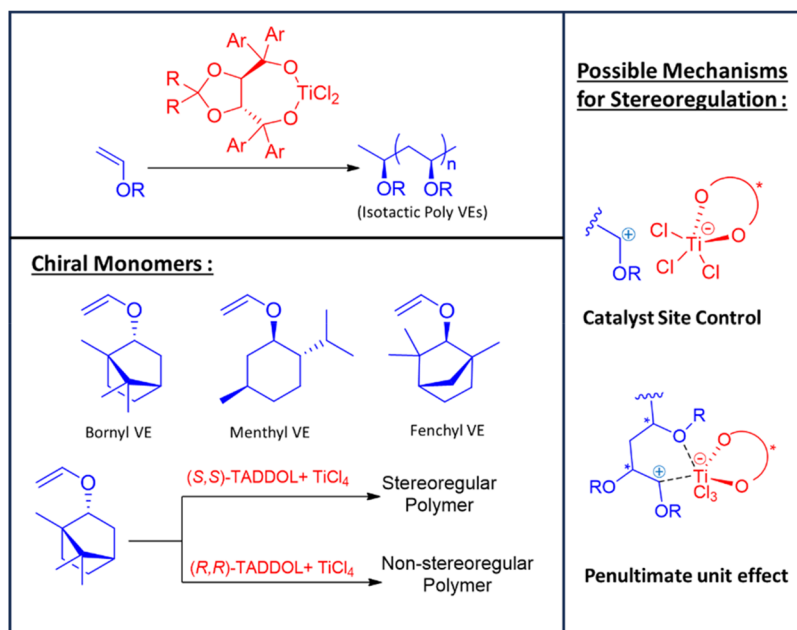
In 2020, Watanabe and co-workers used  $\alpha,\alpha,\alpha',\alpha'$ -tetraarylethylene-1,3-dioxolane-4,5-dimethanol (TADDOL) molecules as ligands to form chiral titanium catalysts.<sup>100</sup> These Ti-TADDOLate complexes were utilized to initiate cationic polymerization in the presence of *i*BVE-HCl adduct. The presence of chiral counteranions systematically influenced the stereoregularity within the complexes. An initiating system formed by the straightforward mixture of TADDOL,  $\text{TiCl}_4$ , and the *i*BVE monomer enabled the successful generation of poly(*i*BVE) with a high degree of isotacticity (90% *m*). Similarly, significant levels of isotacticity were achieved in the polymerization of various other vinyl ethers, including *n*PVE (*m* = 83%) and 2-phenylethyl vinyl ether (Ph-EVE) (*m* = 94%). Chiral VE monomers are also polymerized using the  $\text{TiCl}_4$  adducts of (*R,R*)- and (*S,S*)-TADDOL (Figure 18). It was observed that the polymers resulting from one enantiomer of Ti-TADDOLate complexes displayed solubility in a range of solvents, whereas the polymers obtained from the alternative enantiomer remained insoluble or very less soluble. A



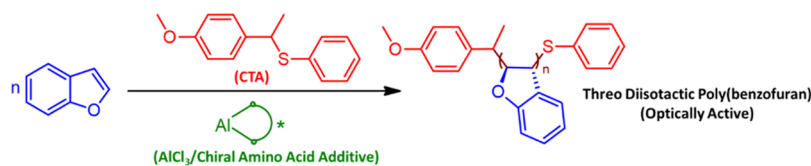
**Figure 16.** (A) Mechanism of stereocontrol in VE polymerization. (B) Development of catalyst systems to synthesize isotactic poly(VE)s.



**Figure 17.** BINOL-based CPAs for the synthesis of stereoregular poly(VE)s Adapted with permission from ref 98. Copyright 2019 The American Association for the Advancement of Science.



**Figure 18.** Ti-TADDOLate complexes for the stereoregular cationic polymerization of VEs. Adapted with permission from ref 100. Copyright 2020 Royal Society of Chemistry.



**Figure 19.** Stereoselective cationic RAFT polymerization of benzofuran using AlCl<sub>3</sub> along with amino acid additives.

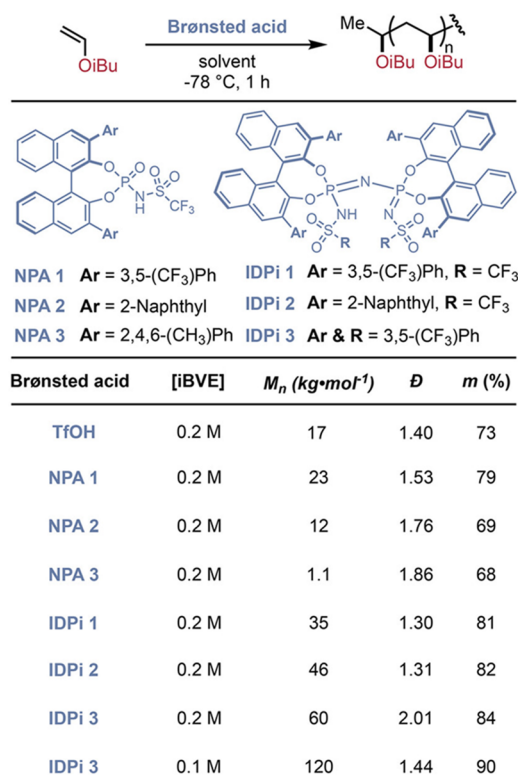
hypothesis was put forward suggesting that, this distinction might be attributed to match–mismatch effects, wherein solubility was linked to isotacticity, with materials exhibiting higher stereoregularity being less soluble across a range of solvents.

The Kamigaito group used BF<sub>3</sub>·OEt<sub>2</sub> or EtAlCl<sub>2</sub> in 2020, along with dithiocarbamate CTAs, to polymerize various bulky VE monomers which resulted in the formation of stereocontrolled polymers with an active chain end.<sup>101</sup> Subsequently, the active chain end was utilized for the radical RAFT polymerization of vinyl acetates, yielding block copolymers without specific stereo control. Following this, through deprotection of the -OR and -OAc units, isotactic-*block*-atactic poly(vinyl alcohol)s were successfully synthesized. Later in 2022, the same group used several  $\alpha$ - and  $\beta$ - amino acids and their derivatives as chiral additives to generate asymmetry in the catalyst system. They have polymerized benzofuran (BzF) using a thioether-based cationic RAFT agent and AlCl<sub>3</sub> along with various chiral additives to obtain dual control over

molecular weight and optical rotation (Figure 19).<sup>102</sup> However, the polymers obtained from  $\alpha$ -amino acid adducts had very less optical activity. Whereas, the adducts of  $\beta$ -amino acids and their derivatives were found more effective in this case. The optical activity improved when the -NH<sub>2</sub> groups were protected by bulky substituents such as *tert*-butyloxycarbonyl (boc), isopropyl, benzoyl, acetyl, and pivaloyl groups.

However, there have been significant advances in the synthesis of several chiral organocatalyst systems to produce poly(VE)s with improved tacticity (Figure 16B). Although organic Brønsted acids, such as triflic acid (TfOH), bistriflimide (Tf<sub>2</sub>NH) can initiate cationic RAFT polymerization at very low catalyst loading to form poly(VE)s with controlled molecular weight and low dispersity,<sup>22,103</sup> they lack the ability to control the tacticity of the resulting polymers. In the previous work by Teator and Leibfarth,<sup>98</sup> the BINOL-based chiral phosphoric acids alone were not capable of initiating cationic polymerization (due to lower acidity)

without the addition of  $\text{TiCl}_4$  as a Lewis acid cocatalyst. Later, in 2021, their group focused on single-component Brønsted acid catalysts which were sufficiently acidic to initiate vinyl ether polymerization. Besides, due to the presence of chiral conjugate bases, they could also control the stereochemistry of monomer addition to the prochiral oxocarbenium chain end to yield isotactic poly(VE)s.<sup>104</sup> They used BINOL-based chiral *N*-triflylphosphoramides (NPAs) and imidodiphosphorimidates (IDPis), which are derivatives of  $\text{Trf}_2\text{NH}$  (Figure 20).



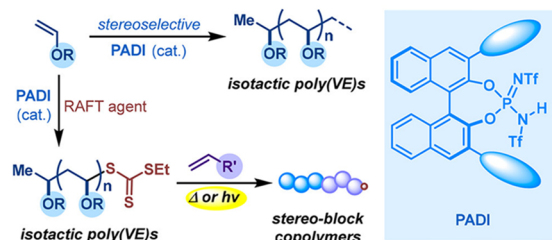
**Figure 20.** BINOL-based organic Brønsted acid catalysts to produce isotactic poly(VE)s. Reproduced with permission from ref 104. Copyright 2021 American Chemical Society.

However, these NPAs produced poly(iBVE)s with comparatively lower molecular weight ( $M_n < 25 \text{ kg mol}^{-1}$ ), higher dispersity ( $\mathcal{D} = 1.40\text{--}1.86$ ), and moderate tacticity (70–80%  $m$ ). The IDPis were found more beneficial as they produced polymers having a comparatively high molecular weight ( $M_n = 35\text{--}120 \text{ kg mol}^{-1}$ ,  $\mathcal{D} = 1.30\text{--}1.44$ ) along with an increased amount of tacticity (80–90%  $m$ ), which was considerably better compared to other Lewis acid regulated stereoselective polymerizations. The presence of an electron-deficient group at the 3 and 3' positions of the BINOL group increased tacticity. This IDPi having 3,5-bistrifluoromethyl aryl substituents was further used to polymerize other vinyl ethers. Most of the obtained polymers had a higher molecular weight ( $M_n = 120\text{--}180 \text{ kg mol}^{-1}$ ) and better stereospecificity (75–90%  $m$ ).

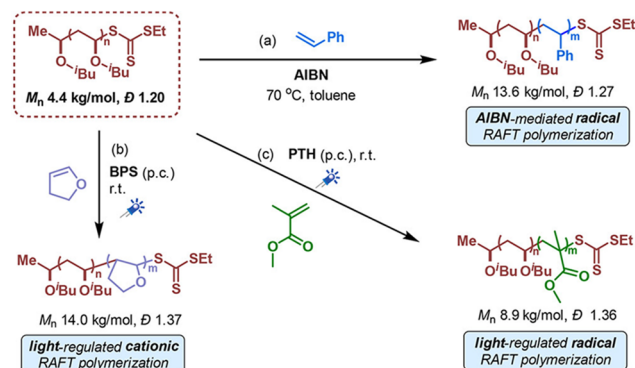
Similarly, the Liao group has reported similar outcomes using IDPis featuring diverse substituents,<sup>105</sup> where the inclusion of an electron-deficient substituent enhanced the stereoregularity of the resultant polymers. They successfully produced poly(iBVE) having up to 91%  $m$  demonstrating enhanced stereocontrol when employing the identical catalyst for the polymerization of other monomers such as EVE (85%  $m$ ), nPVE (90%  $m$ ), nBVE (88%  $m$ ), and 1,2,3,4,5-pentafluoro-

6-(2-(vinylxy)ethoxy)benzene (ArFVE) (90%  $m$ ). Later, their group used BINOL-derived *N,N'*-bis(triflyl)-phosphoramidimidates (PADI)s to develop the first organocatalytic, for the highly stereoselective cationic RAFT polymerization of vinyl ethers.<sup>106</sup> At first, iBVE was polymerized using several PADI acids which produced polymers having high isotacticity (up to above 90%  $m$ ) compared to the polymers obtained by  $\text{Trf}_2\text{NH}$  (60%  $m$ ). Between different PADIs, PADI with two bulky aromatic substituents at 3,3'-positions showed the best result to control the stereoregularity (92%  $m$ ). Further, this stereoselective cationic RAFT polymerization of iBVE was combined with other polymerization methods to obtain different block copolymers (Figure 21).

#### (A) Stereoselective cationic polymerization of VEs using PADI :



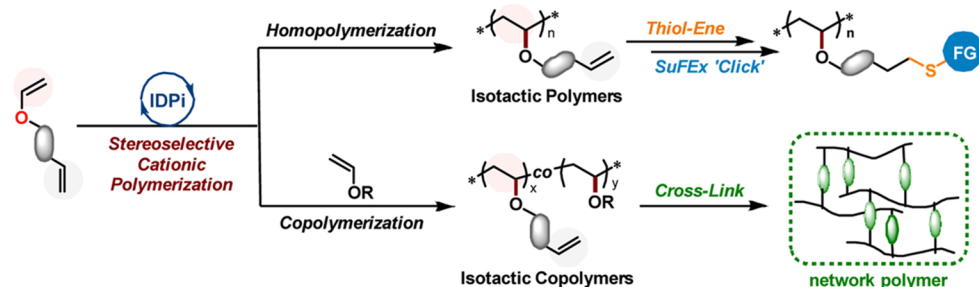
#### (B) Synthesis of different copolymers :



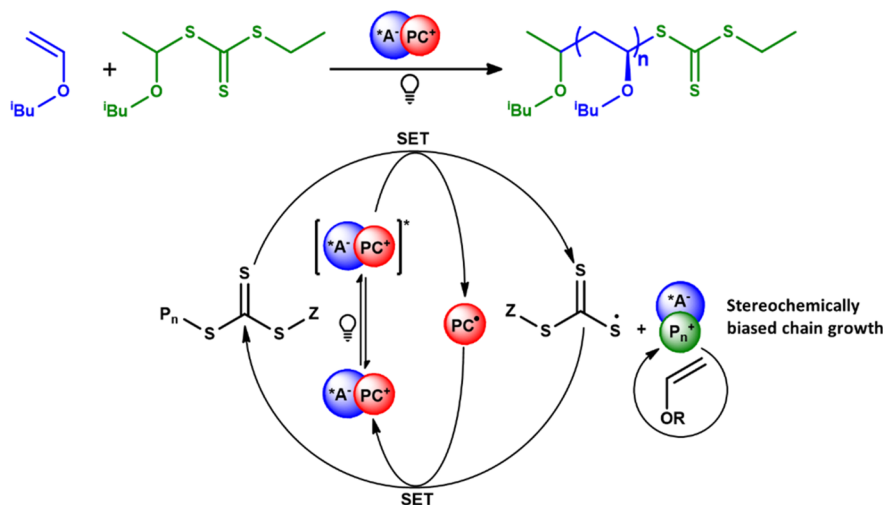
**Figure 21.** (A) Stereoselective cationic polymerization of VEs using PADI. (B) Synthesis of different copolymers. (A) and (B) are reproduced with permission from ref 106. Copyright 2022 American Chemical Society.

Recently, IDPi acids were utilized to undergo stereocontrolled polymerization of alkenyl VEs where the double bond in the alkenyl segment remained intact, resulting in the incorporation of active  $\text{C}=\text{C}$  double bonds into the side chains of poly(VE)s.<sup>107</sup> These terminal  $\text{C}=\text{C}$  bonds can regulate polymer characteristics or introduce any functional group via postpolymerization modifications. This approach integrated the thiol–ene reaction and Sulfur(VI) fluoride exchange (SuFEx) click chemistry in the side-chain allowing the generation of isotactic polymer materials with diverse functional groups in the side-chain terminal positions. Furthermore, this can be applied to synthesize stereoblock copolymers as well as cross-linked network polymers (Figure 22).

An asymmetric ion-pairing strategy was recently employed to undergo the first photocontrolled, stereoselective cationic RAFT polymerization,<sup>108</sup> where the active cationic component of a photoredox catalyst ( $\text{PC}^+$ ) was combined with a steric



**Figure 22.** Stereoselective polymerization of alkenyl VEs and subsequent postpolymerization modification for the synthesis of end group functionalized polymer materials. Reproduced with permission from ref 107. Copyright 2023 Elsevier.



**Figure 23.** Mechanism of photocontrolled stereoregular cationic RAFT polymerization.

hindrance-imposing chiral anion ( $*A^-$ ) to achieve control over the stereochemistry (Figure 23). Here, the anion  $*A^-$  pairs with the propagating carbocationic chains ( $P_n^+$ ) influence the addition of the incoming monomer, leading to the formation of a stereoregular polymer. This approach enabled the effective polymerization of various VE monomers with a remarkably low catalyst loading of 50 ppm, showcasing a notable inclination toward isotactic stereoselectivity for the following monomers: iBVE (90%  $m$ ), nBVE (90%  $m$ ), nPVE (90%  $m$ ), hex-5-enyl vinyl ether (HVE) (91%  $m$ ), benzyl vinyl ether (BnVE) (90%  $m$ ), 2-phenylethyl vinyl ether (PhEtVE) (87%  $m$ ), and 3-phenylpropyl vinyl ether (PhPrVE) (87%  $m$ ).

## CONCLUSIONS AND FUTURE PERSPECTIVE

In conclusion, a detailed overview of the development of cationic polymerization of vinyl ether monomers is discussed here. The polymerization process has evolved from very rigorous conditions to environmentally friendly ambient conditions, presenting substantial potential for its widespread industrial applications. The incorporation of external stimuli, precision in stereo control, and the synthesis of complex block copolymers offer the opportunity to access a variety of polymer architectures, compositions, and properties. Cationic RAFT polymerization, which was initially designed to gain control in the polymerization process, has demonstrated remarkable effectiveness in assimilating diverse external stimuli as initiating and controlling systems to facilitate copolymer synthesis by merging cationic with other polymerization mechanisms. As a result, it has become feasible to create precisely structured

polymeric substances that would otherwise be difficult or unattainable using traditional polymerization methodologies. Incorporating new bulky chiral catalyst systems has led to significant breakthroughs in the pursuit of obtaining stereoregular poly(VE)s, which has been a major focus of research for decades. Additionally, this method has been incorporated with cationic RAFT polymerization to achieve dual control over tacticity and molecular weight without interfering with each other. These recently developed copolymers and stereoregular polymers find utility across an extensive spectrum of uses, encompassing drug delivery systems, applications in the biomedical field, stimuli-responsive materials, adhesives, sealants, nanomaterials, as well as photonic and optoelectronic device developments.

However, certain drawbacks continue to exist, such as, in contrast to other polymerization methods, the scope of applying external stimuli for initiation is still very limited for cationic polymerization. The opportunity for their utilization in large-scale industrial applications is also quite restricted, and yet to be established. Furthermore, the majority of catalysts developed for stereoregular polymerization require a multistep synthesis procedure and are sensitive to air and moisture. As a result, their feasibility for industrial use is hindered by the significant expenses associated with their production and storage. Currently, their usage is also restricted to a few types of monomers, leaving a wide range of monomers unexplored. However, in spite of these drawbacks, ongoing research and innovation are expected to address these challenges and expand its applications in the future. Researchers are actively working on the development of easily synthesizable and

inexpensive initiators and catalyst systems that exhibit tolerance toward air, moisture, and storage. Besides, various research works are going on exploring the scopes of different other monomers, CTAs, and stimuli-initiating systems. We are optimistic that, this comprehensive exploration of the latest advancements in cationic polymerization of VE monomers will strongly motivate the scientific community including polymer chemists, materials scientists, engineers, and other specialists, to persist in their research endeavors, aiming to maximize the potential of cationic polymerization to contribute significantly to the development of advanced materials and sustainable processes, shaping industries and improving various aspects of our daily lives.

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Complete contact information is available at: <https://pubs.acs.org/10.1021/acspolymersau.3c00055>

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### Notes

The authors declare no competing financial interest.

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