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Recent advances in applications of vinyl ether monomers for precise synthesis of custom-tailored polymers

Evgueni Kirillov,^{*,a} Konstantin Rodygin,^{*,b,c} Valentine Ananikov^{*,b,c}

^a University of Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes), UMR 6226, F-35700 Rennes (France), evgueni.kirillov@univ-rennes1.fr

^b Institute of Chemistry, Saint Petersburg State University, Universitetsky prospect 26, Saint Petersburg 198504 (Russia), k.rodygin@spbu.ru

^c N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky Prospect 47 Moscow 119991 (Russia), val@ioc.ac.ru

Abstract: This review highlights recent progress in the synthesis and application of vinyl ethers (VEs) as monomers for modern homo- and co-polymerization processes. VEs can be easily prepared using a number of traditional synthetic protocols including a more sustainable and straightforward manner by reacting gaseous acetylene or calcium carbide with alcohols. The remarkably tunable chemistry of VEs allows designing and obtaining polymers with well-defined structures and controllable properties. Both VE homopolymerization and copolymerization systems are considered, and specific emphasis is given to the novel initiating systems and to the methods of stereocontrol.

Key words: vinyl ethers, poly(vinyl ethers), polymerization mechanism, stereocontrol in polymerization

Abbreviations:

1-(Isobutoxy)ethyl acetate (IBEA)
1-(Methoxyethoxy)ethyl acetate (MOEA)
Ethyl vinyl ether (EVE)
n-Butyl vinyl ether (BVE)
iso-Butyl vinyl ether (IBVE)
iso-Propyl vinyl ether (IPVE)
tert-Butyl vinyl ether (TBVE)
Cyclohexyl vinyl ether (CHVE)
2-Chloroethyl vinyl ether (CEVE)
2-Methoxyethyl vinyl ether (MOVE)
2-ethoxyethyl vinyl ether (EOVE)
(2-ethoxy)ethoxyethyl vinyl ether (EOEOVE)
Dodecyl vinyl ether (DDVE)
8-Vinylxytricyclo[5.2.1.0]decane (TCDVE)
1,4-butanediol divinyl ether (BDVE)
1,6-Hexanediol divinyl ether (HDVE)
Di(ethylene glycol) divinyl ether (DEGDVE)
Tri(ethylene glycol) divinyl ether (TEGDVE)
2-Hydroxyethyl vinyl ether (HEVE)
4-hydroxybutyl vinyl ether (HBVE)
1,4-Cyclohexanedimethanol vinyl ether (CHMVE)
Methyl ethyl ketone (MEK)
1,4-cyclohexane-dimethanol divinyl ether (DVE)
Diethylene glycole monovinyl ether (DEGV)
Chlorotrifluoroethylene (CTFE)
Chain-transfer agent (CTA)
Cyanomethyl methyl(phenyl)carbomodithioate (CMPCD)
2,6-di-*tert*-butyl-pyridine (DTBP)
Near-infrared region (NIR)
Dichloromethane (DCM)
Differential scanning calorimetry (DSC)
Thermogravimetric analysis (TGA)

Contents

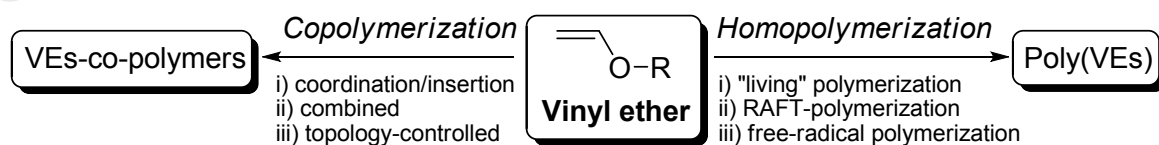
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1. Introduction

Amazing achievements in vinyl ether (VE) chemistry, from the first example of VE polymerization [1] to a plethora of recent research [2-10], facilitated enormous progress in VEs synthesis and in design of advanced polymer materials. The fundamentally important point in this subject is the remarkable versatility of VE structures that resonates with the tunability of the corresponding polymeric systems. To exemplify, industrially manufactured *iso*-butyl vinyl ether (IBVE) has been ubiquitously utilized as monomer in a diverse range of research projects [11-17]. At the same time, many VEs and poly(VE)s are now ton-scale products of the chemical industry [18].

A new wave of interest to VEs was raised by sustainability demands. For instance, VEs can be obtained from various sources of carbon using calcium-carbide-based technologies from fossil carbon (coal, etc.), regenerated carbon (wastes and end-of-life sources), biomass (including biomass processing wastes), as well as from carbon dioxide in a future perspective (via conversion of carbon dioxide to carbon) [19]. Potential ability to access VEs from virtually any carbon source including renewable biomass [20] identified these monomers as highly promising candidates to design bio-based and sustainable plastics.

The classical chain-growth polymerization protocols provide major advantages over the step-growth (e.g., polycondensation) processes in accessing functional polymers with enhanced control over the organization of repeating units. This supremacy, once declared [21], has been substantiated by regular upgrades of the chain-growth polymerization methods and conditions. The regular protocols of VE polymerization include (Scheme 1): i) living cationic polymerization; ii) reversible addition-fragmentation chain transfer (RAFT) and related polymerization reactions; iii) free radical polymerization. Another option is copolymerization of VEs by using coordination/insertion catalysts or combined composition- and topology-controlled polymerization techniques.



Scheme 1. Methods of VE polymerization.

For a long time, methods of cationic polymerization of VEs lacked control over the molecular weight distributions and also resulted in the poorly controlled nature of the chain-end groups in poly(VE)s. The failure was due to excessive activity of the carbenium end groups. A solution came with the discovery of long-lived cationic species [22,23] and their application in polymerization of VEs [24] and other vinylic monomers [11,25]. Thus, the new approach allowed suppressing the reactivity of the chain-ends thus significantly reducing the rates of chain termination without inhibiting the initiation and propagation processes. The proposed methodology allowed syntheses of well-defined products [26,27], including stimuli-responsive polymers [28] and cyclic polymers [29]. Controlled polymerization requires a catalyst (initiator) to promote chain initiation and propagation; the properties of this agent can largely define efficiency of the overall process, which provides chemists with reliable means for its control. Besides chemical initiation, a controlled release of initiating cations can be triggered by external light or electrical stimuli [30,31].

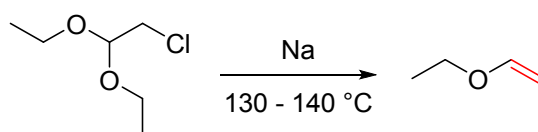
The RAFT approach in both cationic and radical polymerization reactions was found suitable for poly(VE) synthesis [32]. Initiation with thiocarbonylthio or xanthate compounds in combination with a Lewis acid (LA) and a base resulted in well-defined synthetic polymers and was advantageous in terms of simplicity of the experimental procedure. Polymerization of VEs by free-radical protocols, once considered impossible, is now well established; we will highlight the recent achievements in this area as well.

The use of VEs as monomers expands rapidly, and many reviews have been focused on the mechanistic studies of VE polymerization [33-36]. In this review, we do not intend surveying the mechanistic details, rather we give a scope of the most recent and relevant examples of VE involvement in different polymerization protocols. We also highlight advanced procedures for the preparation of VE monomers underscoring their potential as building blocks for sustainable and eco-friendly syntheses.

2. Advanced green syntheses of vinyl ether monomers

Reactions that lead to vinyl ethers can be divided into four groups: *i*) of laboratory interest only; *ii*) affording vinyl ethers as side products; *iii*) used in industry to produce vinyl ether monomers; *iv*) potentially upgradable for reasonable production of vinyl ether monomers.

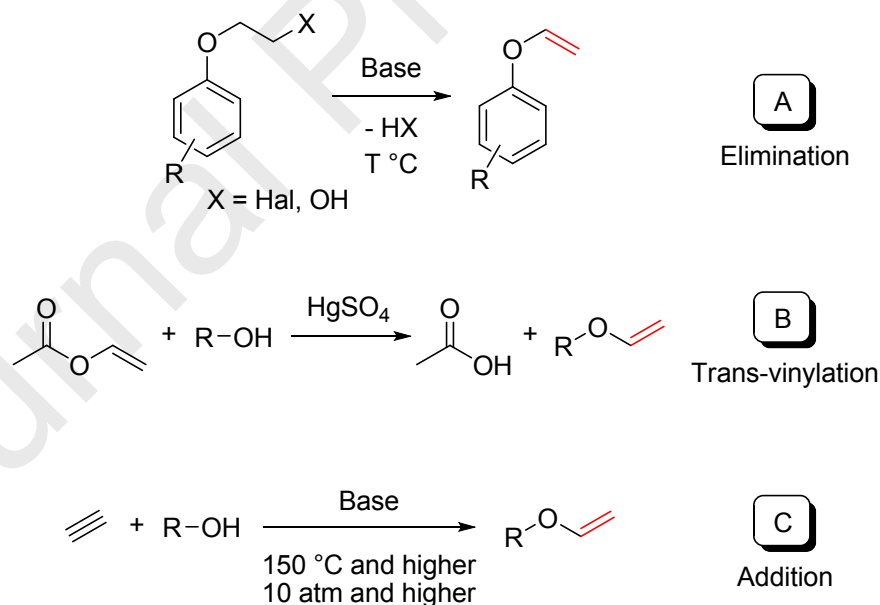
The first synthesis of vinyl ether was reported by Wislizenus in 1878 [1]. The method was based on addition of sodium metal to hot monochloroacetal (Scheme 2) since it was essentially an elimination reaction in the presence of a strong base.



Scheme 2. The first synthesis of vinyl ether.

Improved by subsequent studies [37-39], this versatile synthesis allowed obtaining a wide range of vinyl derivatives. The two-stage methodology yields a halogenated derivative (or an alcohol) at the first stage, which is followed by elimination under basic conditions (Scheme 3, part A). Although being efficient in a lab, the approach is unsuitable for industrial applications.

Another strategy developed for the generation of vinyl functionality is based on the reaction of primary aliphatic alcohols with vinyl acetate in the presence of a mercury catalyst at -60 – 10 °C [40]. The reaction proceeds by dissociation of vinyl acetate into acetylene-mercury complex ion and acetic acid in the presence of mercury sulfate (Scheme 3, part B). *Trans*-vinylation is fairly common, but their use implies availability of vinylated substrates.

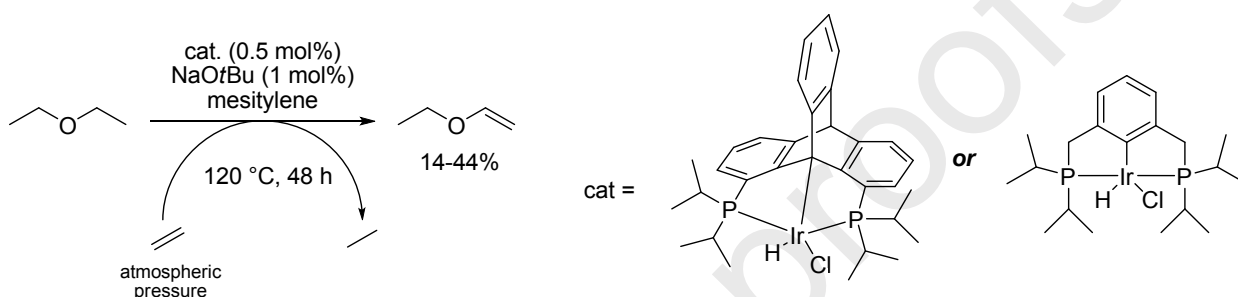


Scheme 3. Common strategies for the vinyl functionality incorporation.

A fundamental breakthrough in the chemistry of vinyl ethers was made in 1888 by Favorskii who discovered nucleophilic addition of alcohols to acetylenes in the presence of bases [41]. Allyl bromide, synthesized by elimination of hydrogen bromide from propylene bromide, was absorbed by cold absolute ethanol with dry potassium hydroxide added in advance. The vessel

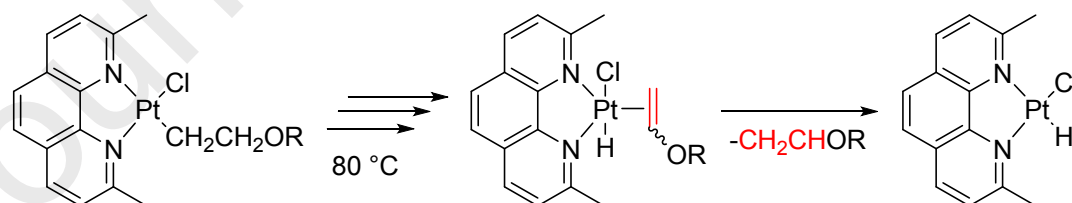
was sealed and heated at 170–180 °C for 12 h; the ether was subsequently purified by distillation.

Nowadays, vinyl ethers are commonly synthesized in laboratory practice to be applied as synthons and precursors. An interesting iridium-catalyzed dehydrogenation with ethylene as a hydrogen acceptor affords unsaturated vinyl ethers from non-functionalized ethers, mixed or simple (e.g. diethyl ether) [42]. Iridium pincer complexes $i\text{Pr}^4\text{PC}(\text{sp}^3)\text{P}-\text{Ir}(\text{H})(\text{Cl})$ and $(i\text{Pr}^4\text{PCP})-\text{Ir}(\text{H})(\text{Cl})$ catalyze dehydrogenation-reduction reactions in the presence of a base under a pressure of ethylene equal to the ambient atmospheric pressure (Scheme 4).



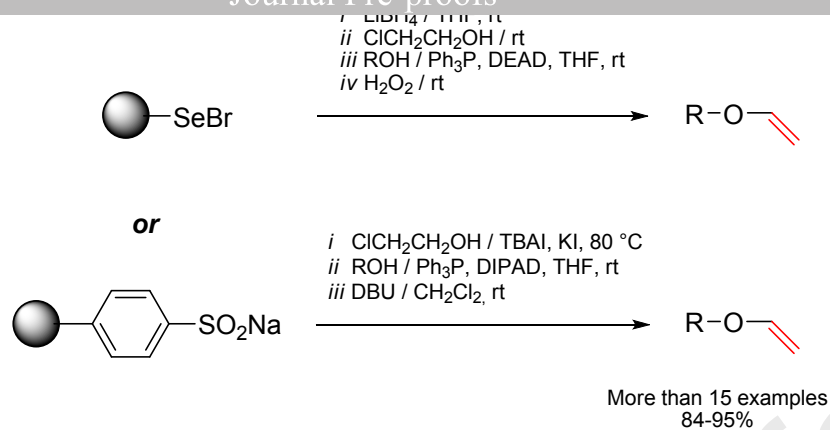
Scheme 4. Iridium-catalyzed dehydrogenation of ethers.

Another organometallic route involves spontaneous decomposition of planar platinum complexes $[\text{PtCl}(\text{N}-\text{N})(\eta^1-\text{CH}_2\text{CH}_2\text{OR})]$ by a pseudo-Wacker-type mechanism [43]. The complexes are stable in the solid state at room temperature; however, upon dissolution in CH_2Cl_2 , CHCl_3 or benzene they slowly decompose to give methyl vinyl ether and a Pt-containing precipitate. The described method is convenient for preparation of challenging vinyl ethers in a lab due to the simplicity of both decomposition and isolation procedures (Scheme 5).



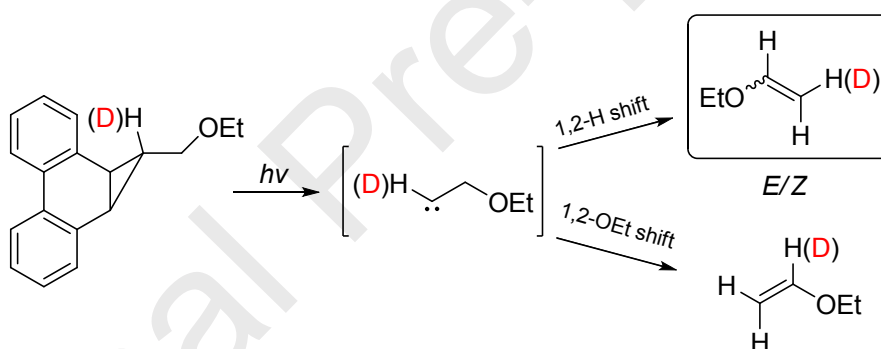
Scheme 5. Plausible mechanism of vinyl ether formation from $[\text{PtCl}(\text{Me}_2\text{phen})\eta^1-\text{CH}_2\text{CH}_2\text{OR}]$.

A solid-phase reaction of polystyrene-supported β -phenylselenoethanol or 2-phenylsulfonylethanol with phenols under the Mitsunobu reaction conditions with subsequent oxidation-elimination affords a scope of vinyl ethers in 84–95% yields [44,45]. Despite the multistep protocol (Scheme 6), the procedure is universal for a wide range of products.



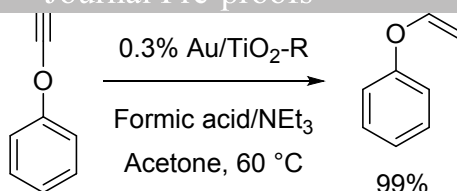
Scheme 6. Solid-phase polystyrene-supported synthesis of aryl vinyl ethers.

A similar principle is employed in biosynthetic implementation of desired organic functionalities in living organisms. A photochemically generated carbene precursor undergoes rearrangement to give the corresponding vinyl ether (Scheme 7). While vinyl ethyl ether can be produced by either 1,2-H or 1,2-ethoxy shift in the carbene [46], both theoretical calculations and deuterium labeling experiments supported the 1,2-H route.



Scheme 7. Rearrangement pathways for ethylidene and its deuterated analog.

A number of industrial processes yielding VEs as side products are certainly worth mentioning in this context. Thus, semireduction of acetylene during ethylene manufacturing and the corresponding semireduction of other alkynes to alkenes with the avoidance of complete reduction to alkanes is a hot topic in catalysis [47-52]. The use of highly efficient metal and polymetal catalysts prevents exhaustive reduction, thus, enabling isolation of alkenes. A selective transfer semireduction of phenoxyacetylene with supported gold nanoparticles as a catalyst has been reported [52]. The catalytic system fed with formic acid as a hydrogen source affords 99% yield of phenyl vinyl ether in 30 min (Scheme 8).



Scheme 8. Semireduction of phenoxyacetylene using a gold catalyst.

The above methods of VEs synthesis are interesting from the point of view of fundamental chemistry, however, their industrial implementations are limited due to poor availability of the starting materials. The potential of VEs in chemistry and materials science was recognized quite early with continuous efforts to develop a procedure for efficient massive production of these monomers.

The real rise of vinyl ethers started with the outstanding work by Reppe [53]. The experiment consisted of various alcohols added to gaseous acetylene in an autoclave in the presence of a strong base (Scheme 3, part C). This approach is efficient but highly hydrocarbon-dependent. It has been recently transformed into new acetylene gas-independent methodologies that have crucial advantages and may attain industrial significance in the nearest future.

Certain enzymes in living organisms are capable of dehydrating long-chain bases (LCBs) to corresponding vinyl ethers [54]. Enzymatic conversion of odd chain-length tracers C-17-dihydrospingosine (dehydro-PHS) and C17-sphingosine (PHS) into corresponding LCB vinyl ether derivatives in yeasts has been described (Scheme 9). The conversion proceeds without toxic over-accumulation of LCBs.

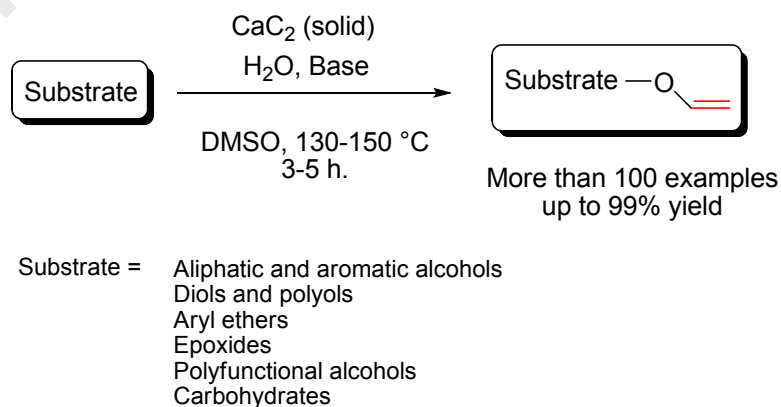


Scheme 9. Plausible sequence of the of PHS vinyl derivative biosynthesis.

All of these methods, including the workup under high pressure in an autoclave, are readily reproducible in laboratory settings. However, nucleophilic addition of alcohols to acetylene in the presence of a base (KOH, CsOH, KF or CsF) remains the only industrially relevant method. Acetylene can be directly manufactured from oil or fossil gas; alternatively, it is accessible

through carbide-based technologies [55]. Acetylene manufacturing from calcium carbide emerged at the end of XIX century [56]. This approach significantly enhanced the industrial relevance of vinyl derivatives by providing efficient route to vinyl ethers as starting materials [57].

Due to their low toxicity [58] and efficient manufacturing, vinyl ethers have been extensively used in research and industry without any significant amendments to the concept of their synthesis [59,60]. A number of modifications have been introduced, including variation of eliminating agents [61], upgrade of the catalysts and conditions for *trans*-vinylation processes [62-65], adjustment of the solvents and expansion of the substrate scope for the addition technique [66,67]. The increasing demand for vinyl monomers requires a sustainable and scalable manufacturing methodology, preferably based on renewables. These requirements are met by the syntheses of vinyl functionalities starting from calcium carbide [19]. Utilization of calcium carbide instead of bulk gaseous acetylene is actively promoted in recent studies [68-73]. In addition to operational safety, this approach provides a sustainable route to vinyl derivatives. The carbide methodology allows to vinylate both aliphatic and benzylic alcohols [74], polyols and phenols [69], aryl ethers and epoxides [75], various multifunctional substrates [76] and carbohydrates [77], with alkalis (KOH, CsOH) or salts (KF, CsF) as bases and water as a hydrolyzing agent. The use of deuterated water leads to deuterated vinyl ethers [78]. The reaction proceeds at 100 °C or higher for 3–5 hours in air-tight ampoules to prevent the release of gaseous acetylene from the mixture. Acetylene gas is generated *in situ* and dissolved in DMSO; subsequent addition of an alcohol leads to the corresponding vinyl ether. As the external pressure is rather small, there is no need to use an autoclave. The substrate scope for this process is very wide (Scheme 10).



Scheme 10. The use of calcium carbide in vinyl ether synthesis.

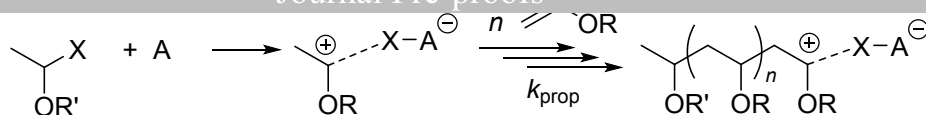
Certain vinyl ethers obtained through the carbide route can be utilized as monomers in polymerization by cationic and free-radical mechanisms [68,76,77]. Usage of calcium carbide for vinylation reaction is a rapidly expanding area with numerous research efforts to produce VEs from alcohols, thiols, amines, among many other examples [69,71,74,79-82].

3. Methods for controlled synthesis of poly(vinyl ether)s

Physicochemical and thermomechanical properties of polymers significantly depend on their size (molecular weight, polydispersity) and macromolecular structure (architecture, topology, regio- and stereochemistry). A number of recent studies are specifically aimed at achieving a better control over polymerization of vinyl ether monomers. The intrinsic “living” character of cationic polymerization provides exclusive opportunity of precise control over the length and structure of monomer sequences. This opportunity has been intensively used for the construction of macromolecules with predefined structures and also for the production of polymers with functional chain-ends for subsequent assembly and/or use as building units. Successful implementation of the new initiation and chain-transfer protocols combining cationic polymerization with free-radical processes (e.g. the RAFT-like and degenerative chain transfer polymerizations) is complemented by advanced means to control initiation and propagation by applying external stimuli (light, electrical, etc.).

3.1. Living cationic polymerization

Early examples of IBVE cationic polymerization with ionic salts $[\text{Ph}_3\text{C}]^+[\text{X}]^-$ [83] and hydrogen iodine/iodine [11] as initiators was reported in 1971 and 1984 respectively. Among different types of initiating systems identified later on, the two-component combinations of initiator (proto- or cationogen) and coinitiator (Lewis acids (LA), metal halides, ammonium salts) were shown to efficiently trigger the living polymerization mechanism (Scheme 11). Such well-defined systems as HI/I_2 , HI/ZnX_2 ($\text{X} = \text{halogen}$), $\text{IBEA}/\text{EtAlCl}_2$ or $\text{CH}_3\text{CH}(\text{O}i\text{Bu})\text{Cl}/\text{SnCl}_4$, etc. were efficiently employed for the controlled synthesis of poly(VE)s. This subject has been comprehensively reviewed by Sawamoto in 1991 [27] and by Aoshima *et al.* in 2009/2010 [33,34].



X = halogen, OC(O)CH₃, OC(O)CF₃ etc

A = coin initiator (Lewis acid LA; LA/base; LA/X⁻[NR₄]⁺)

Scheme 11. Controlled cationic polymerization of vinyl ethers initiated by a cationogen/coin initiator combination

During the last decade, several newly described multi-component initiating systems facilitated the emergence of new types of poly(VE)-based polymers. First, initiating systems combining metal precursors with various sources of cations were successfully refined and upgraded. For example, Sawamoto *et al.* reported the application of a tri-component system consisting of alcohol, BF₃·(Et₂O) and a base (alcohol = MeOH, *s*BuOH, *i*BuOH, *t*BuOH, DMBOH, AdOH; base = ethyl acetate, 1,4-dioxane, THF, Et₂O, Me₂S) to initiate controlled polymerization of IBVE, EVE, CHVE, TBVE or CEVE at -15 °C in CH₂Cl₂ to afford the corresponding polymers of predictable molecular weight [84]. Alternative combinations of alcohol with MCl_x and a base (alcohol = MeOH, *i*PrOH, *t*BuOH; M = Ti–Hf (x = 4); Nb, Ta (x = 5); Mo (x = 5); W (x = 6); Fe, Al, Ga (x = 3), Zn (x = 2); Sn (x = 4); Bi (x = 3)); base = ethyl acetate, 1,4-dioxane, THF) were studied as precursors for living polymerization of IBVE at 0 °C in toluene [17,85,86]. Among those, Fe- and Ga-based initiators afforded poorly controlled polymerization (PDI, 2.11–3.73), whereas the Zn, In- and Bi-based congeners were inactive. Under the living polymerization conditions, poly(IBVE) samples having *M_n* of 2,400–32,000 g·mol⁻¹ and narrow polydispersities (PDI, 1.10–1.62) were prepared. The same group studied polymerization of IBVE under similar experimental conditions, with MCl_x (M = Ti–Hf (x = 4), Nb, Ta (x = 5), W (x = 6), Fe, Al (x = 3) and Sn (x = 4)) combined with a base (ethyl acetate, 1,4-dioxane, THF) and pyrrole as a chain-transfer agent [87]. In this case, the adventitious H₂O was identified as a proton donor. In this study, the initiating systems with Si, Ge, Ga, Zn, In and Bi chloride salts were inactive. The other systems were found active but allowing low degree of control in terms of PDI of the polymers (1.20–2.82).

Different substituted triazines reacting with a Lewis acid (TiCl₄, SnCl₄) afforded corresponding *N*-methyleneamines to be used *in situ* as cationic initiators of TBVE polymerization (-78 °C, CH₂Cl₂) [88]. Only a moderate degree of control was achieved in the most polymerization experiments (PDI of 1.18–3.4), including those carried out in the presence of additives (*n*Bu₄NCl or 1,4-dioxane).

A study of polymerization of IBVE initiated with $\text{H}_2\text{O}/\text{BF}_3 \cdot (\text{Et}_2\text{O})$ in aqueous media demonstrated a varying degree of control over molecular weights and distributions depending on the conditions (notably for suspensions, dispersions and emulsions) [89].

$\text{AuCl}/\text{AgPF}_6$ at $-78\text{ }^\circ\text{C}$ in DCM produced poly(BVE)s of moderate molecular weight (M_n , 4,500–44,000 $\text{g}\cdot\text{mol}^{-1}$) and narrow to broad polydispersity (PDI, 1.41–8.28); the reaction proceeded at high rates (TOF up to 675 h^{-1}) [90]. Another coinage metal-based initiating system $\text{AgClO}_4/\text{C}_6\text{H}_5\text{CH}_2\text{Br}/\text{base}$ (base = Et_2O , iPr_2O , CPME, Me_2S) was shown to provide a similar degree of control (PDI of 1.36–5.63) at $-41 - 0\text{ }^\circ\text{C}$ in different solvents (CH_2Cl_2 , Et_2O , toluene) [91,92]. Better results were achieved with $\text{Cp}_2\text{MMe}_2/\text{activator}$ ($\text{M} = \text{Zr, Hf}$; activator = $\text{B}(\text{C}_6\text{F}_5)_3$, $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, $[\text{PhNMe}_2\text{H}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$) in polymerization of EVE, BE and IBVE carried out at $-10\text{ }^\circ\text{C}$ in CH_3CN [93]. The system allowed obtaining corresponding polymers with narrower PDI (1.18–2.38) and broader M_n (5,600–206,000). Statistical copolymers of EVE and BE were prepared under the same experimental conditions and studied by DSC and TGA techniques.

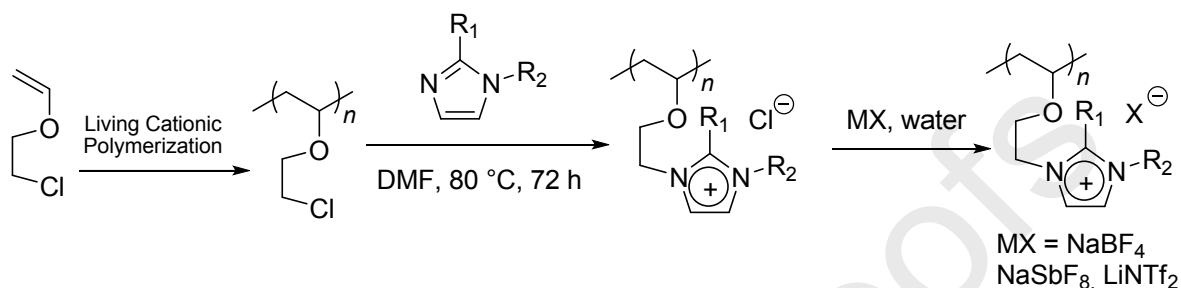
In situ generation of cationogen $\text{CH}_3\text{CH}(\text{OR})\text{X}$ from parent monomers IBVE, IPVE and TBVE with a Lewis acid-free initiating system $\text{CF}_3\text{SO}_3\text{H}/n\text{Bu}_4\text{NX}$ ($\text{X} = \text{Cl, Br, I, CF}_3\text{SO}_3$) was examined under a range of conditions ($-78 - 0\text{ }^\circ\text{C}$, 1 min–600 h, CH_2Cl_2) [94]. The nature of halide anion X^- in $n\text{Bu}_4\text{NX}$ was demonstrated to influence the degree of polymerization control as $\text{I}^- > \text{Br}^- > \text{Cl}^-$; the narrowest PDI distributions (1.13–1.16) were achieved in polymerizations of IPVE and TBVE with $n\text{Bu}_4\text{NI}$ as coinitiator.

Lewis acid-free triflate ester-based systems were reported to initiate carbocationic polymerization of IBVE at room temperature in CH_2Cl_2 providing access to polymers with a narrow range of M_n (8,320–9,620 $\text{g}\cdot\text{mol}^{-1}$) and PDI (1.8–2.1) [95].

A series of systems containing various thienyl chlorides $\text{RS}-\text{Cl}$ in combination with different LAs (SnCl_4 , ZnCl_2 , TiCl_4 , FeCl_3 , AlCl_3) were used for initiation of cationic polymerization of IBVE, BVE and HBVE-TBS in CH_2Cl_2 at $-78\text{ }^\circ\text{C}$ [96]. The corresponding poly(VE)s with M_n of 2,900–31,500 $\text{g}\cdot\text{mol}^{-1}$) and PDI of 1.06–1.19 bearing functional chain-ends were obtained.

Another initiating system containing $\text{IBEA}/\text{Et}_{1.5}\text{AlCl}_{1.5}/1,4\text{-dioxane}$ was used for the highly controlled polymerization of CEVE, and its copolymerization with IBVE as well, to produce di- and tri-block copolymers [97]. Treatment of the resulted polymers with different alkyl-imidazolium bases allowed preparation of corresponding uniform polymeric ionic liquids of narrow polydispersity (PDI 1.06–1.22) (Scheme 12). The same initiating systems were applied for the synthesis of fluorinated poly(VE)s from the parent fluorine-containing monomers

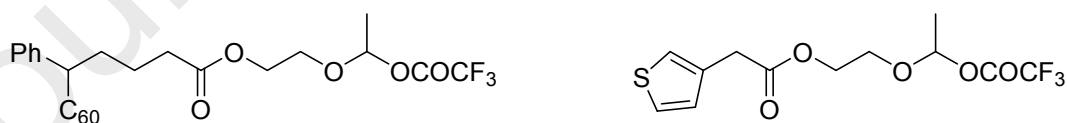
[98,99]. The use of fluorinated solvents (hydrofluorocarbons, chlorocarbons, ethers and aromatics) appeared to be mandatory to provide solubility of the resulting materials. Under the same conditions, fluorine-containing and fluorine-free star-shaped crosslinked polymers were produced upon addition of difunctional DVEs as cross-linking agents. Temperature-dependent sol-gel transitions of these reticulated polymers were also investigated.



Scheme 12. Synthesis of polymeric ionic liquids.

The use of IBEA/cointiator/ethyl acetate (cointiator = TiCl₄, SnCl₄, Et_{1.5}AlCl_{1.5}) in the presence of proton trap (2,6-di-*tert*-butyl-pyridine) for polymerization of IBVE in ionic liquids was reported by the same authors [100] and others [101] as well. IBEA-like initiators with diverse functional groups were successfully employed in controlled syntheses (PDI 1.05–1.14) of end-functionalized thermosensitive poly(MOVE)s featuring a range of temperature-induced phase-separation behaviors [102].

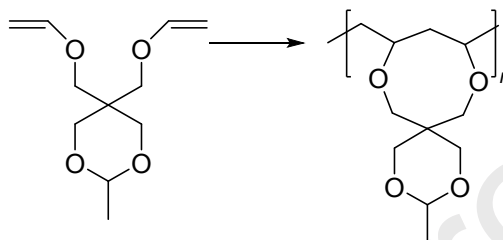
A combination of [60]fullerene- [103,104] or thiophene- [105] substituted triflate esters (Scheme 13) with EtAlCl₂ and 1,4-dioxane for living polymerization of IBVE, MOVE and methoxy ethoxy ethyl vinyl ether (MEEVE) was applied to prepare the corresponding unsaturated group-end-capped polymers. Self-assembly behavior of C₆₀-poly(MOVE) in aqueous solution and in the presence of γ -cyclodextrine was also studied.



Scheme 13. Examples of cationogens for cationic polymerization of vinyl ethers.

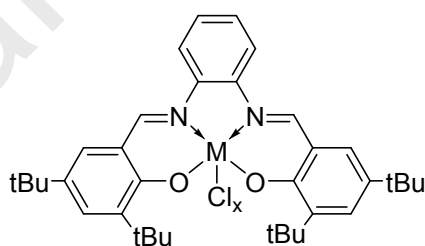
Highly-controlled polymerization of IBVE was achieved by utilizing an unusual initiating system HCl/LA/base (base = 1,4-dioxane or ethyl acetate) [106]. In this case, the chain-growth process was initiated at the Lewis acidic (LA) centers of Fe₃O₄ synthesized by magnetotactic bacteria or α -Fe₂O₃ prepared by a microbial-mineralization-inspired approach, or oxides of other metals. Heteropolyacid H₃PW₁₂O₄₀ and its various salts (AlPW₁₂O₄₀, FePW₁₂O₄₀,

$\text{K}_3\text{PW}_{12}\text{O}_{40}$, $\text{Na}_3\text{PW}_{12}\text{O}_{40}$) acted as coinitiators of the HCl-triggered cationic polymerization of IBVE to produce isotactic-enriched ($[m]$ of 60%) polymers with poorly controlled PDI (2.4–4.4) [107]. Well-controlled cyclopolymerization (PDI 1.20–2.18) of divinyl ethers, e.g. 2-methyl-5,5-bis(vinyloxymethyl)-1,3-dioxane (Scheme 14) and its likes, was achieved by using HCl/ ZnCl_2 in toluene or CH_2Cl_2 at $-30\text{ }^\circ\text{C}$ [108–110]. The resulting gel-free linear polymers, composed of cyclic repeating units, exhibited a range of high glass-transition points ($T_g = 163\text{--}231\text{ }^\circ\text{C}$) and high thermal stability ($T_{\text{decomp}} > 338\text{ }^\circ\text{C}$).



Scheme 14. Example of cationic cyclopolymerization of divinyl ether.

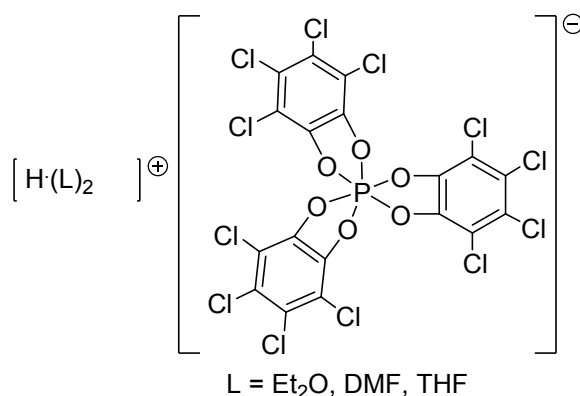
Initiating systems containing HCl and the *in situ* generated Salphen complexes of transition or main-group metals (Scheme 15) were successfully used for living polymerization of IBVE at $0\text{ }^\circ\text{C}$ in toluene [111,112]. Combinations of SnCl_4 , FeCl_3 or ZnCl_2 with Salphen resulted in poorly controlled polymerization (PDI 1.37–1.94), while the Ti- and Al-based analogs appeared to be sluggishly active. The ZrCl_4 /Salphen-derived system afforded poly(IBVE) in a controlled manner (M_n 3,200–17,300 $\text{g}\cdot\text{mol}^{-1}$, PDI 1.15–1.49).



M = Zr, Sn, Fe, Zn, Ti, Al

Scheme 15. Examples of metal-based coinitiators for cationic polymerization of vinyl ethers.

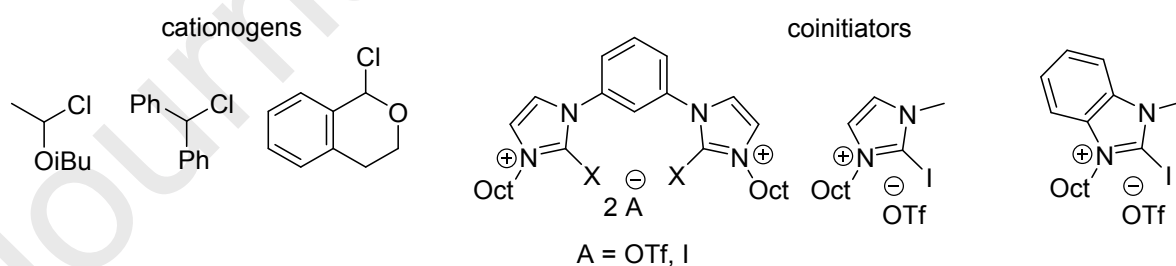
Diverse metal-free initiating systems have been reported recently. For example, apart from ubiquitous Brønsted acids ($\text{HCl}\cdot\text{Et}_2\text{O}$ [113,114] or HNTf_2 [115]), more sophisticated congeners can be utilized (Scheme 16) [116,117]. Polymerization of BVE in CH_2Cl_2 proceeded at low temperatures ($-84\text{--}19\text{ }^\circ\text{C}$) with the optimum at $-50\text{ }^\circ\text{C}$ affording poly(BVE) (M_n 15,000–29,300 $\text{g}\cdot\text{mol}^{-1}$, PDI 1.05–1.83) in high yields.



Scheme 16. Examples of discrete cationogens.

Graphite oxide was introduced as a heterogeneous catalyst for cationic polymerization of BVE under solvent-free conditions ($T_{\text{pol}} = 22\text{ }^{\circ}\text{C}$) affording poly(BVE)-carbon composites featuring diverse molecular weight distributions (M_n 700–8,100 $\text{g}\cdot\text{mol}^{-1}$, PDI 1.45–13.88, depending on the monomer/initiator ratio used) and high decomposition temperature ($T_{\text{dec}} = 354\text{ }^{\circ}\text{C}$) [118]. Graphene oxide was found to initiate cationic polymerization of IBVE in the same manner [119].

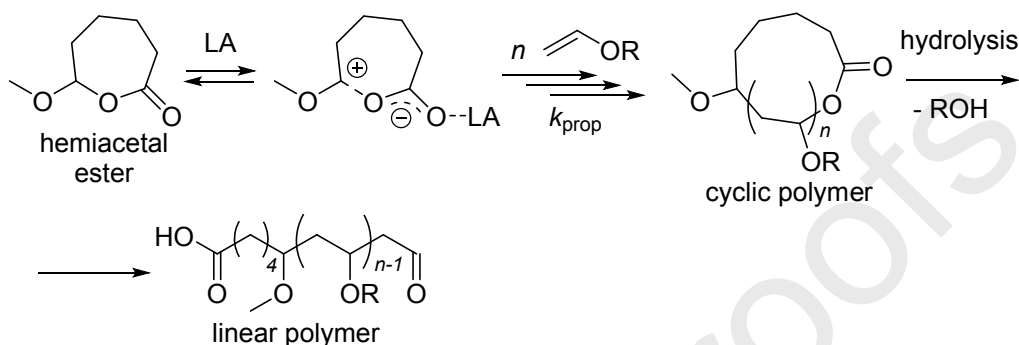
The halogen bonding-mediated cationic polymerization of IBVE involved initiating systems on the basis Cl-substituted cationogens and imidazolium salts (Scheme 17) [120]. Polymerization experiments, carried out at -40 – $20\text{ }^{\circ}\text{C}$ in CH_2Cl_2 , afforded poly(IBVE)s with low molecular weights M_n and broadened M_w/M_n values, 570–5,040 $\text{g}\cdot\text{mol}^{-1}$ and 1.52–5.61, respectively.



Scheme 17. Initiating systems for cationic polymerization of vinyl ethers based on organic cationogens and imidazolium derivatives.

Another protocol of well-defined initiation with cyclic cationogens was introduced by Sawamoto, Ouchi *et al.* (Scheme 18) [36]. The ring-expansion cationic cyclopolymerization mediated by hemiacetal ester in combination with a Lewis acid (e.g. SnCl_4) afforded macrocyclic polymers of broadened molecular weight distributions from IBVE at $0\text{ }^{\circ}\text{C}$ in CH_2Cl_2 , and TCDVE

or DDVE at $-40\text{ }^{\circ}\text{C}$ in toluene [121-124]. However, linear macromolecules exhibiting highly controlled molecular weight characteristics (M_n 3,500–18,500 $\text{g}\cdot\text{mol}^{-1}$, PDI 1.10–1.36) were eventually produced from these samples by hydrolysis. Yet, the use of halogen (Br)-end-capped vinyl ether monomers enabled the synthesis of macrocyclic initiators for the ring-linear graft copolymers with polystyrene by radical polymerization.

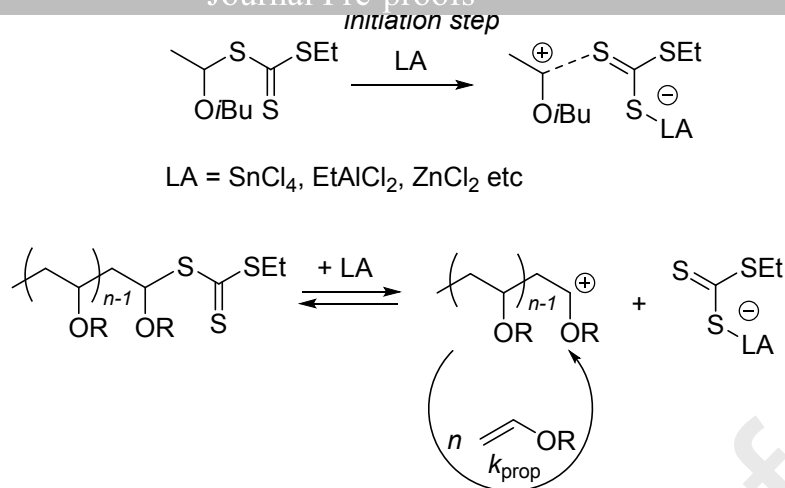


Scheme 18. Ring-expansion living cationic polymerization of vinyl ethers.

Cationic polymerization of vinyl ethers in a microflow reactor was attempted as a means of enhanced control over the propagation step. For example, initiation of IBVE polymerization with electrogenerated dendritic dicarbenium ion, followed by propagation in a flow microreactor and controlled entrapment of the reactive end-capped polymer with DTBP, yielded highly uniform polymers (PDI 1.08–1.19) [125,126]. The approach also worked with IBVE-HCl/ MCl_x /base ($\text{MCl}_x = \text{SnCl}_4, \text{FeCl}_3$; base = 1,4-dioxane, 1,3-dioxolane) initiating systems at $0\text{ }^{\circ}\text{C}$ in toluene, producing poly(IBVE)s of PDI 1.09–1.21 [127,128].

3.2. RAFT polymerization

Converting the living cationic polymerization into RAFT was firstly proposed by Kamigato *et al* [129]. Initiating system containing trithiocarbonate initiator, LA and a base (ethyl acetate, Scheme 19) was shown to induce the reversible termination cationic polymerization of IBVE at $20\text{ }^{\circ}\text{C}$ in toluene affording narrowly dispersed polymers (PDI 1.18–1.49). The group also explored the influence of metal salts (AgOTf , AgPF_6 , AgSF_6 , $\text{Na}^+[\text{B}(\text{C}_6\text{H}_3(\text{CF}_3)_2)_4]^-$, etc.) on the IBVE/HCl-initiated RAFT and the related degenerative chain transfer polymerization reactions of IBVE and EVE [130].



Scheme 19. RAFT-like cationic polymerization of vinyl ethers.

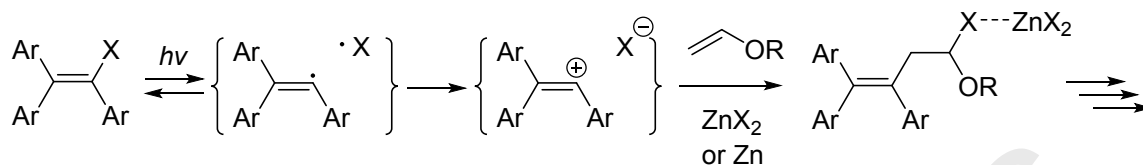
Since then, different metal-free initiating systems for cationic RAFT via degenerative chain-transfer have been developed. For example, binary systems combining triflic acid (TfOH) as cationogen and a RAFT agent, e.g. thiocarbonyl [131], thioether [132], phosphate or phosphinate [133], were used for highly controlled polymerization of vinyl ethers (IBVE, EVE, CEVE or CHVE). The resulting polymers featured high molecular weights (M_n up to 10^5 g·mol⁻¹) with very narrow distributions (PDI < 1.1). Another metal-free system, competent of IBVE, nitrophenyl vinyl ether or EOVE polymerization, consisted of HCl·Et₂O adduct and thioester and provided a slightly lower degree of control (PDI of 1.20–1.28) [2]. Besides, the intrinsic ability of trithiocarbonates as RAFT agents [32] to mediate both cationic and radical polymerization mechanisms was exploited to promote *in situ* switch from one type of polymerization to another. The approach afforded diblock polymers consisting of a poly(VE) segment obtained by cationic polymerization (e.g. poly(IBVE) or poly(MOVE)) and another segment derived from radically polymerizable monomers (acrylates, acrylamides, vinyl acetate, styrenics, etc.) [121,122,129,133-136].

3.3. Novel photo- and electro-controlled methods of polymerization

The externally stimulated initiation of VE cationic polymerization has been receiving increased attention in recent years. The traditional Brønsted or Lewis acids-based initiating systems can be replaced with the systems capable of the controlled release of initiating cations under external stimuli (light, electrical, chemical, etc.) [137].

For example, Yagci *et al.* used binary systems composed of aryl-substituted vinyl halides and ZnX₂ or metallic Zn (Scheme 20) for the photoinitiated living cationic polymerization of IBVE or

divinyl ethers (BDVE, HDVE, DEGDVE, TEGDVE) at 0 °C in CH₂Cl₂ [138-140]. The resulting poly(IBVE) polymers featured M_n 9,950–67,900 g·mol⁻¹ and PDI 1.35–2.03, whereas polymerization of difunctionalized monomers resulted in crosslinked materials with high gel content (70–100 %).



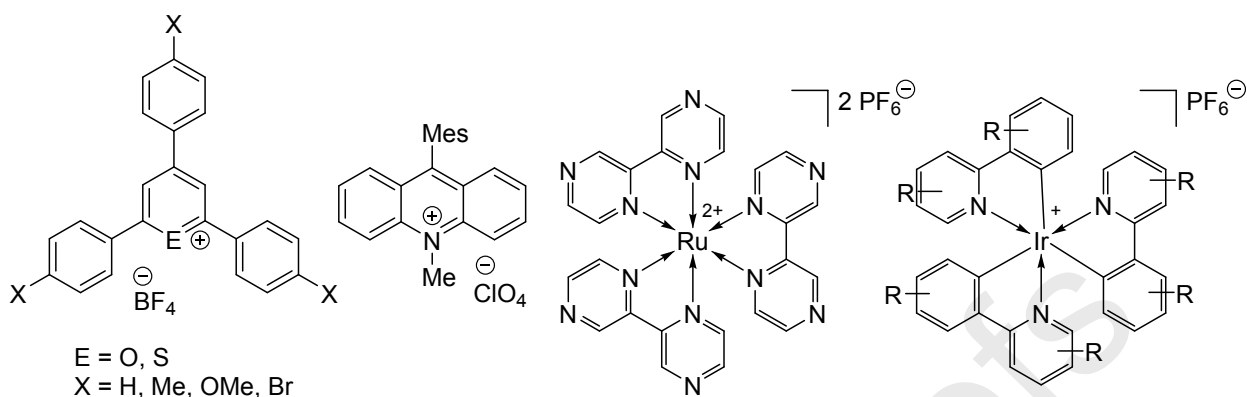
Scheme 20. The mechanism of vinyl halide-mediated photoinitiation-dependent cationic polymerization of vinyl and divinyl ethers.

A number of recently introduced photoinitiating systems comprise functionalized carbazoles [141,142], pyrenes [143], di- and polythiophenes [144] and disulfones [145], C₆₀-fullerene [146], allylic ammonium or phosphonium salts [147,148], acylgermanes [149] or different dyes [150,151], in the presence of oxidants/coinitiators AgPF₆ or [Ph₂I]⁺[PF₆]⁻. Light-controlled catalytic polymerization of EVE (M_n 10,000 g·mol⁻¹, PDI 1.74) was achieved with a photosensitizing BINAP complex of palladium [152]. Supramolecular complexes of diaryliodonium salts with crown ethers were tested as initiators of cationic polymerization of triethyleneglycole divinyl ether [153].

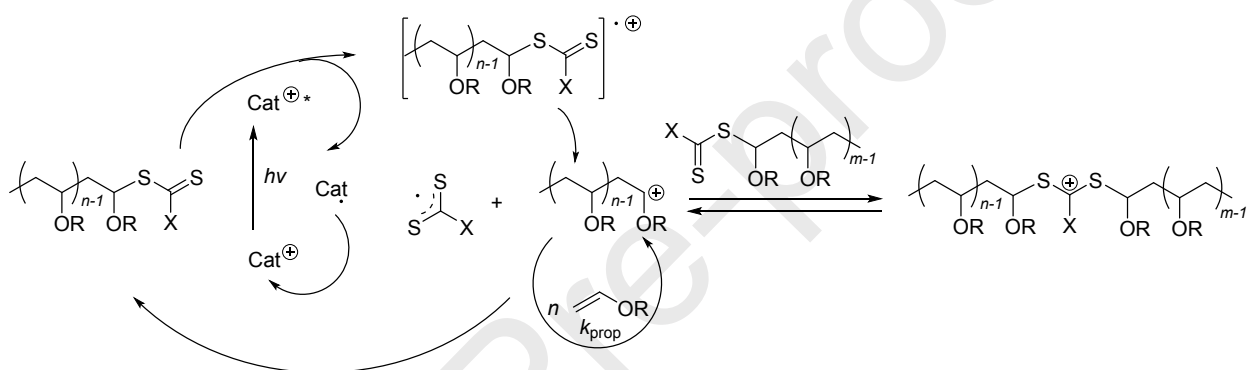
The intermediacy of radical species was specifically exploited in photogeneration of active systems for cationic polymerization. For example, a classical combination of benzyl bromide with Mn₂(CO)₁₀ affords benzyl radical. Under UV irradiation, upon activation with [Ph₂I]⁺[Br]⁻ or [Ph₂I]⁺[PF₆]⁻, it produced benzyl cation that promoted polymerization of IBVE in a controlled living manner [6]. Another initiating mechanism involves either upconverting glass with fluorescein and PMDETA [154] or lanthanide-doped upconverting nanoparticles/Cp₂TiAr₂ [155] as sources of radicals emitted under near-infrared irradiation. Such techniques were employed for polymerization of IBVE and BVE in the presence of [Ph₂I]⁺[PF₆]⁻ [154].

Photocontrolled VE polymerization processes with initiation by visible or blue light were studied as well. Fors *et al.* reported application of both metal-based and metal-free photocatalysts (Scheme 21) in complex initiating systems with thioester or trithiocarbonate as a chain transfer agent (CTA) [156-159]. Single-electron transfer from CTA or CTA-terminated polymer to the excited photocatalyst afforded radical-cation which split into CTA radical and

active cationic center (Scheme 22). The generated cation can be reversibly engaged in the degenerative chain transfer by RAFT-type mechanism.

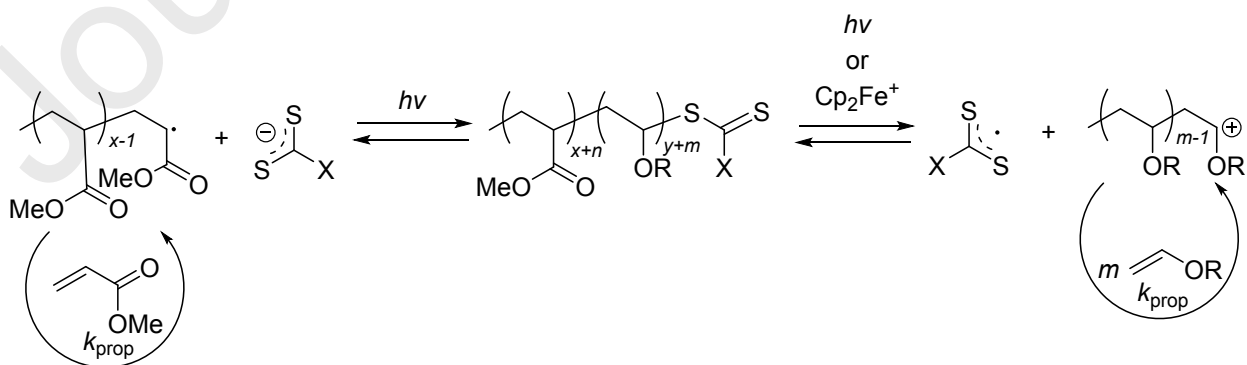


Scheme 21. Examples of photocatalysts that promote photocontrolled cationic polymerization.



Scheme 22. The mechanism of photocontrolled cationic polymerization.

A similar system involving photoinitiator combined with CTA enabled interconversion between the cationic and radical polymerization mechanisms (Scheme 23) thus promoting copolymerization of IBVE with methyl acrylate (MA) [160,161]. This new type of initiation afforded multiblock copolymers composed of poly(IBVE) and poly(MA) sequences in a highly controlled manner.

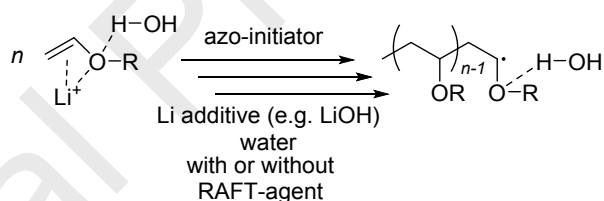


Scheme 23. Controlled interconversion of polymerization mechanisms.

Electrocontrolled VE cationic polymerization protocols are also available. A new cationic RAFT-type mechanism involved dithiocarbamate as CTA in the presence of electron-carrier or mediator (TEMPO, DDQ); by reversible transfer at the electrode, CTA is oxidized to produce carbocation [162,163]. With this method, different vinyl ethers (BVE, IPVE, EVE and CEVE) were successfully polymerized in a highly controlled manner (PDI 1.11–1.24). In the absence of electroredox agent, the process was poorly controlled and afforded polymers of broad polydispersity.

3.4. Free-radical polymerization

A rare example of polymerization of vinyl ethers by a radical mechanism was reported by Sugihara *et al.* Polymerization of several vinyl ethers was triggered by azo-initiators (e.g. 2,2'-azobis(2-methylpropionate)); the scope included IBVE, DEAVE, and hydroxy-functionalized HEVE, HBVE, CHMVE and DEGV [164-166]. The presence of RAFT agent (cyanomethyl methyl(phenyl)carbamdithioate, CMPCD) conveyed living behavior to the system and enabled block-copolymerization of poly(VE) macromonomers with vinyl acetate or N-vinylpyrrolidone (PDI < 1.38). Yet, HEVE homopolymers obtained by radical polymerization were found to be poorly isotactic ($[m] = 51\%$).



Scheme 24. Controlled radical polymerization of vinyl ethers.

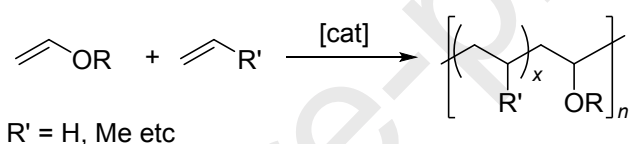
The same group developed an advanced protocol enabling controlled radical polymerization of MOVE and IBVE (Scheme 24) [167]. Polymerization reactions, conducted at 60–70 °C in the presence of water and LiOH for stabilization of the radical centers and activation of the double bonds in monomers, respectively, afforded corresponding polymers in high yields. Utilization of RAFT agents (e.g. cyanomethyl methyl(phenyl)carbamdithioate) resulted in controlled preparation of poly(MOVE) homopolymers and poly(MOVE)-*b*-poly(Vac) block copolymers with PDI 1.20–1.52.

4. Copolymerization of vinyl ethers with various monomers

Control of monomer sequence in copolymerization reactions is the holy grail of macromolecular engineering. Contributions of sequential vs. statistic copolymerization for different polymerization mechanisms (living cationic, coordination/insertion polymerization, ring-opening polymerization) have been explored by using appropriate initiating or catalytic systems.

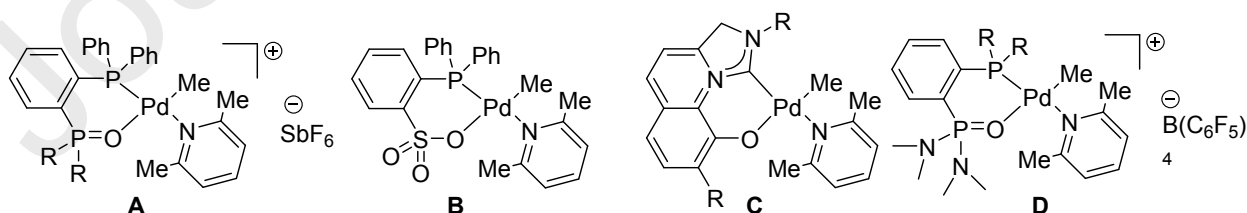
4.1. Ethylene and alkenes. The late transition metal-based coordination/insertion catalysts favor statistical copolymers

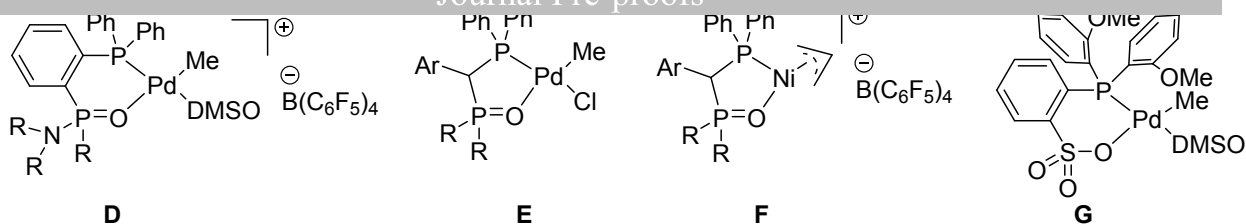
Homopolymerization of vinyl ethers by coordination/insertion mechanisms has been extensively studied [92,163,168-174]. Many contributions over the past decade dealt with the synthesis of functional polyolefins by catalytic copolymerization of alkenes (ethylene, propylene, etc.) with polar monomers (e.g. VEs, Scheme 25).



Scheme 25. Copolymerization of vinyl ethers with alkenes.

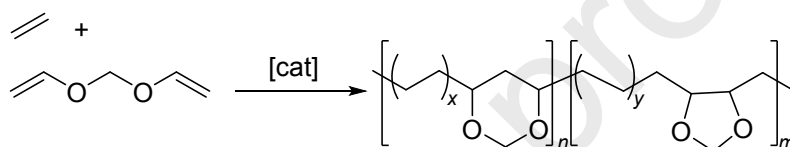
Nozaki *et al.* and Carrow *et al.* developed palladium catalysts (Scheme 26, **A–C** and **D**, respectively) for copolymerization of ethylene with BVE [170,175-178]. The copolymerization reactions proceeded under moderate conditions ($P_{\text{ethylene}} = 10\text{--}40$ bar, $T_{\text{pol}} = 80\text{--}100$ °C) affording PE-*co*-BVE copolymers (M_n 8,000–39,000 g·mol⁻¹, PDI 1.6–4.1) containing 0.1–7.7 mol% of randomly incorporated VE. Comparable results, in terms of molecular weight characteristics and BVE incorporation, were reported by Chen *et al.* for palladium- and nickel-based catalytic systems **D–F** [3,9,179].





Scheme 26. Examples of catalysts used for copolymerization of vinyl ethers with alkenes.

Copolymerization of ethylene with BVE or divinyl formal (DVF) was studied by Mecking *et al.*; the authors used a neutral palladium system **G** [172]. Thus, copolymerization of ethylene with BVE afforded PE-*co*-BVE copolymers with similar characteristics (M_n 1,300–1,900 g·mol⁻¹, PDI 1.3–1.7, incorporated BVE (2.1–6.9 mol%). Copolymerization of ethylene with DVF afforded linear polymers (M_n 1,300–4,700 g·mol⁻¹, PDI 1.2–2.3) containing five- and six-membered cyclic acetal units with the total DVF content reaching 12.9 mol% (Scheme 27).



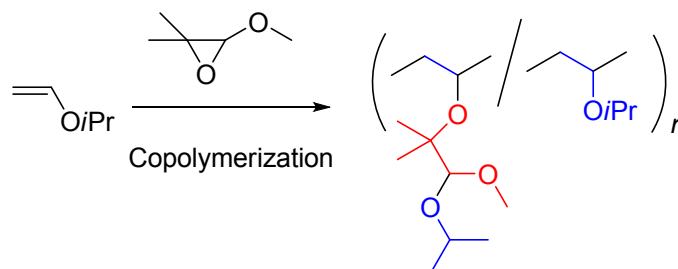
Scheme 27. Copolymerization of ethylene with divinyl formal.

4.2. Other combined copolymerization techniques

A straightforward access to di- and multiblock copolymers can be gained by sequential addition of different monomers to the same living polymerization system. For example, ABA-triblock copolymers of adamantyl vinyl ether with NBVE were produced by cationic polymerization with a difunctional initiating system 1,4-bis(1-acetoxy)butane/ $\text{Et}_{1,5}\text{AlCl}_{1,5}$ /ethyl acetate [180], while introducing cyclohexanedimethanol divinyl ether to this system afforded star-diblock copolymers featuring improved rubber elastic properties. A similar sequential protocol afforded tri- and pentablock copolymers of NBVE, CEVE and tert-butyldimethylsilyl ethylene glycol vinyl ether (SiEGVE) [181]. Diblock copolymers of IBVE and α -methylstyrene were also produced by sequential approach with initiation by $\text{HBr}/\text{FeCl}_3/n\text{Bu}_4\text{NBr}$ [182].

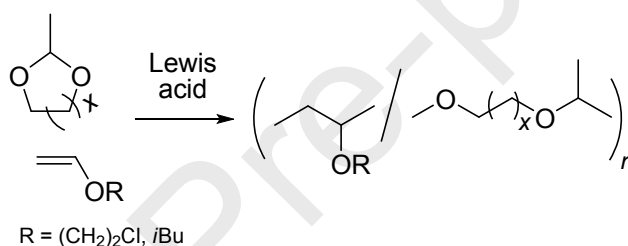
Copolymerization of IPVE with 1-methoxy-2-methylpropylene oxide (MOMPO) was accomplished using a specific initiating system composed of $\text{CF}_3\text{SO}_3\text{H}$ and $n\text{Bu}_4\text{NI}$ [183] (Scheme 28). The ring-opening copolymerization resulted in IPVE-*co*-MOMPO product with unimodal molecular weight distribution ($M_n = 6,500$ g·mol⁻¹, PDI = 1.73) subsequently hydrolyzed under acidic conditions to a low molecular weight product ($M_n = 1,700$ g·mol⁻¹, PDI = 1.7). Noteworthy, the IPVE-IPVE junctions appeared to be resistant to acidic hydrolysis.

incorporation of the ring-opened MOMPO unit into IPVE chain by alkoxy-group transfer was confirmed by ^1H , ^{13}C , and ^2D NMR spectroscopic studies.



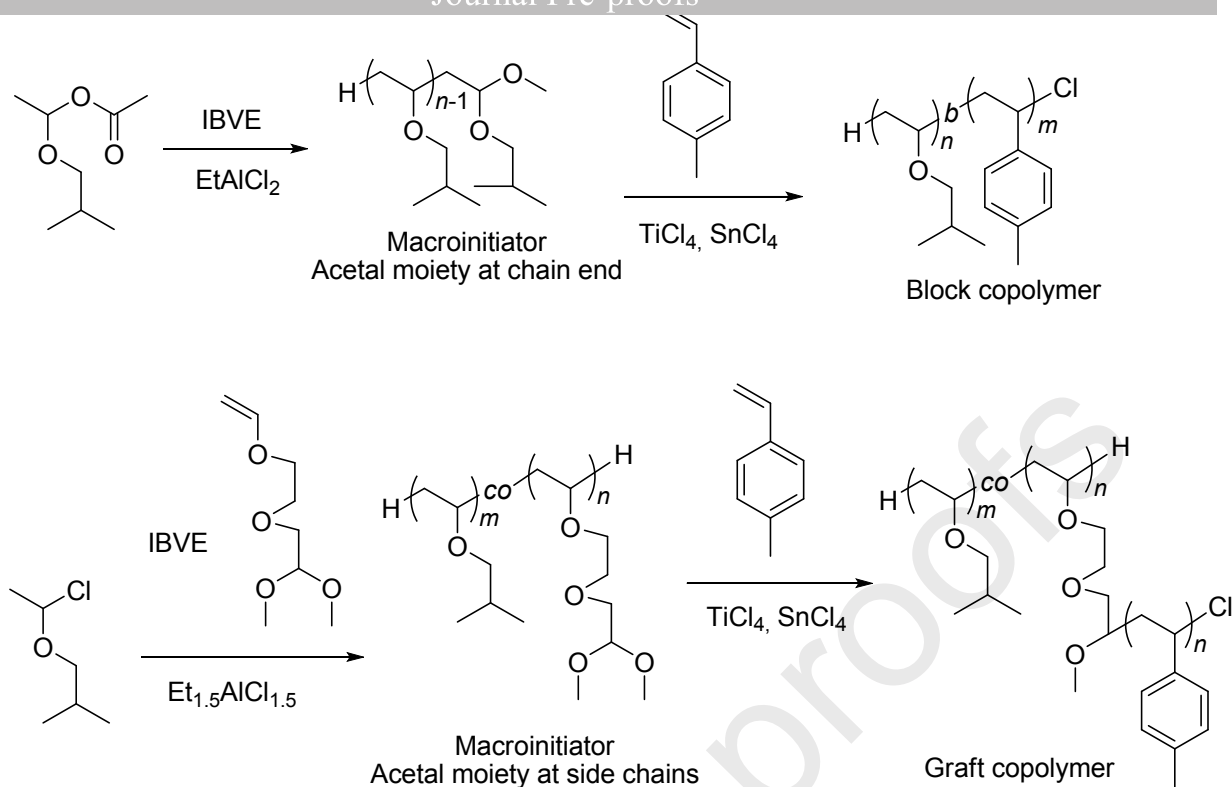
Scheme 28. Copolymerization of IPVE with MOMPO. Reaction conditions: $[\text{IPVE}] = 0.80 \text{ M}$, $[\text{MOMPO}]_0 = 0.20 \text{ M}$, $[\text{CF}_3\text{SO}_3\text{H}]_0 = 4.0 \text{ mM}$, $[\text{nBu}_4\text{NI}]_0 = 4.2 \text{ mM}$, in dichloromethane at $-40 \text{ }^\circ\text{C}$.

Cyclic acetals were also copolymerized by ring opening reactions with CEVE and IBVE; the SnCl_4 -promoted process yielded multiblock-like copolymers [184]. Propagating species were provided by both VE- and cyclic acetal-derived end groups. The distribution of comonomers within the chains was defined by the nature of cyclic acetal and VE.



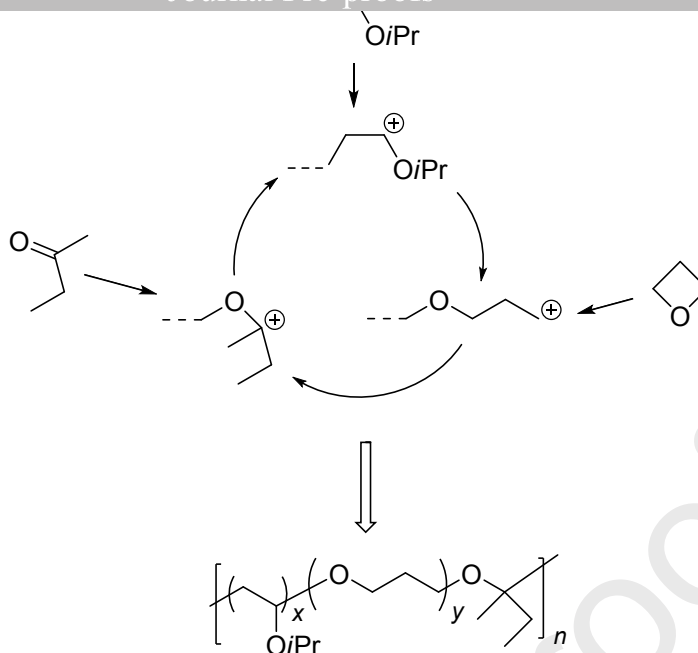
Scheme 29. Ring-opening copolymerization of vinyl ethers and cyclic acetals.

The use of acetals as initiators in living cationic polymerization afforded block and graft copolymers containing poly(*p*-methylstyrene) and poly(VE) segments [185]. IBVE and *p*-methylstyrene, conventionally incompatible with each other, were successfully copolymerized in the presence of $\text{TiCl}_4/\text{SnCl}_4$ initiating system and macroinitiators having acetal moieties. Linear macroinitiators with acetal moieties at chain termini provided block copolymers (Scheme 30, top), whereas macroinitiators with acetal moieties at side chains facilitated formation of graft copolymers (Scheme 30, bottom). The macroinitiators were prepared by quenching the living cationic polymerization of IBVE with methanol or by promoting the living cationic copolymerization of IBVE with 2-(2,2-dimethoxy)ethoxyethyl vinyl ether.



Scheme 30. Block and graft copolymer preparation using macroinitiators.

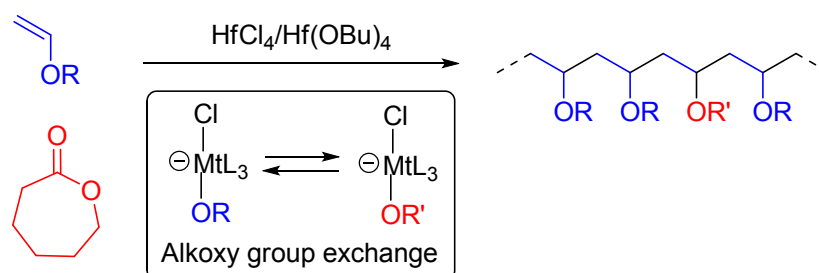
Concurrent cationic vinyl-addition, ring-opening, and carbonyl-addition mechanisms were described for terpolymerization of IPVE, oxetane, and methyl ethyl ketone (MEK) [186]. Given each of the monomers is capable of providing propagating chain ends, formation of statistical multiblock polymers was the result of this polymerization reaction. During the reaction, the non-homopolymerizable ketone monomer reacted with the oxetane-derived oxonium ion giving rise to carbocation capable of reacting with VE only (Scheme 31).



Scheme 31. Terpolymerization of VE, Oxetane and MEK.

Discovery of such cross-reactivity led to successful copolymerization of vinyl ethers (IPVE, EVE) with various oxiranes (IBO, ISPO, BDO, DMBO, BO) in the presence of TfOH or $B(C_6F_5)_3$ initiators [187,188] to afford linear random or alternating-rich copolymers exhibiting a range of molecular weight characteristics (M_n 300–43,200 $g \cdot mol^{-1}$, PDI 1.53–4.49).

Vinyl-addition polymerization of VE and simultaneous ring-opening polymerization of ϵ -caprolactone under hafnium-mediated control afforded graft copolymers [189,190]. Copolymerization of the conventionally incompatible monomers occurred by virtue of orthogonal propagating reactions and transient merging, yielding the poly(VE) main chain and several poly(caprolactone) side chains. The growing alkoxide ends attached to the Hf-metal center promoted both cationic vinyl-addition and ring-opening polymerizations. Exchange reactions between the terminal alkoxy groups of polyester chains and the VE-derived alkoxy groups, combined with the repetitive mode of propagation, provided graft copolymer composed of a poly(VE) chain with several inserted polyester chains (Scheme 32).



Scheme 32. The alkoxy group exchange mechanism and graft copolymer construction.

An approach based on successive living cationic polymerization of MOVE, EOVE or EOVEVE, followed by ring-opening polymerization of L-lactide, enabled precision synthesis of block copolymers exhibiting well-defined organization of poly(VE) and poly(lactide) blocks [191].

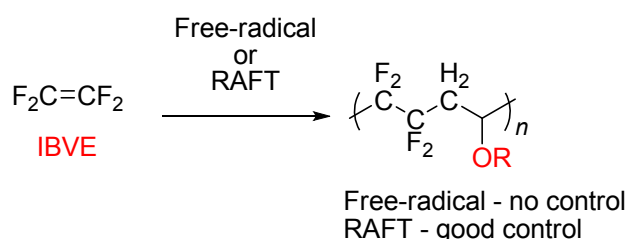
Yagci *et al* applied the photoinduced $\text{Ph}_3\text{CBr}/\text{Mn}_2(\text{CO})_{10}/[\text{Ph}_2]^+[\text{Br}]^-$ -mediated initiation to prepare a Ph_3C -capped poly(IBVE) macroinitiator by living cationic polymerization. Subsequent thermally promoted radical polymerization of acrylates or styrene yielded diblock copolymers [192].

An alkoxyamine-based TEMPO/ SnBr_4 initiating system promoted cationic polymerization of IBVE producing a TEMPO-terminated macroinitiator. Used at the next step to initiate radical polymerization of styrene, this macroinitiator afforded well-defined copolymer of narrow polydispersity (PDI 1.2) [193].

A combination of living cationic polymerization with RAFT in a three-step protocol afforded diblock brush-like copolymers of MEEVE and N-isopropylacrylamide featuring thermoresponsive properties [194].

Tetrafluoroethylene (TFE) was for the first time copolymerized with IBVE by conventional radical and RAFT (RAFT/MADIX) methods [195] using *O*-ethyl-*S*-(1-methyloxycarbonyl)ethyl xanthate as a chain transfer agent and benzoyl peroxide as an initiator. As expected, copolymers obtained by radical copolymerization were heavier (M_n 4,400–11,000 $\text{g}\cdot\text{mol}^{-1}$) and of broader polydispersity (PDI > 2) than copolymers obtained by controlled processes (M_n 1,200–2,000 $\text{g}\cdot\text{mol}^{-1}$, PDI 1.08–1.11) (Scheme 33).

Photoorganocatalyzed reversible-deactivation radical alternating copolymerization of CTFE and vinyl ethers (EVE, BVE, IBVE, CEVE, SiBVE and SiEGVE) was recently reported [[196]]. Utilization of functionalized 10-phenylphenothiazine as photoinitiator in combination with RAFT agents (xanthates) allowed synthesis of various alternated copolymers under mild conditions (LED irradiation, room temperature, 1 bar pressure) and in controlled manner (M_n 2,000–45,300 $\text{g}\cdot\text{mol}^{-1}$, PDI 1.12–1.32).



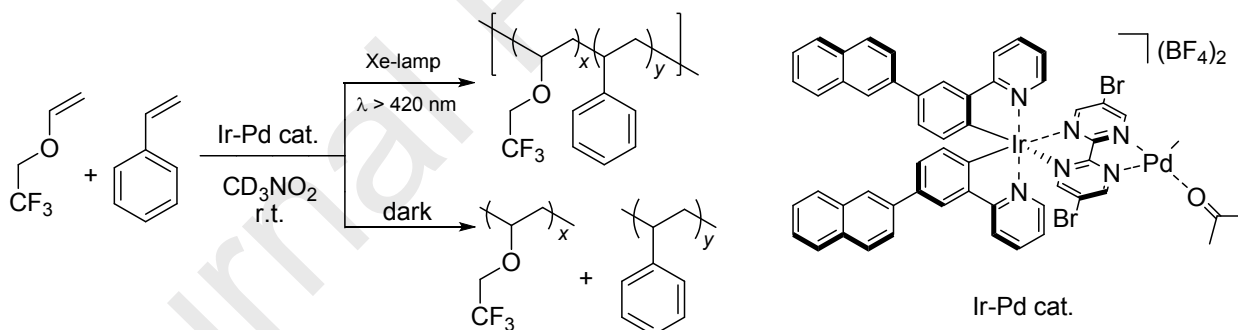
Scheme 33. Copolymerization of TFE with IBVE by conventional and RAFT/MADIX approaches.

LIVING NOMOPOLYMERIZATION OF FLUORINATED VINYL ETHERS (FVE, WITH F₉, F₁₂ AND F₁₃ GROUPS IN THE side chains) AND THEIR COPOLYMERIZATION WITH IBVE OR MOVE WERE ACHIEVED IN FLUORINATED solvents under regular conditions (IBEA/Et_{1.5}AlCl_{1.5}/1,4-dioxane, 0 °C) [197]. The thermally reversed micellization and sol-gel transition properties of the resulting di- and tri-block copolymers were investigated.

Comb-like poly(VE) polymers with fluorinated side chains were studied to determine their macromolecular organization and interrelated physicochemical and thermal characteristics [198].

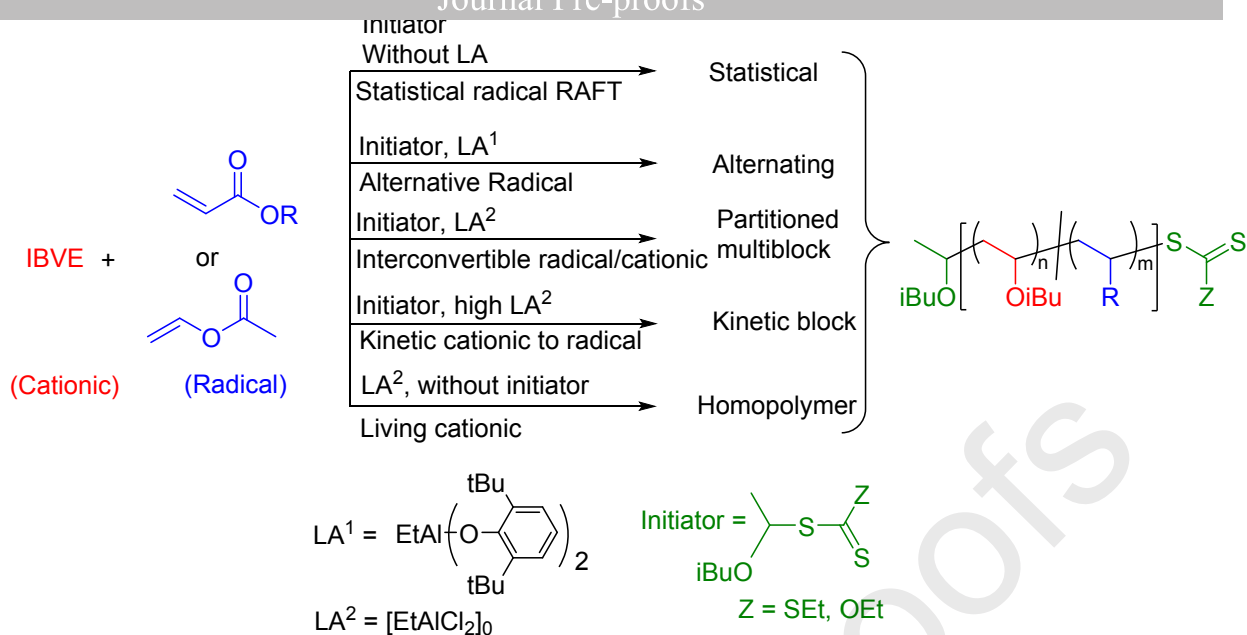
In a search for alternative biosourced polymers, several ribose-derived vinyloxy monomers were copolymerized with diethyl fumarate and diethyl maleate and alkoxy monomers [199]. Detailed kinetic investigations confirmed higher reactivity of the sugar-derived VEs as compared to that of alkyl VEs in the free radical-mediated donor-acceptor copolymerization with butadienoates.

A highly active Ir-Pd catalyst facilitated copolymerization of styrene with 2,2,2-trifluoroethyl vinyl ether (TFEVE) under Xe irradiation [199]. The isolated copolymer was clearly a co-polymer; the reaction carried out in the dark produced a mixture of homopolymers (Scheme 34). Turning on the lamp in the course of the reaction altered the type of synthesized polymers.



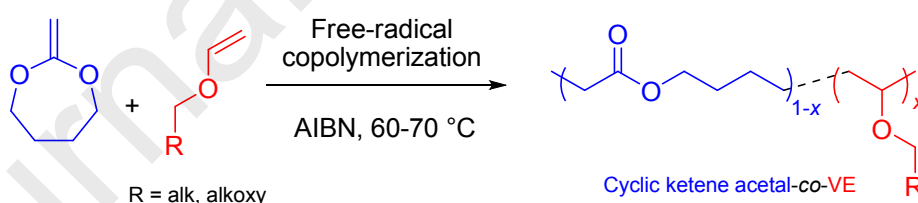
Scheme 34. Homopolymerization and copolymerization of styrene and TFEVE in the presence of Ir-Pd catalyst under different light conditions.

The tunable nature of VEs allowed involving them into copolymerization reactions with acrylates or with vinyl ethers proceeding by totally different mechanisms. The identity of final products varied depending on the type of Lewis acid used and the presence of the coinitiator [200]. Weak and bulky Lewis acids promoted the alternating radical RAFT copolymerization of IBVE with acrylates, while strong Lewis acids led to the controlled living copolymerization (Scheme 35).



Scheme 35. A system for controllable VE (co)polymerization.

Functional aliphatic copolymers of cyclic ketene acetals (CKAs) with VEs were synthesized by a simple free-radical approach (Scheme 36) [201]; it provided access to functionalized fluorescent probe copolymers, amphiphilic copolymers grafted with poly(ethylene glycol) side chains, antibacterial films and crosslinked bioelastomers. Interestingly, di(ethylene glycol) divinyl ether was successfully integrated into CKA chain yielding a linear copolymer instead of a crosslinked homopolymer. The isolated copolymers revealed potential for tissue engineering applications.



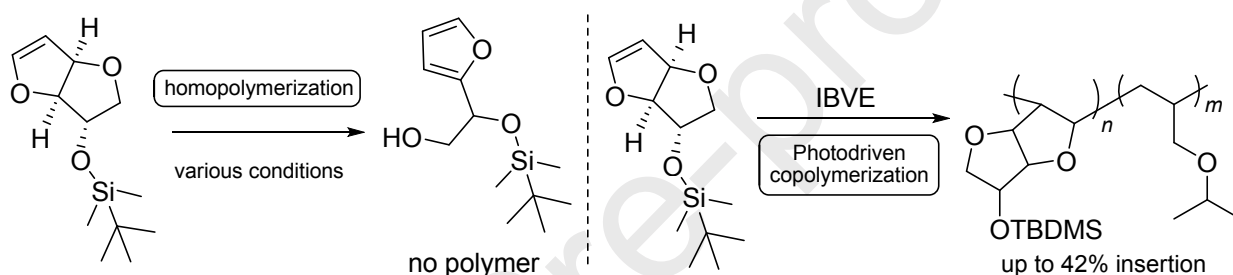
Scheme 36. Copolymerization of CKAs and VEs via free-radical mechanism.

Another promising access to linear diblock copolymers incorporating poly(vinyl ether) and poly(styryl) or poly(acryl) fragments is based on a two-step approach [202,203]. Thus, a conventional living polymerization is switched to a different mode (cationic or radical) by introducing a chain end-capped initiating function at the first step.

Similar results in the synthesis of poly(vinyl ether)-poly(styrene) diblock copolymers were achieved by introducing a hybrid initiator composed of $OCH(Me)^+X^-$ and AIBN capable of

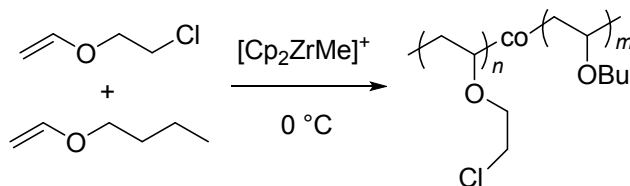
initiating cationic and radical polymerizations, respectively, and trinitrocarbonate as RAFT agent [204].

The inherent reactivity of VEs in polymerization reactions can be developed in relation to monomers incapable of homopolymerization. According to this strategy, desired fragments can be inserted into the main chain to modify the final properties of the resulting polymers. For example, straightforward homopolymerization of biomass-derived isosorbide is impossible. However, it readily undergoes cationic copolymerization with IBVE in the presence of Lewis acids, giving up to 42 mol% of isosorbide derivative incorporated into the copolymer structure (Scheme 37) [205]. Conventional cationic copolymerization promoted a competing process of ring-opening polymerization and rearrangement, whereas photo-driven cationic polymerization protocol with a RAFT agent facilitated chain propagation against the rearrangement.



Scheme 37. Homo- and copolymerization of iso-sorbide derivatives under conventional and photo-driven polymerization conditions.

Bis(η^5 -cyclopentadienyl)dimethyl zirconium (Cp_2ZrMe_2) in combination with $[\text{PhMe}_2\text{NH}]^+$ $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ catalyzed statistical cationic copolymerization of BVE and CEVE [206]. Regardless of different monomers ratios used for polymerization, the reaction yielded polymers with similar characteristics (M_n 10,000–14,000 $\text{g}\cdot\text{mol}^{-1}$, PDI 1.5) (Scheme 38). The structure of the copolymers was confirmed by NMR spectroscopy. The same group reported preparation of block copolymers based on zirconocenium-promoted cationic copolymerization of perfluoro ethyl vinyl ether with 2-R-oxazolines (R = Me, Ph) and ϵ -caprolactone [207].

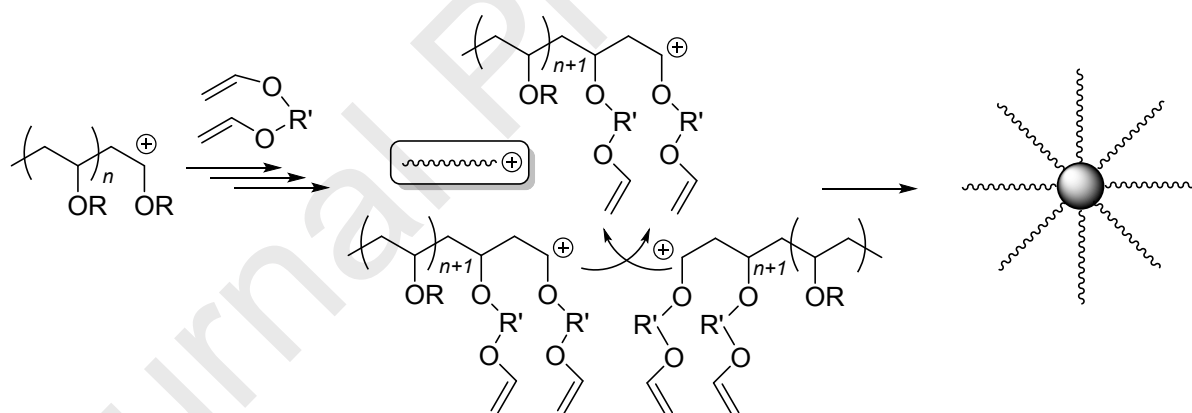


Scheme 38. Cationic copolymerization of BVE and CEVE.

4.3. Composition- and topology-controlled copolymerization of vinyl ethers

A number of well-controlled cationic polymerization techniques allowed synthesis of copolymers featuring several particular types of topological motifs [208]. Conventional living polymerization of monofunctional monomers affords a linear polymer, whereas controlled incorporation of difunctional monomers can produce a variety of topologies e.g. star-, beaded- or brush-shaped polymers.

For example, Aoshima *et al.* succeeded in synthesis of well-defined star-shaped copolymers (Scheme 39) from monovinyl and divinyl ethers (respectively, IBVE, MOVE, EOVE, EOEOVE, CHVE, PIVE, and DVE, BVP) using cationic initiating systems composed of IBEA, LA and a base (LA = Et_{1.5}AlCl_{1.5}, EtAlCl₂, SnCl₄; base = 1,4-dioxane) [209-212]. The resulting materials exhibited a range of stimuli-responsive behaviors (temperature, pH) depending on the nature of comonomer functionalities. Introduction of aldehydes (e.g. *p*-methylbenzaldehyde, isophthalaldehyde, (1*R*)-(-)-myrtenal) during the EtSO₃H/GaCl₃/1,4-dioxane-promoted polymerization of CEVE, IBVE and linear or cyclic enol ethers allowed sequence-controlled preparation of both linear and star-shaped polymers [213,214]. Under mildly acidic conditions, these polymers underwent degradation into lower molecular weight polymers.



Scheme 39. Synthesis of star-shaped (co)polymers.

A non-aqueous inverse suspension copolymerization approach enables formation of beaded-like poly(VE) gels with low crosslinking levels [215]. A combination of CEVE or 4-acetoxybutyl vinyl ether with methoxybutyl vinyl ether and a divinyl ether was induced into copolymerization promoted by a cationic initiating system (BF₃·Et₂O, CH₂BrCl, -78 °C). The resulting solid gels featured improved swelling characteristics in different solvents.

Minoda *et al.* designed new monomers with both vinyl ether and phenyl acetylene functionalities [216,217]. Living cationic polymerization (TFA/Et₂AlCl/1,4-dioxane) of the vinyl

ether functionalities afforded linear poly(VE)s, which were then subjected to polymerization involving the acetylene moieties by either Cu-catalyzed oxidative coupling or a Rh-catalyzed process, with both catalytic systems promoting formation of brush-shaped polymers. The same research group reported a synthesis of hydrophilic glycerol-functionalized poly(VE)s for the use in preparation of monodispersed core-shell polymer particles via dispersion polymerization with styrene [218].

Syntheses of biosourced vinyl ethers, derived from different plant oils (soybean, linseed, camelina), and their homo- and copolymerization by a cationic mechanism (IBEA/ $\text{Et}_{1.5}\text{AlCl}_{1.5}$ or $\text{SnCl}_4/1,4$ -dioxane) were reported by Chisholm *et al.* [64,219-222]. Some of the resulting materials were tested as alkyd-type surface coatings.

A number of poly(VE) homo- and copolymers obtained by cationic polymerization of various functional group-capped VE monomers were reported by Sakaguchi *et al.* The products were probed for diverse applications including preparation of hydrophilic thermoresponsive polyurethanes, development of gas-selective permeable membranes and production of transparent polymeric materials for optical lenses [223-231].

Living cationic copolymerization was used by Aoshima *et al.* to prepare amphiphilic copolymers of IBVE and aminoethyl vinyl ether [232,233]; the products featured antibacterial and hemolytic activity. Linear diblock copolymers of poly(CHVE-*b*-MOVE) and poly(CHVE-*b*-EOVE), showing enhanced blood-compatibility, were proposed as candidate materials for construction of bioinert interfaces [234-236].

4.4. Miscellaneous

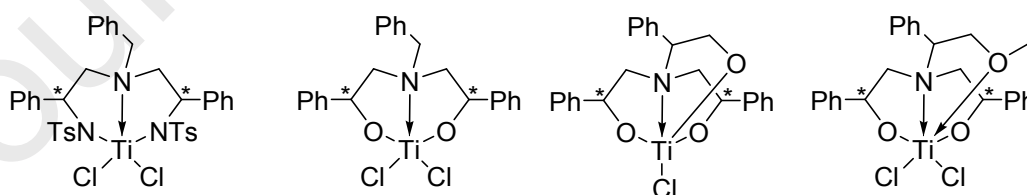
Poly(VE)s with azobenzene functionalities in the repeating unit, synthesized by living cationic polymerization, were blended with poly(ϵ -caprolactone) to provide a material with unique anisotropic photomechanical response properties [237]. Cationic polymerization of a TEMPO-capped vinyl ether monomer afforded a hydrophilic polymer proposed as a cathode active material for rechargeable devices [238]. Linear poly(VE)s are considered for diverse applications including production of advanced materials for hydrogen generation [239] and chitin nanofiber composites embedded with gold nanoparticles [240].

5. Stereocontrol in polymerization of vinyl ethers

From a more applied viewpoint, structure of the macromolecules is the crucial parameter that determines the properties of polymer materials. Enhancement of the stereoselectivity control will eventually allow fine tuning for a broad range of plastic materials with diverse thermal, mechanical and other physicochemical properties.

Several pioneering reports described the efforts to maintain stereocontrol of VE polymerization. Stereoselective polymerization of IBVE was demonstrated to proceed by cationic mechanism at -80 – 60 °C under control of $\text{BF}_3 \cdot (\text{Et}_2\text{O})$ initiating system [241]. The structure of the resulting solid thermoplastic materials was studied by X-ray diffraction analysis showing that the polymers were isotactic by nature [242,243]. Isotactic poly(IBVE)s with similar properties were obtained by coordination/insertion mechanism in a $\text{TiCl}_4/\text{R}_3\text{Al}$ Ziegler-Natta-type catalytic system [244]; in the presence of titanium-based LAs [245]; phosphoric acid derivatives coupled with SnCl_4 [246]; and aromatic acetals in conjunction with tin halides [247].

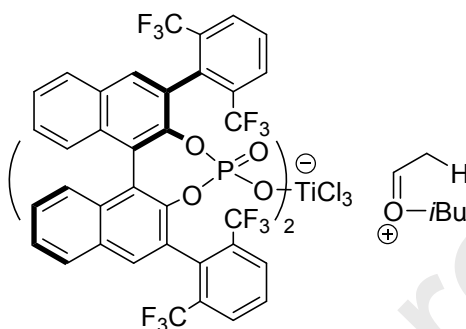
More recent contributions featured isoselective polymerization of IBVE and TBVE achieved with both metallocene and post-metallocene systems e.g. CpTiCl_3 , Cp_2MCl_2 ($\text{M} = \text{Ti, Zr, V}$) or phenoxy-imino precatalysts $[\text{ON}]_2\text{MCl}_2$ ($\text{M} = \text{Ti, Zr, Hf}$), combined with methylaluminoxane (MAO) [248]. However, the level of isotacticity for these systems was quite moderate; in particular, the dyads $[m]$ constituted 63–68% and 45–52% for poly(IBVE) and poly(TBVE), respectively. Chiral precatalysts (Scheme 40), in combination with MAO or molecular activator $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_5\text{F}_5)_4]^-$, afforded at relatively high polymerization temperatures (-10 – 30 °C) poly(BVE) with a good degree of control in terms of molecular weight distributions (M_n 2,400–59,400, PDI 1.08–2.01) and improved isotacticity ($[m]$ of 45–90 %) [249-251].



Scheme 40. Chiral titanium-based precatalysts studied in VE polymerization.

The $t\text{BuOH}/\text{FeSO}_4$ binary system [252] revealed multi-site behavior in IBVE polymerization at 0 °C; the reaction afforded mixtures of isotactic and atactic poly(IBVE) fractions. Subsequent fractionation with MEK allowed isolation of the minor isotactic fraction containing up to 82% of $[m]$ dyads.

A new cationic initiating system featuring chiral anion (Scheme 4.1) was optimized in order to provide a higher degree of stereocontrol in IBVE, IPVE, BVE and EVE polymerization [253]. The most promising products, with up to 93 % of isotactic dyads [*m*], were obtained upon polymerization of IBVE at $-78\text{ }^{\circ}\text{C}$ in a toluene/hexane mixture. The resulted crystalline materials featured high melting points (138–152 $^{\circ}\text{C}$), valuable thermomechanical properties and improved adhesion to polar surfaces.



Scheme 41. A chiral ion-pair used in isoselective cationic polymerization of vinyl ethers.

6. Conclusions

The review highlights recent advances in polymerization of VEs, including the means for precise structural and functional design of the polymers. The mainstream living polymerization protocols, ubiquitously applied to synthesize poly(vinyl ethers), become actively supplemented by new methods of controlled synthesis. The rapidly developing area of initiating systems and precise control eventually gained over polymerization reactions allows the involvement of unconventional VE substrates as monomers and co-monomers thus expanding the variety of polymers with desired features and properties.

The remarkable versatility of VEs makes them highly valuable monomers not only providing polymeric materials with unique properties, but also conferring clues to understanding of a complicated nature of polymerization processes. At the same time, the easy access to VE from available and sustainable raw materials (acetylene or calcium carbide) makes them highly relevant to our industrial future. Of special importance are the efforts to produce calcium carbide from biomass and biomass refining wastes, which could associate production of plastics with natural photosynthetic cycle.

7. References

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