



HAL
open science

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

E. Kirillov, K. Rodygin, Valentine P. Ananikov

► To cite this version:

E. Kirillov, K. Rodygin, Valentine P. Ananikov. Recent advances in applications of vinyl ether monomers for precise synthesis of custom-tailored polymers. *European Polymer Journal*, 2020, 136, pp.109872. 10.1016/j.eurpolymj.2020.109872 . hal-02931999

HAL Id: hal-02931999

<https://hal.science/hal-02931999>

Submitted on 11 Sep 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

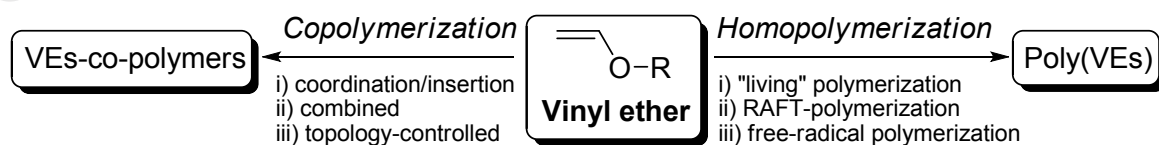
1. Introduction.....	3
2. Advanced green syntheses of vinyl ether monomers	4
3. Methods for controlled synthesis of poly(vinyl ether)s.....	10
3.1. Living cationic polymerization	10
3.2. RAFT polymerization.....	16
3.3. Novel photo- and electro-controlled methods of polymerization	17
3.4. Free-radical polymerization.....	20
4. Copolymerization of vinyl ethers with various monomers	21
4.1. Ethylene and alkenes. The late transition metal-based coordination/insertion catalysts favor statistical copolymers	21
4.2. Other combined copolymerization techniques.....	22
4.3. Composition- and topology-controlled copolymerization of vinyl ethers.....	29
4.4. Miscellaneous.....	31
5. Stereocontrol in polymerization of vinyl ethers.....	31
6. Conclusions	33
7. References.....	34

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].

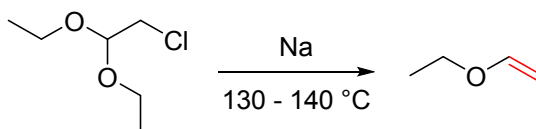
The RAFT approach in both cationic and radical polymerization reactions was found suitable for poly(VE) synthesis [32]. Initiation with thiocarbonylthio or xanthate compounds in combination with a Lewis acid (LA) and a base resulted in well-defined synthetic polymers and was advantageous in terms of 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.

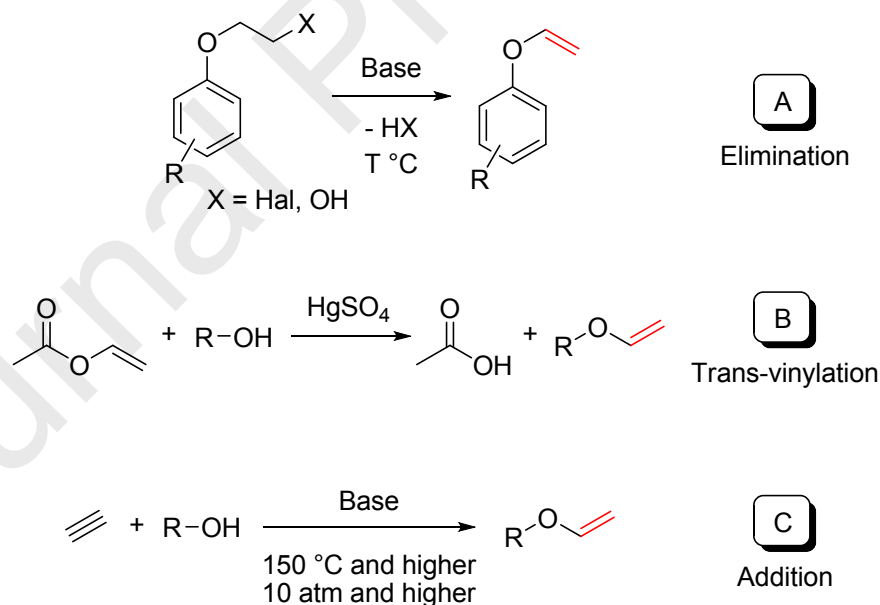
The first synthesis of vinyl ether was reported by Wislizenus in 1878 [1]. The method was based on addition of sodium metal to hot monochloroacetal (Scheme 2) since it was essentially an elimination reaction in the presence of a strong base.



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.

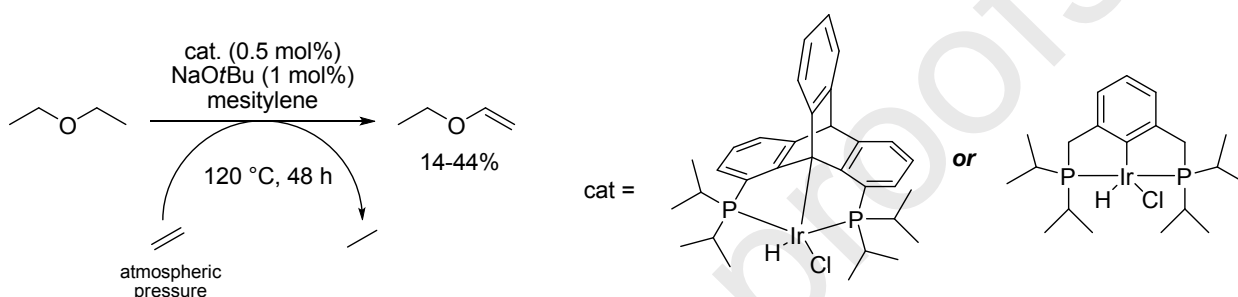


Scheme 3. Common strategies for the vinyl functionality incorporation.

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

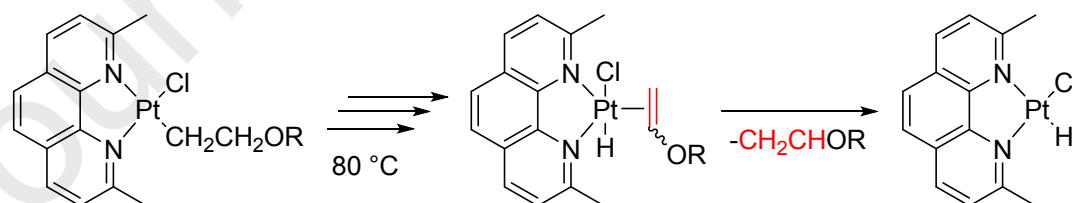
was sealed and heated at 170–180 °C for 12 h; the ether was subsequently purified by distillation.

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).



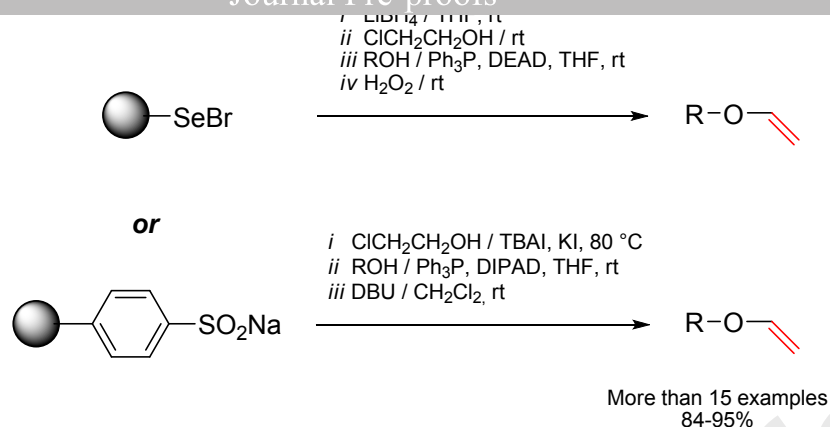
Scheme 4. Iridium-catalyzed dehydrogenation of ethers.

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).



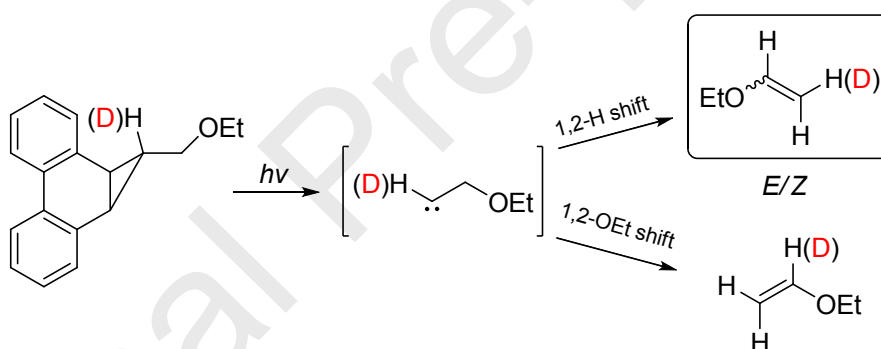
Scheme 5. Plausible mechanism of vinyl ether formation from $[\text{PtCl}(\text{Me}_2\text{phen})\eta^1-\text{CH}_2\text{CH}_2\text{OR}]$.

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.



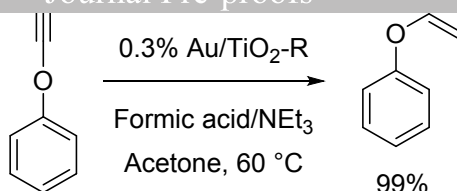
Scheme 6. Solid-phase polystyrene-supported synthesis of aryl vinyl ethers.

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.

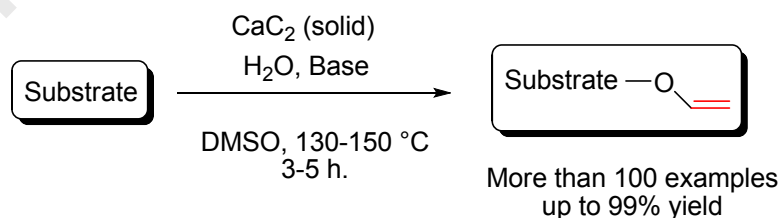


Scheme 9. Plausible sequence of the of PHS vinyl derivative biosynthesis.

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).



Substrate = Aliphatic and aromatic alcohols
Diols and polyols
Aryl ethers
Epoxides
Polyfunctional alcohols
Carbohydrates

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

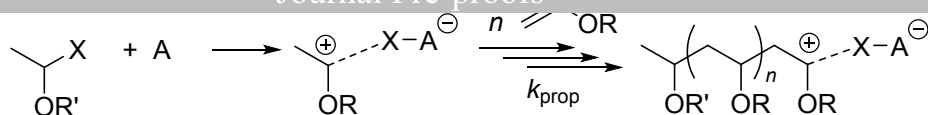
Certain vinyl ethers obtained through the carbide route can be utilized as monomers in polymerization by cationic and free-radical mechanisms [68,76,77]. Usage of calcium carbide for vinylation reaction is a rapidly expanding area with numerous research efforts to produce VEs from alcohols, thiols, amines, 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 = coinitiator (Lewis acid LA; LA/base; LA/X⁻[NR₄]⁺)

Scheme 11. Controlled cationic polymerization of vinyl ethers initiated by a cationogen/coinitiator 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 $\text{Cp}_2\text{MMe}_2/\text{activator}$ ($M = \text{Zr, Hf}$; 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.

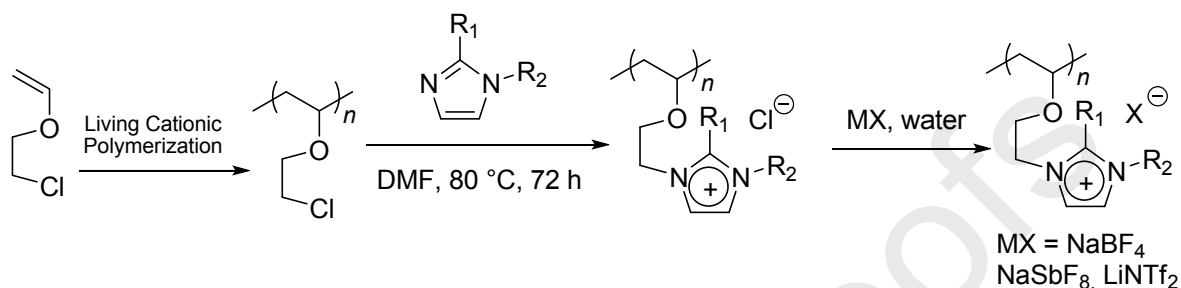
In situ generation of cationogen $\text{CH}_3\text{CH}(\text{OR})\text{X}$ from parent monomers IBVE, IPVE and TBVE with a Lewis acid-free initiating system $\text{CF}_3\text{SO}_3\text{H}/n\text{Bu}_4\text{NX}$ ($X = \text{Cl, Br, I, CF}_3\text{SO}_3$) was examined under a range of conditions ($-78 - 0\text{ }^\circ\text{C}$, 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

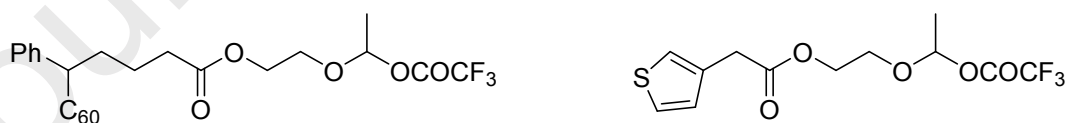
[98,99]. The use of fluorinated solvents (hydrofluorocarbons, chlorocarbons, ethers and aromatics) appeared to be mandatory to provide solubility of the resulting materials. Under the same conditions, fluorine-containing and fluorine-free star-shaped crosslinked polymers were produced upon addition of 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].

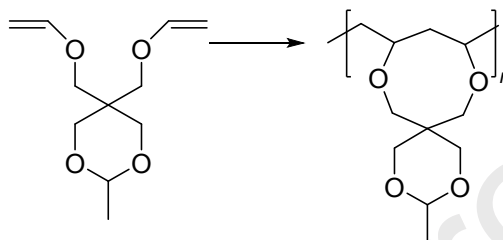
A combination of [60]fullerene- [103,104] or thiophene- [105] substituted triflate esters (Scheme 13) with EtAlCl₂ and 1,4-dioxane for living polymerization of IBVE, MOVE and methoxy ethoxy ethyl vinyl ether (MEEVE) was applied to prepare the corresponding unsaturated group-end-capped polymers. Self-assembly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

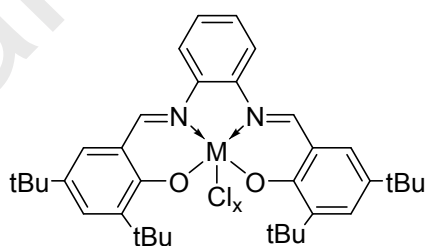
Highly-controlled polymerization of IBVE was achieved by utilizing an unusual initiating system HCl/LA/base (base = 1,4-dioxane or ethyl acetate) [106]. In this case, the chain-growth process was initiated at the Lewis acidic (LA) centers of Fe₃O₄ synthesized by magnetotactic bacteria or α -Fe₂O₃ prepared 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.

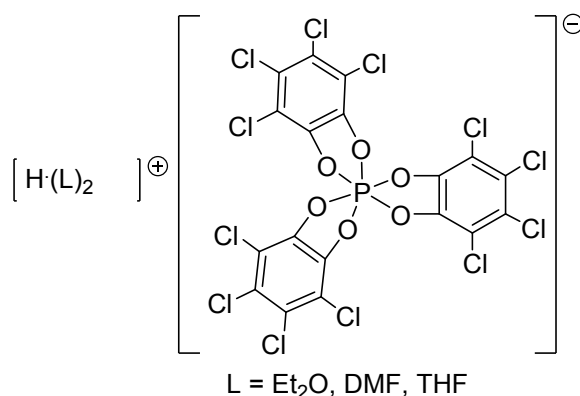
Initiating systems containing HCl and the *in situ* generated Salphen complexes of transition or main-group metals (Scheme 15) were successfully used for living polymerization of IBVE at $0\text{ }^\circ\text{C}$ in toluene [111,112]. Combinations of SnCl_4 , FeCl_3 or ZnCl_2 with Salphen resulted in 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.

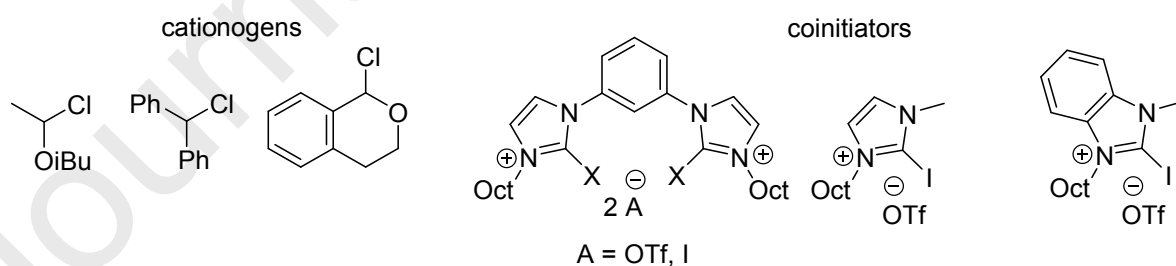
Diverse metal-free initiating systems have been reported recently. For example, apart from ubiquitous Brønsted acids ($\text{HCl}\cdot\text{Et}_2\text{O}$ [113,114] or HNTf_2 [115]), more sophisticated congeners can be utilized (Scheme 16) [116,117]. Polymerization of BVE in CH_2Cl_2 proceeded at low 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].

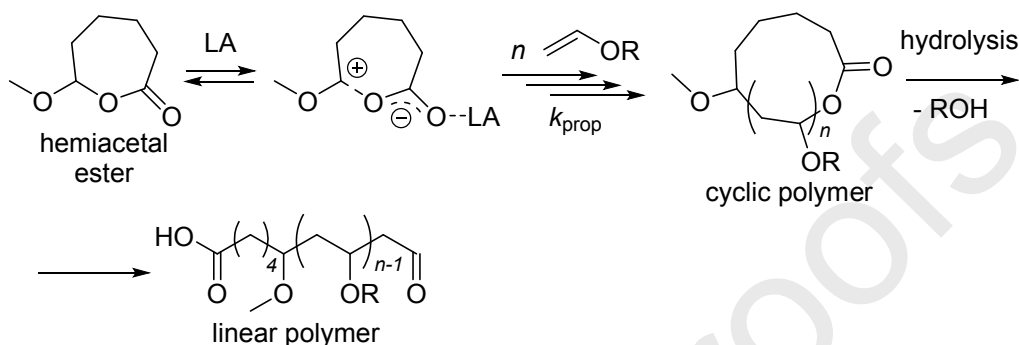
The halogen bonding-mediated cationic polymerization of IBVE involved initiating systems on the basis Cl-substituted cationogens and imidazolium salts (Scheme 17) [120]. Polymerization experiments, carried out at -40 – $-20\text{ }^{\circ}\text{C}$ in CH_2Cl_2 , afforded poly(IBVE)s with low molecular 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.

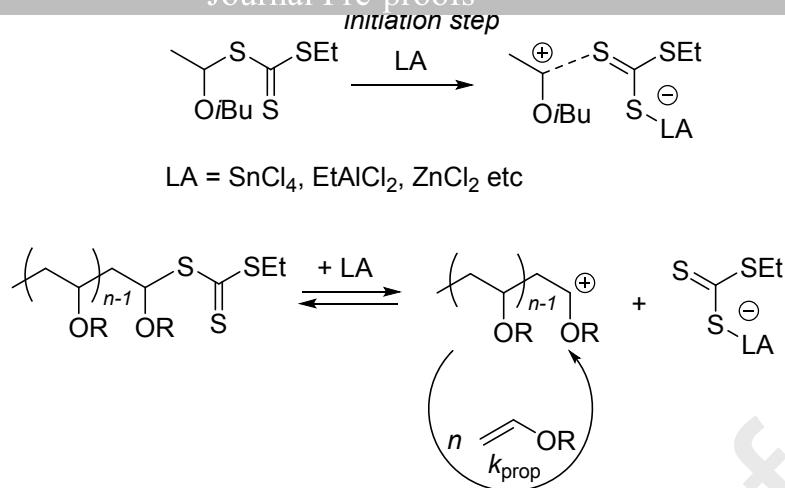


Scheme 18. Ring-expansion living cationic polymerization of vinyl ethers.

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.

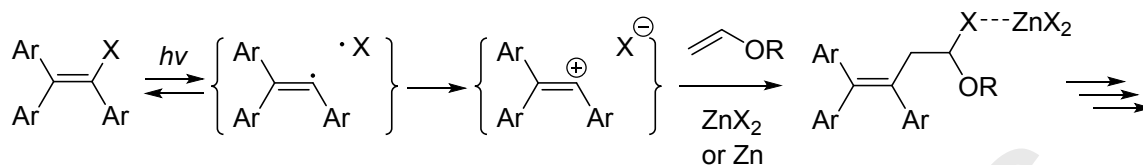
Since then, different metal-free initiating systems for cationic RAFT via degenerative chain-transfer have been developed. For example, binary systems combining triflic acid (TfOH) as cationogen and a RAFT agent, e.g. thiocarbonyl [131], thioether [132], phosphate or phosphinate [133], were used for 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 %).



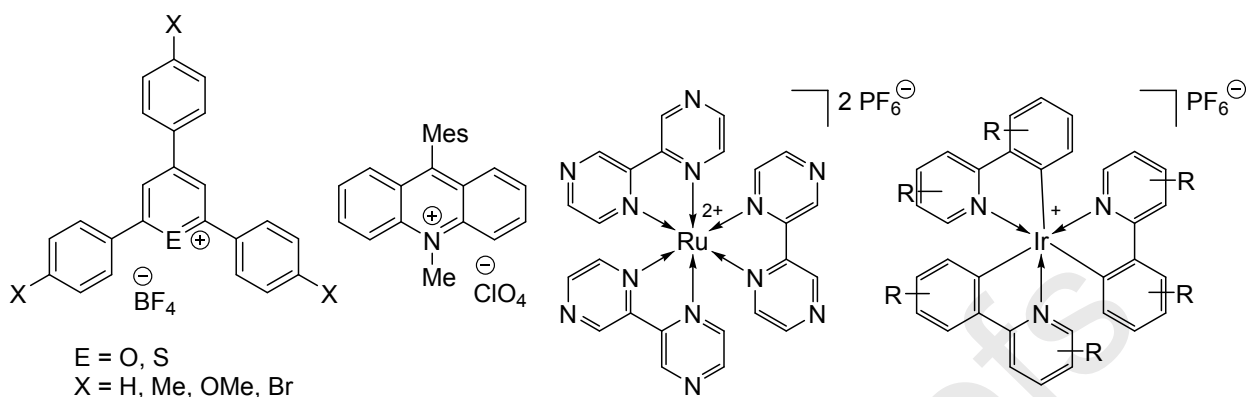
Scheme 20. The mechanism of vinyl halide-mediated photoinitiation-dependent cationic polymerization of vinyl and divinyl ethers.

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].

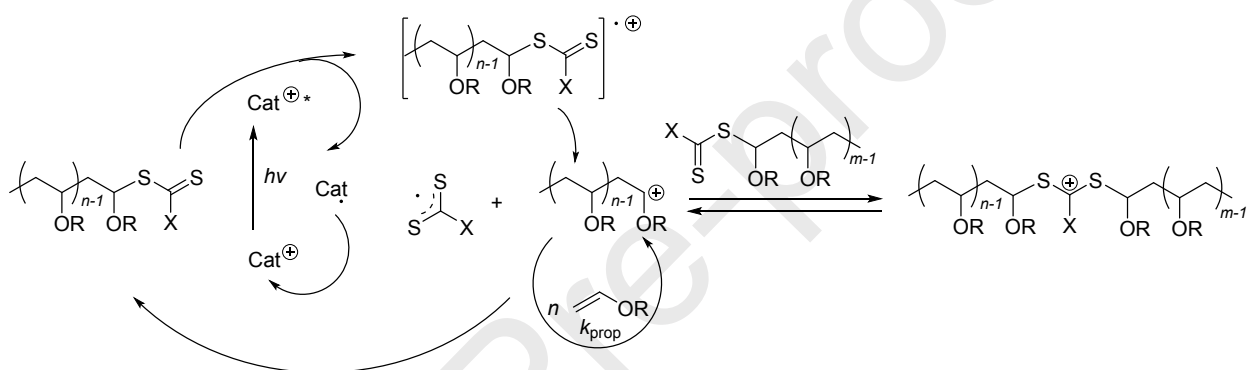
The intermediacy of radical species was specifically exploited in photogeneration of active systems for cationic polymerization. For example, a classical combination of benzyl bromide with Mn₂(CO)₁₀ affords benzyl radical. Under UV irradiation, upon activation with [Ph₂I]⁺[Br]⁻ or [Ph₂I]⁺[PF₆]⁻, it produced 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.

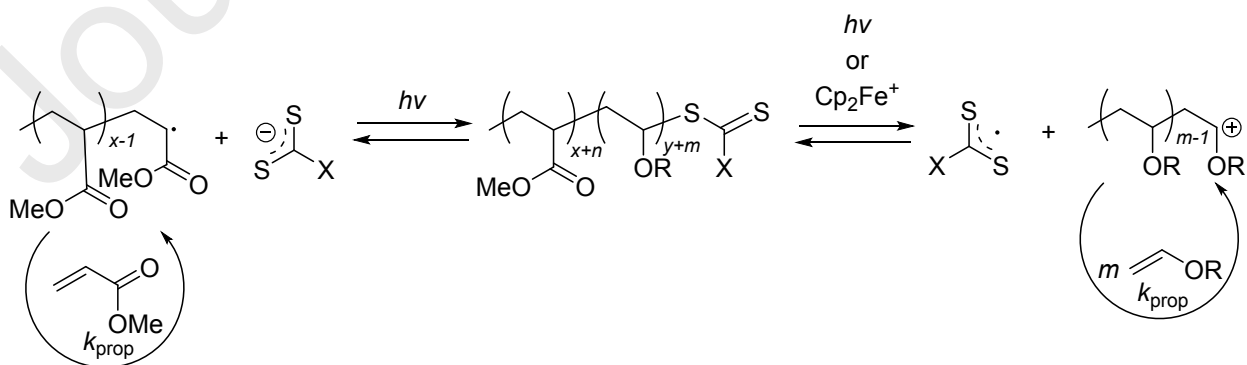


Scheme 21. Examples of photocatalysts that promote photocontrolled cationic polymerization.



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.

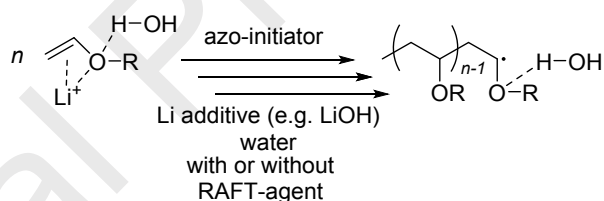


Scheme 23. Controlled interconversion of polymerization mechanisms.

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.

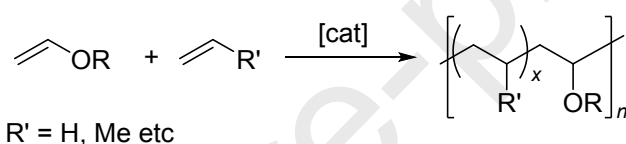
The same group developed an advanced protocol enabling controlled radical polymerization of MOVE and IBVE (Scheme 24) [167]. Polymerization reactions, conducted at 60–70 °C in the presence of water and LiOH for stabilization of the radical centers and activation of the double bonds in monomers, respectively, 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.

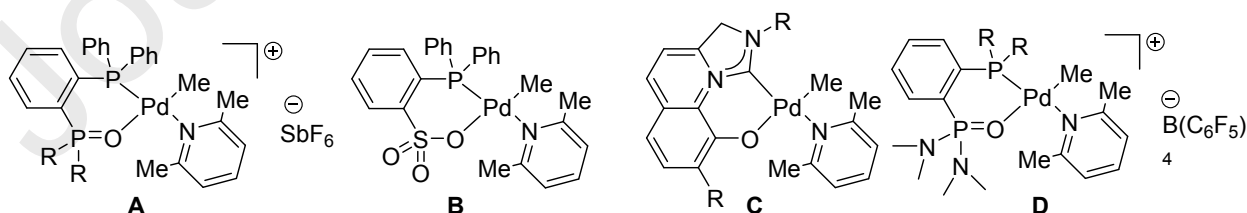
4.1. Ethylene and alkenes. The late transition metal-based coordination/insertion catalysts favor statistical copolymers

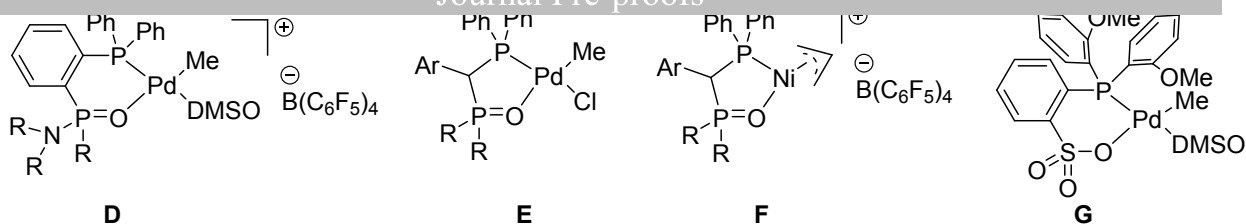
Homopolymerization of vinyl ethers by coordination/insertion mechanisms has been extensively studied [92,163,168-174]. Many contributions over the past decade dealt with the synthesis of functional polyolefins by catalytic copolymerization of alkenes (ethylene, propylene, etc.) with polar monomers (e.g.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



Scheme 25. Copolymerization of vinyl ethers with alkenes.

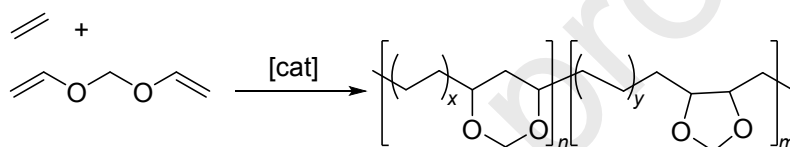
Nozaki *et al.* and Carrow *et al.* developed palladium catalysts (Scheme 26, **A–C** and **D**, respectively) for copolymerization of ethylene with BVE [170,175-178]. The copolymerization reactions proceeded under moderate conditions ($P_{\text{ethylene}} = 10\text{--}40$ bar, $T_{\text{pol}} = 80\text{--}100$ °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).



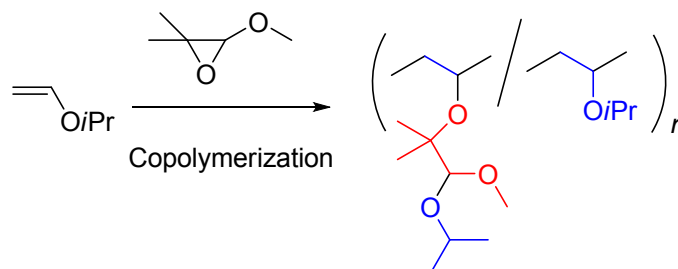
Scheme 27. Copolymerization of ethylene with divinyl formal.

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 HBr/ FeCl_3 / $n\text{Bu}_4\text{NBr}$ [182].

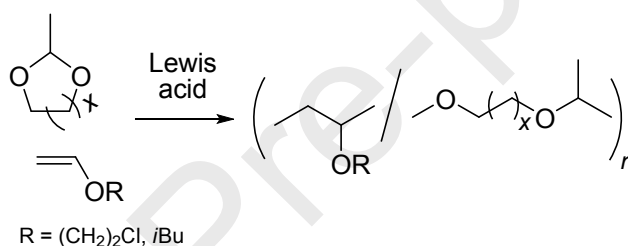
Copolymerization of IPVE with 1-methoxy-2-methylpropylene oxide (MOMPO) was accomplished using a specific initiating system composed of $\text{CF}_3\text{SO}_3\text{H}$ and $n\text{Bu}_4\text{Ni}$ [183] (Scheme 28). The ring-opening copolymerization resulted in IPVE-*co*-MOMPO product with unimodal molecular 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.



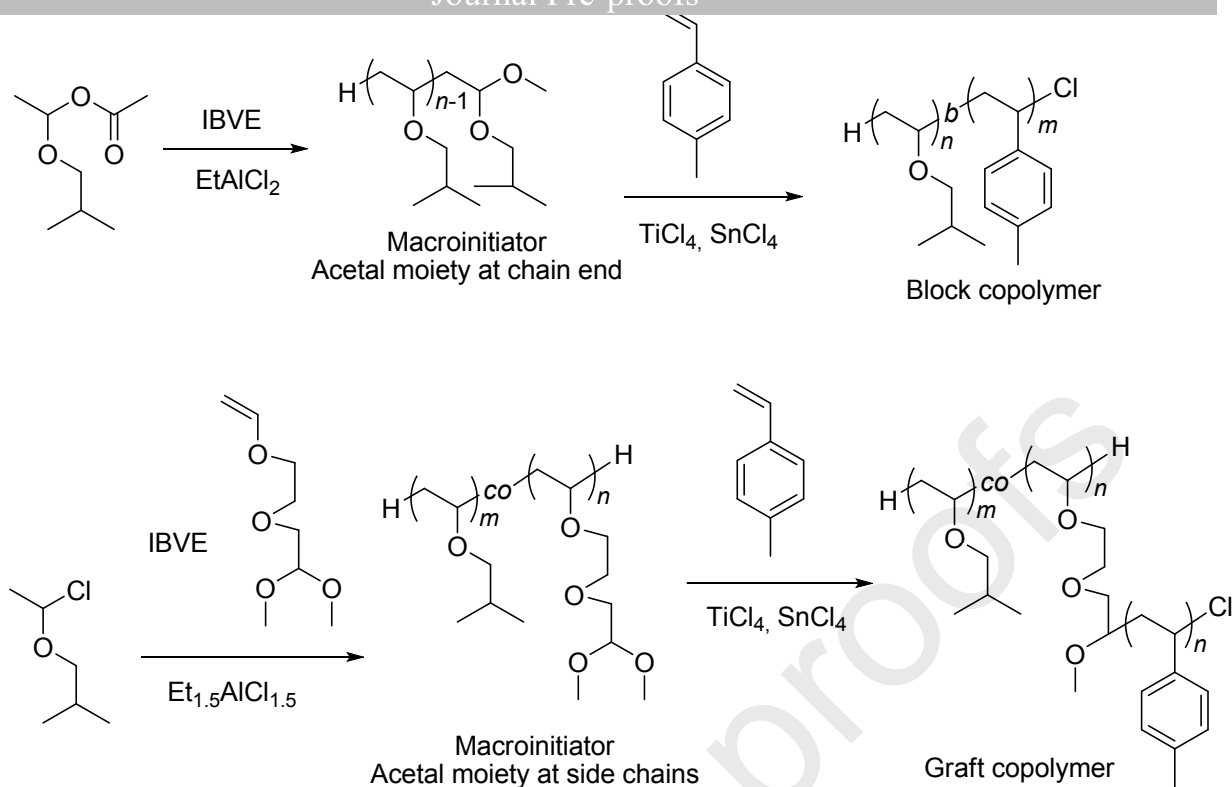
Scheme 28. Copolymerization of IPVE with MOMPO. Reaction conditions: $[\text{IPVE}] = 0.80 \text{ M}$, $[\text{MOMPO}]_0 = 0.20 \text{ M}$, $[\text{CF}_3\text{SO}_3\text{H}]_0 = 4.0 \text{ mM}$, $[\text{nBu}_4\text{NI}]_0 = 4.2 \text{ mM}$, in dichloromethane at $-40 \text{ }^\circ\text{C}$.

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.



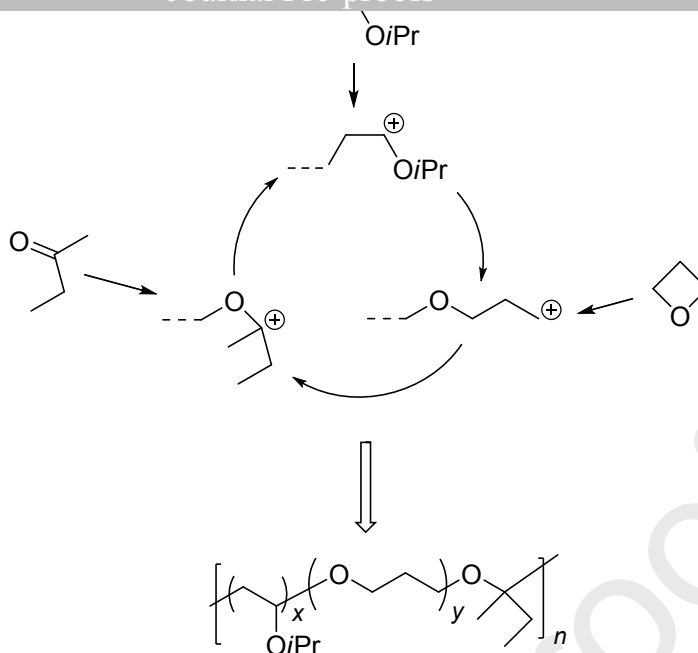
Scheme 29. Ring-opening copolymerization of vinyl ethers and cyclic acetals.

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.

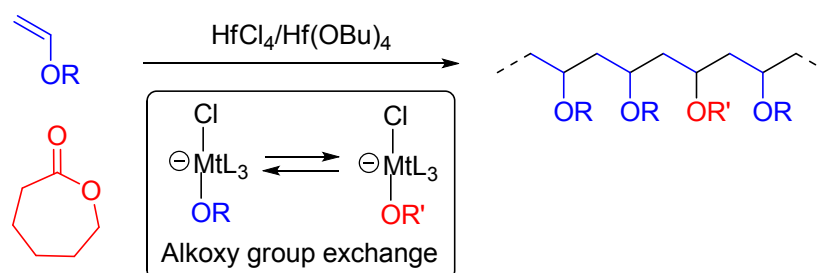
Concurrent cationic vinyl-addition, ring-opening, and carbonyl-addition mechanisms were described for terpolymerization of IPVE, oxetane, and methyl ethyl ketone (MEK) [186]. Given each of the monomers is capable of providing propagating chain ends, formation of statistical multiblock polymers was the 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].

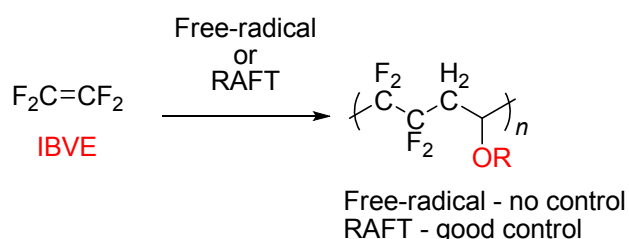
Yagci *et al* applied the photoinduced $\text{Ph}_3\text{CBr}/\text{Mn}_2(\text{CO})_{10}/[\text{Ph}_2]^+[\text{Br}]^-$ -mediated initiation to prepare a Ph_3C -capped poly(IBVE) macroinitiator by living cationic polymerization. Subsequent thermally promoted radical polymerization of acrylates or styrene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



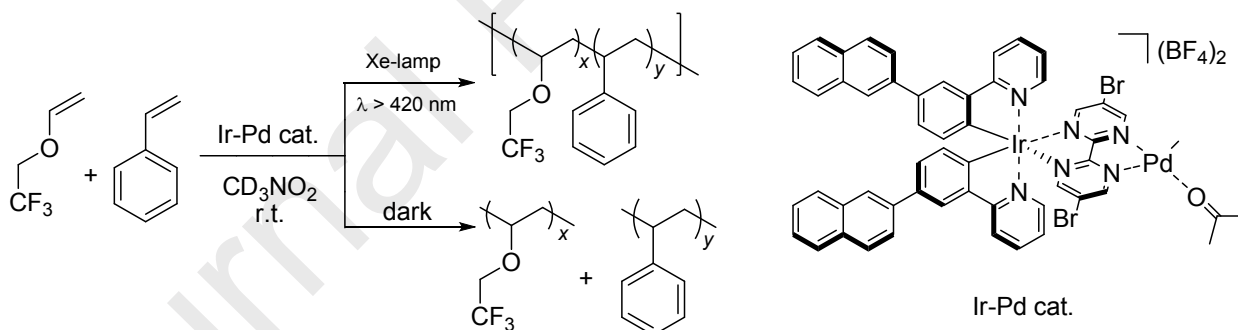
Scheme 33. Copolymerization of TFE with IBVE by conventional and RAFT/MADIX approaches.

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].

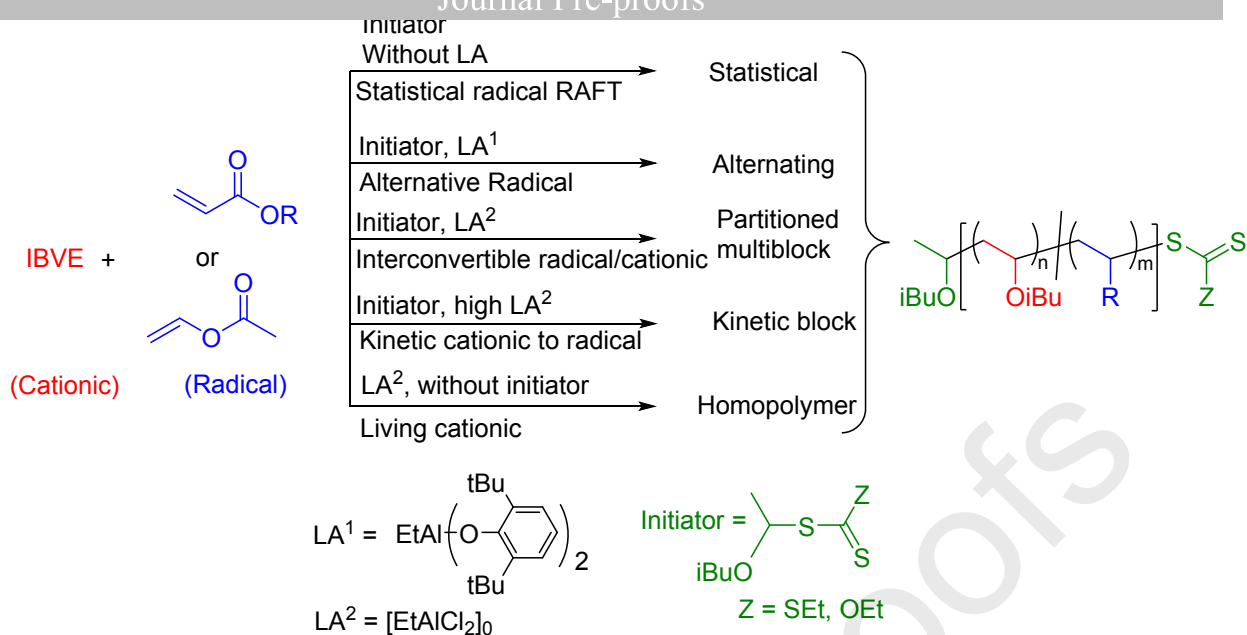
In a search for alternative biosourced polymers, several ribose-derived vinyloxy monomers were copolymerized with diethyl fumarate and diethyl maleate and alkoxy monomers [199]. Detailed kinetic investigations confirmed higher reactivity of the sugar-derived VEs as compared to that of alkyl VEs in the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



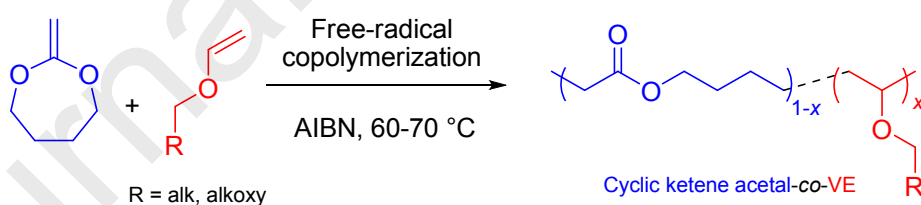
Scheme 34. Homopolymerization and copolymerization of styrene and TFEVE in the presence of Ir-Pd catalyst under different light conditions.

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.



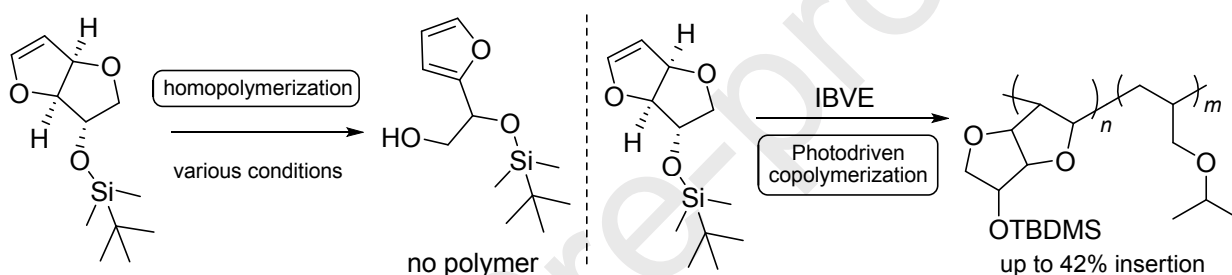
Scheme 36. Copolymerization of CKAs and VEs via free-radical mechanism.

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

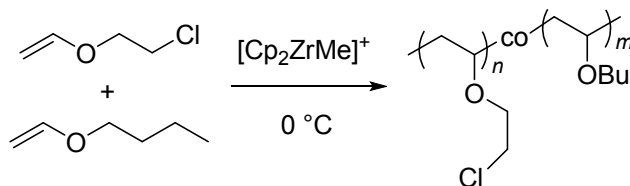
initiating cationic and radical polymerizations, respectively, and trinitrocarbonate as RAFT agent [204].

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].

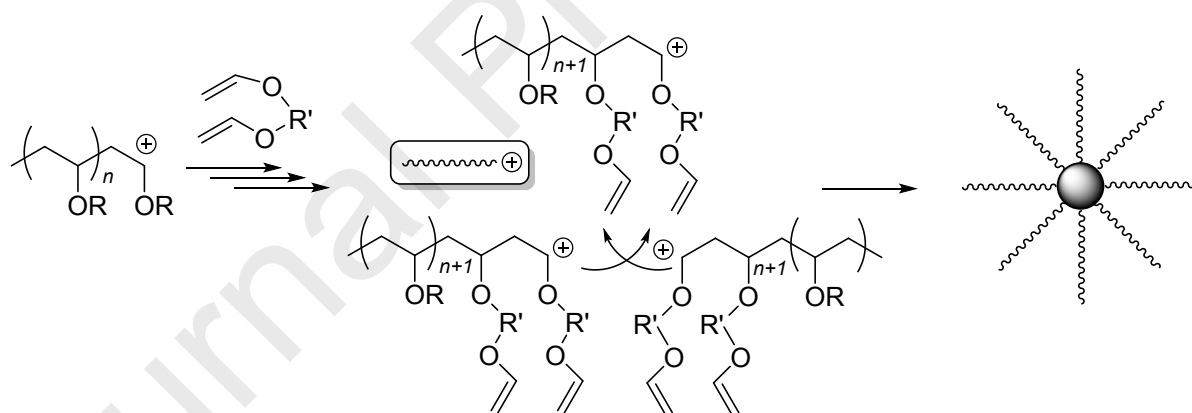


Scheme 38. Cationic copolymerization of BVE and CEVE.

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

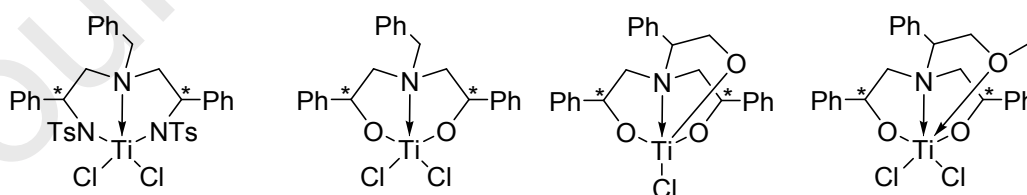
Poly(VE)s with azobenzene functionalities in the repeating unit, synthesized by living cationic polymerization, were blended with poly(ϵ -caprolactone) to provide a material with unique anisotropic photomechanical response properties [237]. Cationic polymerization of a TEMPO-capped vinyl ether monomer 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].

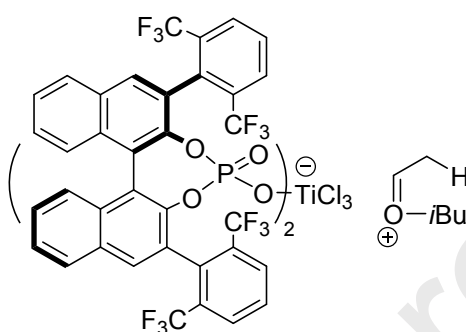
More recent contributions featured isoselective polymerization of IBVE and TBVE achieved with both metallocene and post-metallocene systems e.g. CpTiCl_3 , Cp_2MCl_2 ($\text{M} = \text{Ti, Zr, V}$) or phenoxy-imino precatalysts $[\text{ON}]_2\text{MCl}_2$ ($\text{M} = \text{Ti, Zr, Hf}$), combined with 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

- [1] J. Wislicenus, Ueber Vinyläthyläther, *Liebigs Ann. Chem.*, 192 (1878) 106-128. <https://doi.org/10.1002/jlac.18781920108>
- [2] S. Sugihara; N. Konegawa; Y. Maeda, HCl·Et₂O-Catalyzed Metal-Free RAFT Cationic Polymerization: One-Pot Transformation from Metal-Free Living Cationic Polymerization to RAFT Radical Polymerization, *Macromolecules*, 48 (2015) 5120-5131. <https://doi.org/10.1021/acs.macromol.5b01071>
- [3] X. Sui; S. Dai; C. Chen, Ethylene Polymerization and Copolymerization with Polar Monomers by Cationic Phosphine Phosphonic Amide Palladium Complexes, *ACS Catalysis*, 5 (2015) 5932-5937. <https://doi.org/10.1021/acscatal.5b01490>
- [4] M. Uchiyama; K. Satoh; M. Kamigaito, Cationic RAFT Polymerization Using ppm Concentrations of Organic Acid, *Angew. Chem. Int. Ed.*, 54 (2015) 1924-1928. <https://doi.org/10.1002/anie.201410858>
- [5] V. Kottisch; Q. Michaudel; B. P. Fors, Cationic Polymerization of Vinyl Ethers Controlled by Visible Light, *J. Am. Chem. Soc.*, 138 (2016) 15535-15538. <https://doi.org/10.1021/jacs.6b10150>
- [6] M. Ciftci; Y. Yoshikawa; Y. Yagci, Living Cationic Polymerization of Vinyl Ethers through a Photoinduced Radical Oxidation/Addition/Deactivation Sequence, *Angew. Chem. Int. Ed.*, 56 (2017) 519-523. <https://doi.org/10.1002/anie.201609357>
- [7] V. Kottisch; Q. Michaudel; B. P. Fors, Photocontrolled Interconversion of Cationic and Radical Polymerizations, *J. Am. Chem. Soc.*, 139 (2017) 10665-10668. <https://doi.org/10.1021/jacs.7b06661>
- [8] Q. Michaudel; T. Chauviré; V. Kottisch; M. J. Supej; K. J. Stawiasz; L. Shen; W. R. Zipfel; H. D. Abruña; J. H. Freed; B. P. Fors, Mechanistic Insight into the Photocontrolled Cationic Polymerization of Vinyl Ethers, *J. Am. Chem. Soc.*, 139 (2017) 15530-15538. <https://doi.org/10.1021/jacs.7b09539>
- [9] M. Chen; C. Chen, A Versatile Ligand Platform for Palladium- and Nickel-Catalyzed Ethylene Copolymerization with Polar Monomers, *Angew. Chem. Int. Ed.*, 57 (2018) 3094-3098. <https://doi.org/10.1002/anie.201711753>
- [10] B. M. Peterson; S. Lin; B. P. Fors, Electrochemically Controlled Cationic Polymerization of Vinyl Ethers, *J. Am. Chem. Soc.*, 140 (2018) 2076-2079. <https://doi.org/10.1021/jacs.8b00173>
- [11] M. Miyamoto; M. Sawamoto; T. Higashimura, Living polymerization of isobutyl vinyl ether with hydrogen iodide/iodine initiating system, *Macromolecules*, 17 (1984) 265-268. <https://doi.org/10.1021/ma00133a001>
- [12] S. Aoshima; T. Higashimura, Living cationic polymerization of vinyl monomers by organoaluminum halides. 3. Living polymerization of isobutyl vinyl ether by ethyldichloroaluminum in the presence of ester additives, *Macromolecules*, 22 (1989) 1009-1013. <https://doi.org/10.1021/ma00193a001>
- [13] M. Kamigaito; Y. Maeda; M. Sawamoto; T. Higashimura, Living cationic polymerization of isobutyl vinyl ether by hydrogen chloride/Lewis acid initiating systems in the presence of salts: in-situ direct NMR analysis of the growing species, *Macromolecules*, 26 (1993) 1643-1649. <https://doi.org/10.1021/ma00059a023>
- [14] K. Yamada; M. Miyazaki; K. Ohno; T. Fukuda; M. Minoda, Atom Transfer Radical Polymerization of Poly(vinyl ether) Macromonomers, *Macromolecules*, 32 (1999) 290-293. <https://doi.org/10.1021/ma981415w>
- [15] S. Sugihara; S. Kanaoka; S. Aoshima, Thermosensitive Random Copolymers of Hydrophilic and Hydrophobic Monomers Obtained by Living Cationic Copolymerization, *Macromolecules*, 37 (2004) 1711-1719. <https://doi.org/10.1021/ma034730d>
- [16] T. Shibata; S. Kanaoka; S. Aoshima, Quantitative Synthesis of Star-Shaped Poly(vinyl ether)s with a Narrow Molecular Weight Distribution by Living Cationic Polymerization, *J. Am. Chem. Soc.*, 128 (2006) 7497-7504. <https://doi.org/10.1021/ja057611h>
- [17] A. Kanazawa; S. Kanaoka; S. Aoshima, Major Progress in Catalysts for Living Cationic Polymerization of Isobutyl Vinyl Ether: Effectiveness of a Variety of Conventional Metal Halides, *Macromolecules*, 42 (2009) 3965-3972. <https://pubs.acs.org/doi/abs/10.1021/ma900116s>
- [18] W. G. S. Reyntjens; E. J. Goethals, New Materials from poly(vinyl ethers), *Polym. Adv. Technol.*, 12 (2001) 107-122. [https://doi.org/10.1002/1099-1581\(200101/02\)12:1/2<107::AID-PAT948>3.0.CO;2-R](https://doi.org/10.1002/1099-1581(200101/02)12:1/2<107::AID-PAT948>3.0.CO;2-R)
- [19] K. S. Rodygin; Y. A. Vikenteva; V. P. Ananikov, Calcium-Based Sustainable Chemical Technologies for Total Carbon Recycling, *ChemSusChem*, 12 (2019) 1483-1516. <https://doi.org/10.1002/cssc.201802412>
- [20] K. Rodygin; K. Lotsman; V. P. Ananikov, Calcium carbide looping system for acetaldehyde manufacturing from virtually any carbon source, *ChemSusChem*, (2020) <https://doi.org/10.1002/cssc.202000760>

- [21] G. Odian, Principles of Polymerization, John Wiley & Sons, Inc., Hoboken, New Jersey, 2004, pp. 812
- [22] T. Higashimura; O. Kishiro, Possible Formation of Living Polymers of p-Methoxystyrene by Iodine, *Polym. J.*, 9 (1977) 87-93. <https://doi.org/10.1295/polymj.9.87>
- [23] T. Higashimura; M. Mitsuhashi; M. Sawamoto, Synthesis of p-Methoxystyrene-Isobutyl Vinyl Ether Block Copolymers by Living Cationic Polymerization with Iodine, *Macromolecules*, 12 (1979) 178-182. <https://doi.org/10.1021/ma60068a003>
- [24] T. Ohtori; Y. Hirokawa; T. Higashimura, Studies on the Nature of Propagating Species in Cationic Polymerization of Isobutyl Vinyl Ether by Iodine, *Polym. J.*, 11 (1979) 471-476. <https://doi.org/10.1295/polymj.11.471>
- [25] M. Miyamoto; M. Sawamoto; T. Higashimura, Synthesis of monodisperse living poly(vinyl ethers) and block copolymers by the hydrogen iodide/iodine initiating system, *Macromolecules*, 17 (1984) 2228-2230. <https://doi.org/10.1021/ma00141a005>
- [26] C. G. Cho; B. A. Feit; O. W. Webster, Cationic polymerization of isobutyl vinyl ether: livingness enhancement by dialkyl sulfides, *Macromolecules*, 23 (1990) 1918-1923. <https://doi.org/10.1021/ma00209a006>
- [27] M. Sawamoto, Modern cationic vinyl polymerization, *Prog. Polym. Sci.*, 16 (1991) 111-172. [https://doi.org/10.1016/0079-6700\(91\)90008-9](https://doi.org/10.1016/0079-6700(91)90008-9)
- [28] S. Aoshima; S. Kanaoka, (Eds.). (2008) Synthesis of Stimuli-Responsive Polymers by Living Polymerization: Poly(N-Isopropylacrylamide) and Poly(Vinyl Ether)s, In *Wax Crystal Control · Nanocomposites · Stimuli-Responsive Polymers*, pp. 169-208, Springer Berlin Heidelberg, Berlin, Heidelberg.
- [29] D. Pasini; D. Takeuchi, Cyclopolymerizations: Synthetic Tools for the Precision Synthesis of Macromolecular Architectures, *Chem. Rev.*, 118 (2018) 8983-9057. <https://doi.org/10.1021/acs.chemrev.8b00286>
- [30] N. Corrigan; S. Shanmugam; J. Xu; C. Boyer, Photocatalysis in organic and polymer synthesis, *Chem. Soc. Rev.*, 45 (2016) 6165-6212. <http://dx.doi.org/10.1039/C6CS00185H>
- [31] M. Chen; M. Zhong; J. A. Johnson, Light-Controlled Radical Polymerization: Mechanisms, Methods, and Applications, *Chem. Rev.*, 116 (2016) 10167-10211. <https://doi.org/10.1021/acs.chemrev.5b00671>
- [32] T. G. McKenzie; Q. Fu; M. Uchiyama; K. Satoh; J. Xu; C. Boyer; M. Kamigaito; G. G. Qiao, Beyond Traditional RAFT: Alternative Activation of Thiocarbonylthio Compounds for Controlled Polymerization, *Advanced Science*, 3 (2016) 1500394. <https://doi.org/10.1002/advs.201500394>
- [33] A. Kanazawa; S. Kanaoka; S. Aoshima, Recent Progress in Living Cationic Polymerization of Vinyl Ethers, *Chem. Lett.*, 39 (2010) 1232-1237. <https://doi.org/10.1246/cl.2010.1232>
- [34] S. Aoshima; S. Kanaoka, A Renaissance in Living Cationic Polymerization, *Chem. Rev.*, 109 (2009) 5245-5287. <https://doi.org/10.1021/cr900225g>
- [35] M. Ouchi; T. Terashima; M. Sawamoto, Transition Metal-Catalyzed Living Radical Polymerization: Toward Perfection in Catalysis and Precision Polymer Synthesis, *Chem. Rev.*, 109 (2009) 4963-5050. <https://doi.org/10.1021/cr900234b>
- [36] M. Ouchi; H. Kammiyada; M. Sawamoto, Ring-expansion cationic polymerization of vinyl ethers, *Polymer Chemistry*, 8 (2017) 4970-4977. <http://dx.doi.org/10.1039/C7PY00638A>
- [37] A. Wohl; E. Berthold, Über die Darstellung der aromatischen Alkohole und ihrer Acetate, *Berichte der deutschen chemischen Gesellschaft*, 43 (1910) 2175-2185. <https://doi.org/10.1002/cber.191004302170>
- [38] J. v. Braun; G. Kirschbaum, Halogen-alkylierte aromatische Amine, V.: Darstellung von Aryl-vinyläthern, *Berichte der deutschen chemischen Gesellschaft (A and B Series)*, 53 (1920) 1399-1408. <https://doi.org/10.1002/cber.19200530815>
- [39] W. M. Lauer; M. A. Spielman, The Thermal Decomposition of Phenyl Vinyl Ether, *J. Am. Chem. Soc.*, 55 (1933) 1572-1574. <https://doi.org/10.1021/ja01331a042>
- [40] R. L. Adelman, The Reactions of Vinyl Acetate with Aliphatic Hydroxy Compounds. A New Synthesis of Vinyl Ethers, *J. Am. Chem. Soc.*, 75 (1953) 2678-2682. <https://doi.org/10.1021/ja01107a037>
- [41] A. E. Favorskii, The phenomena of isomerization in the series of hydrocarbons C_nH_{2n-2} (in Russian), *Journal of the Russian Chemical Society*, 20 (1888) 518-523.
- [42] T. W. Lyons; D. Bézier; M. Brookhart, Iridium Pincer-Catalyzed Dehydrogenation of Ethers Featuring Ethylene as the Hydrogen Acceptor, *Organometallics*, 34 (2015) 4058-4062. <https://doi.org/10.1021/acs.organomet.5b00501>
- [43] M. Benedetti; D. Antonucci; S. A. De Pascali; G. Ciccarella; F. P. Fanizzi, Alkyl-vinyl-ethers from alcoholic substrates and the Zeise's salt, via square planar [PtCl(N-N)(η¹-CH₂CH₂OR)] complexes, *J. Organomet. Chem.*, 714 (2012) 104-108. <https://doi.org/10.1016/j.jorganchem.2012.04.008>

- [44] L. Yu, N. Tang, S. Sheng, K. Chen, X. Liu, M. Cai, Solid-Phase Organic Synthesis of Aryl Vinyl Ethers Using Sulfone-Linking Strategy, *Chin. J. Chem.*, 30 (2012) 1027-1030. <https://doi.org/10.1002/cjoc.201100451>
- [45] J.-L. Zhang; S.-R. Sheng; X. Liu; S.-Y. Lin, Solid-phase synthesis of aryl vinyl ethers based on polystyrene-supported β -phenylselenoethanol, *J. Chem. Res.*, 2009 (2009) 287-289. <https://doi.org/10.3184/030823409X447682>
- [46] K. S. Graves; D. M. Thamattoor; P. R. Rablen, Experimental and Theoretical Study of the 2-Alkoxyethylidene Rearrangement, *J. Org. Chem.*, 76 (2011) 1584-1591. <https://doi.org/10.1021/jo1020536>
- [47] V. V. Voronin; M. S. Ledovskaya; A. S. Bogachenkov; K. S. Rodygin; V. P. Ananikov, Acetylene in Organic Synthesis: Recent Progress and New Uses, *Molecules*, 23 (2018) 2442. <https://doi.org/10.3390/molecules23102442>
- [48] C. Belger; N. M. Neisius; B. Plietker, A Selective Ru-Catalyzed Semireduction of Alkynes to Z Olefins under Transfer-Hydrogenation Conditions, *Chemistry – A European Journal*, 16 (2010) 12214-12220. <https://doi.org/10.1002/chem.201001143>
- [49] A. M. Whittaker; G. Lalic, Monophasic Catalytic System for the Selective Semireduction of Alkynes, *Org. Lett.*, 15 (2013) 1112-1115. <https://doi.org/10.1021/ol4001679>
- [50] P.-A. Deyris; T. Cañeque; Y. Wang; P. Retailleau; F. Bigi; R. Maggi; G. Maestri; M. Malacria, Catalytic Semireduction of Internal Alkynes with All-Metal Aromatic Complexes, *ChemCatChem*, 7 (2015) 3266-3269. <https://doi.org/10.1002/cctc.201500729>
- [51] E. Richmond; J. Moran, Ligand Control of E/Z Selectivity in Nickel-Catalyzed Transfer Hydrogenative Alkyne Semireduction, *J. Org. Chem.*, 80 (2015) 6922-6929. <https://doi.org/10.1021/acs.joc.5b01047>
- [52] S.-S. Li; L. Tao; F.-Z.-R. Wang; Y.-M. Liu; Y. Cao, Heterogeneous Gold-Catalyzed Selective Semireduction of Alkynes using Formic Acid as Hydrogen Source, *Adv. Synth. Catal.*, 358 (2016) 1410-1416. <https://doi.org/10.1002/adsc.201501183>
- [53] W. Reppe, Vinylierung, *Liebigs Ann. Chem.*, 601 (1956) 81-138. <https://doi.org/10.1002/jlac.19566010106>
- [54] F. Martínez-Montañés; M. A. Lone; F.-F. Hsu; R. Schneiter, Accumulation of long-chain bases in yeast promotes their conversion to a long-chain base vinyl ether, *J. Lipid Res.*, 57 (2016) 2040-2050. <https://doi.org/10.1194/jlr.M070748>
- [55] P. Pässler; W. Hefner; K. Buckl; H. Meinass; A. Meiswinkel; H.-J. Wernicke; G. Ebersberg; R. Müller; J. Bässler; H. Behringer; D. Mayer, Acetylene, in: *Ullmann's Encyclopedian of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA., Weinheim, 2011, pp. 277-326
- [56] K. S. Rodygin; G. Werner; F. A. Kucherov; V. P. Ananikov, Calcium Carbide: A Unique Reagent for Organic Synthesis and Nanotechnology, *Chem. Asian J.*, 11 (2016) 965-976. <https://doi.org/10.1002/asia.201501323>
- [57] W. Reppe, Polyvinylpyrrolidon, *Angew. Chem.*, 65 (1953) 577-578. <https://doi.org/10.1002/ange.19530652302>
- [58] H. F. Smyth; C. P. Carpenter; C. S. Well; U. C. Pozzani; J. A. Striegel, Range-Finding Toxicity Data: List VI, *Am. Ind. Hyg. Assoc. J.*, 23 (1962) 95-107. <https://doi.org/10.1080/00028896209343211>
- [59] M. S. Ledovskaya; V. V. Voronin; K. S. Rodygin, Methods for the synthesis of O-, S- and N-vinyl derivatives, *Russ. Chem. Rev.*, 87 (2018) 167-191.
- [60] D. J. Winternheimer; R. E. Shade; C. A. Merlic, Methods for Vinyl Ether Synthesis, *Synthesis*, 2010 (2010) 2497-2511. <https://doi.org/10.1055/s-0030-1258166>
- [61] A. Hamdi; A. S. Mostafa; C. N. Watat; M. Y. Laurent; K. Ben Ayed; K. B. Selim; G. Dujardin, Acetylene-free synthesis of vinyloxy pyridine and quinoline, *Tetrahedron Lett.*, 57 (2016) 5825-5829. <https://doi.org/10.1016/j.tetlet.2016.11.061>
- [62] A. Alaaeddine; G. Couture; B. Ameduri, An efficient method to synthesize vinyl ethers (VEs) that bear various halogenated or functional groups and their radical copolymerization with chlorotrifluoroethylene (CTFE) to yield functional poly(VE-alt-CTFE) alternated copolymers, *Polymer Chemistry*, 4 (2013) 4335-4347. <http://dx.doi.org/10.1039/C3PY00443K>
- [63] M. Finnveden; S. Brännström; M. Johansson; E. Malmström; M. Martinelle, Novel sustainable synthesis of vinyl ether ester building blocks, directly from carboxylic acids and the corresponding hydroxyl vinyl ether, and their photopolymerization, *RSC Advances*, 8 (2018) 24716-24723. <http://dx.doi.org/10.1039/C8RA04636K>
- [64] D. J. Kalita; I. Tarnavchyk; M. Sibi; B. R. Moser; D. C. Webster; B. J. Chisholm, Biobased poly(vinyl ether)s derived from soybean oil, linseed oil, and camelina oil: Synthesis, characterization, and properties of crosslinked networks and surface coatings, *Prog. Org. Coat.*, 125 (2018) 453-462. <https://doi.org/10.1016/j.porgcoat.2018.09.033>

- [65] F. Yuan; Z. Tingquan, Synthesis and photo-curing behaviors of silicon-containing (vinyl ether)-(allyl ether) hybrid monomers, *Polym. Int.*, 62 (2013) 1624-1633. <https://doi.org/10.1002/pi.4459>
- [66] B. A. Trofimov, Vinylation of cellulose in superbase catalytic systems: towards new biodegradable polymer materials, *Cellulose*, 20 (2013) 1201-1214. <https://doi.org/10.1007/s10570-013-9890-x>
- [67] D. Steinborn; H. Mosinski; T. Rosenstock, Hochaktive Katalysatorsysteme für die Vinylethersynthese aus Acetylen und Alkoholen—Kaliumalkoholat/Kronenether in Kohlenwasserstoffen, *J. Organomet. Chem.*, 414 (1991) C45-C50. [https://doi.org/10.1016/0022-328X\(91\)86108-3](https://doi.org/10.1016/0022-328X(91)86108-3)
- [68] M. S. Ledovskaya; V. V. Voronin; K. S. Rodygin; V. P. Ananikov, Efficient labeling of organic molecules using ¹³C elemental carbon: universal access to ¹³C₂-labeled synthetic building blocks, polymers and pharmaceuticals, *Org. Chem. Front.*, 7 (2020) 638-647. <http://dx.doi.org/10.1039/C9QO01357A>
- [69] S. P. Teong; A. Y. H. Chua; S. Deng; X. Li; Y. Zhang, Direct vinylation of natural alcohols and derivatives with calcium carbide, *Green Chem.*, 19 (2017) 1659-1662. <http://dx.doi.org/10.1039/C6GC03579E>
- [70] K. S. Rodygin; Y. V. Gyrdymova; V. V. Zarubaev, Synthesis of vinyl thioethers and bis-thioethenes from calcium carbide and disulfides, *Mendeleev Commun.*, 27 (2017) 476-478. <http://www.sciencedirect.com/science/article/pii/S0959943617302018>
- [71] M. Turberg; K. J. Ardila-Fierro; C. Bolm; J. G. Hernández, Altering Copper-Catalyzed A3 Couplings by Mechanochemistry: One-Pot Synthesis of 1,4-Diamino-2-butyne from Aldehydes, Amines, and Calcium Carbide, *Angew. Chem. Int. Ed.*, 57 (2018) 10718-10722. <https://doi.org/10.1002/anie.201805505>
- [72] A. Hosseini; P. R. Schreiner, Synthesis of Exclusively 4-Substituted β -Lactams through the Kinugasa Reaction Utilizing Calcium Carbide, *Org. Lett.*, (2019) <https://doi.org/10.1021/acs.orglett.9b01192>
- [73] L. Gao; Z. Li, Synthesis of Aromatic Terminal Allenes and Aliphatic Terminal Alkynes from Hydrazones Using Calcium Carbide as an Acetylene Source, *Org. Chem. Front.*, 7 (2020) 702-708. <http://dx.doi.org/10.1039/C9QO01400D>
- [74] R. Mataka; Y. Adachi; H. Matsubara, Synthesis of vinyl ethers of alcohols using calcium carbide under superbasic catalytic conditions (KOH/DMSO), *Green Chem.*, 18 (2016) 2614-2618. <http://dx.doi.org/10.1039/C5GC02977E>
- [75] S. P. Teong; J. Lim; Y. Zhang, Vinylation of Aryl Ether (Lignin β -O-4 Linkage) and Epoxides with Calcium Carbide through C–O Bond Cleavage, *ChemSusChem*, 10 (2017) 3198-3201. <https://doi.org/10.1002/cssc.201701153>
- [76] G. Werner; K. S. Rodygin; A. A. Kostin; E. G. Gordeev; A. S. Kashin; V. P. Ananikov, A solid acetylene reagent with enhanced reactivity: fluoride-mediated functionalization of alcohols and phenols, *Green Chem.*, 19 (2017) 3032-3041. <http://dx.doi.org/10.1039/C7GC00724H>
- [77] K. S. Rodygin; I. Werner; V. P. Ananikov, A Green and Sustainable Route to Carbohydrate Vinyl Ethers for Accessing Bioinspired Materials with a Unique Microspherical Morphology, *ChemSusChem*, 11 (2018) 292-298. <https://doi.org/10.1002/cssc.201701489>
- [78] M. S. Ledovskaya; V. V. Voronin; K. S. Rodygin; A. V. Posvyatenko; K. S. Egorova; V. P. Ananikov, Direct Synthesis of Deuterium-Labeled O-, S-, N-Vinyl Derivatives from Calcium Carbide, *Synthesis*, 51 (2019) 3001-3013.
- [79] A. Hosseini; D. Seidel; A. Miska; P. R. Schreiner, Fluoride-Assisted Activation of Calcium Carbide: A Simple Method for the Ethynylation of Aldehydes and Ketones, *Org. Lett.*, 17 (2015) 2808-2811. <https://doi.org/10.1021/acs.orglett.5b01219>
- [80] E. Rattanangkool; T. Vilaivan; M. Sukwattanasinitt; S. Wacharasindhu, An Atom-Economic Approach for Vinylation of Indoles and Phenols Using Calcium Carbide as Acetylene Surrogate, *Eur. J. Org. Chem.*, 2016 (2016) 4347-4353. <https://doi.org/10.1002/ejoc.201600666>
- [81] Y. Yu; W. Huang; Y. Chen; B. Gao; W. Wu; H. Jiang, Calcium carbide as the acetylide source: transition-metal-free synthesis of substituted pyrazoles via [1,5]-sigmatropic rearrangements, *Green Chem.*, 18 (2016) 6445-6449.
- [82] V. Voronin; M. Ledovskaya; K. Rodygin; V. Ananikov, Examining the vinyl moiety as a protecting group for hydroxyl (-OH) functionality under basic conditions, *Org. Chem. Front.*, (2020) <http://dx.doi.org/10.1039/D0QO00202J>
- [83] T. Kunitake; Y. Matsuguma; C. Aso, The Effect of Counteranions in the Polymerization of Isobutyl Vinyl Ether Initiated by Triphenylmethyl Cation, *Polym. J.*, 2 (1971) 345-352. <https://doi.org/10.1295/polymj.2.345>
- [84] K. Nakatani; M. Ouchi; M. Sawamoto, Antithetic function of alcohol in living cationic polymerization: From terminator/inhibitor to useful initiator, *J. Polym. Sci., Part A: Polym. Chem.*, 47 (2009) 4194-4201. <http://dx.doi.org/10.1002/pola.23488>

- [85] A. Kanazawa; S. Kanaoka; S. Aoshima, Living Cationic Polymerization of vinyl Ether with Methanol/metal Chloride Initiating Systems: Relationship between Polymerization Behavior and the Nature of Lewis Acids, *Macromolecules*, 43 (2010) 2739-2747. <https://doi.org/10.1021/ma902616j>
- [86] A. Kanazawa; S. Kanaoka; S. Aoshima, Cationic polymerization of isobutyl vinyl ether using alcohols both as cationogen and catalyst-modifying reagent: Effect of Lewis acids and alcohols on living nature, *J. Polym. Sci., Part A: Polym. Chem.*, 48 (2010) 2509-2516. <https://doi.org/10.1002/pola.24009>
- [87] A. Kanazawa; S. Kanaoka; S. Aoshima, Chain Multiplying Controlled Cationic Polymerization of Isobutyl Vinyl Ether Using Pyrrole: Increment of Propagating Chains by Efficient "Initiator-Like" Transfer Agent, *Macromolecules*, 43 (2010) 3682-3689. <https://doi.org/10.1021/ma100182b>
- [88] J. G. Leasure; C. E. Brinkman; E. S. Tillman; I. W. Monk; N. A. Cohen, Effect of temperature, solvent, Lewis acid and additives on the polymerization of *tert*-butyl vinyl ether using Lewis acid-induced *N*-methylethylenamines as cationic initiators, *Polym. Int.*, (2009) 642-647. <https://doi.org/10.1002/pi.2742>
- [89] A. V. Radchenko; S. V. Kostjuk; F. Ganachaud, Cationic polymerization of isobutyl vinyl ether in aqueous media: physical chemistry tricks to fight against thermal runaway, *Polymer Chemistry*, 4 (2013) 1883-1892. <https://doi.org/10.1039/C2PY20945D>
- [90] A. S. K. Hashmi; S. Schäfer; V. Göker; C. D. Eisenbach; K. Dirnberger; Z. Zhao-Karger; P. Crewdson, Gold Catalysis: AuCl-induced Polymerization of Styrene and *n*-Butylvinylether, *Aust. J. Chem.*, 67 (2014) 500-506. <http://dx.doi.org/10.1071/CH13562>
- [91] L. Lin; G. Zhang; K. Kodama; M. Yasutake; T. Hirose, A benign initiating system for cationic polymerization of isobutyl vinyl ether: Silver salt/aryl(alkyl) halide/lewis base, *J. Polym. Sci., Part A: Polym. Chem.*, 53 (2015) 2050-2058. <https://doi.org/10.1002/pola.27656>
- [92] L. Lin; G. Zhang; K. Kodama; H. Shitara; T. Hirose, Cationic polymerization of vinyl ethers and *p*-methoxystyrene by a benign initiating system: Silver salt/arylmethyl halide/dialkyl sulfide, *J. Polym. Sci., Part A: Polym. Chem.*, 54 (2016) 861-870. <https://doi.org/10.1002/pola.27925>
- [93] E. Batagianni; A. Marathianos; A. Koraki; A.-P. Maroudas; M. Pitsikalis, Metallocene-mediated cationic polymerization of vinyl ethers: Kinetics of polymerization and synthesis and characterization of statistical copolymers, *Journal of Macromolecular Science, Part A*, 53 (2016) 140-151. <https://doi.org/10.1080/10601325.2016.1132908>
- [94] A. Kanazawa; R. Hashizume; S. Kanaoka; S. Aoshima, Design of Benign Initiator for Living Cationic Polymerization of Vinyl Ethers: Facile in Situ Generation of Vinyl Ether-Hydrogen Halide Adducts and Subsequent Controlled Polymerization without a Lewis Acid Catalyst, *Macromolecules*, 47 (2014) 1578-1585. <https://doi.org/10.1021/ma402490f>
- [95] A. V. Radchenko; H. Boucekif; F. Peruch, Triflate esters as in-situ generated initiating system for carbocationic polymerization of vinyl ethers, isoprene, myrcene and ocimene, *Eur. Polym. J.*, 89 (2017) 34-41. <https://doi.org/10.1016/j.eurpolymj.2017.02.001>
- [96] L. Zhang; K. Jiang; X. Shen; Y. Gu; X. Lin; M. Chen, Thieryl Chloride Initiated Living Cationic Polymerization: A General and Efficient Access toward Terminally Functionalized Poly(vinyl ether)s, *Macromolecules*, (2020) <https://doi.org/10.1021/acs.macromol.9b02425>
- [97] H. Yoshimitsu; A. Kanazawa; S. Kanaoka; S. Aoshima, Well-Defined Polymeric Ionic Liquids with an Upper Critical Solution Temperature in Water, *Macromolecules*, 45 (2012) 9427-9434. <https://doi.org/10.1021/ma301746u>
- [98] H. Shimomoto; D. Fukami; S. Kanaoka; S. Aoshima, Fluorine-containing vinyl ether polymers: Living cationic polymerization in fluorinated solvents as new media and unique solubility characteristics in organic solvents, *J. Polym. Sci., Part A: Polym. Chem.*, 49 (2011) 1174-1182. <https://doi.org/10.1002/pola.24534>
- [99] H. Shimomoto; D. Fukami; T. Irita; K.-i. Katsukawa; T. Nagai; S. Kanaoka; S. Aoshima, Synthesis of fluorine-containing star-shaped poly(vinyl ether)s via arm-linking reactions in living cationic polymerization, *J. Polym. Sci., Part A: Polym. Chem.*, 50 (2012) 1547-1555. <https://doi.org/10.1002/pola.25922>
- [100] H. Yoshimitsu; A. Kanazawa; S. Kanaoka; S. Aoshima, Cationic polymerization of vinyl ethers with alkyl or ionic side groups in ionic liquids, *J. Polym. Sci., Part A: Polym. Chem.*, 54 (2016) 1774-1784. <https://doi.org/10.1002/pola.28039>
- [101] Y.-b. Wu; L. Han; X.-q. Zhang; J. Mao; L.-f. Gong; W.-l. Guo; K. Gu; S.-x. Li, Cationic polymerization of isobutyl vinyl ether in an imidazole-based ionic liquid: characteristics and mechanism, *Polymer Chemistry*, 6 (2015) 2560-2568. <https://doi.org/10.1039/C4PY01784F>
- [102] H. Shimomoto; S. Kanaoka; S. Aoshima, Precise synthesis of end-functionalized thermosensitive poly(vinyl ether)s by living cationic polymerization, *J. Polym. Sci., Part A: Polym. Chem.*, 50 (2012) 4137-4144. <https://doi.org/10.1002/pola.26219>

- [103] J. Motoyanagi; K. Miyabara; M. Suzuki; S. Miki; M. Minoda, A novel [60]fullerene-appended initiator for living cationic polymerization and its application to the synthesis of [60]fullerene-end-capped poly(vinyl ether)s, *Polym. Chem.*, 3 (2012) 329-331. <https://doi.org/10.1039/c2py00522k>
- [104] J. Motoyanagi; A. Kurata; M. Minoda, Self-assembly behavior of amphiphilic C₆₀-end-capped poly(vinyl ether)s in water and dissociation of the aggregates by the complexing of the C₆₀ moieties with externally added γ -cyclodextrins, *Langmuir*, 31 (2015) 2256-2261. <https://doi.org/10.1021/la504341s>
- [105] T. Ishikawa; J. Motoyanagi; M. Minoda, Synthesis of Brush-shaped π -Conjugated Polymers Based on Well-defined Thiophene-end-capped Poly(vinyl ether)s, *Chem. Lett.*, 45 (2016) 415-417. <https://doi.org/10.1246/cl.160022>
- [106] A. Kanazawa; S. Kanaoka; N. Yagita; Y. Oaki; H. Imai; M. Oda; A. Arakaki; T. Matsunaga; S. Aoshima, Biologically synthesized or bioinspired process-derived iron oxides as catalysts for living cationic polymerization of a vinyl ether, *Chem Commun (Camb)*, 48 (2012) 10904-10906. <https://doi.org/10.1039/c2cc36218j>
- [107] Q. Huang; Y. Wu; J. Dan, Cationic polymerization of isobutyl vinyl ether cointiated with heteropolyacid or its salts in aqueous medium, *J. Polym. Sci., Part A: Polym. Chem.*, 51 (2013) 546-556. <https://doi.org/10.1002/pola.26431>
- [108] T. Hashimoto; H. Takagi; Y. Hasegawa; H. Matsui; M. Urushisaki; T. Sakaguchi, Living/controlled cationic cyclopolymerization of divinyl ether with a cyclic acetal moiety: Synthesis of poly(vinyl ether)s with high glass transition temperature based on incorporation of cyclized main chain and cyclic side chains, *J. Polym. Sci., Part A: Polym. Chem.*, 48 (2010) 952-958. <https://doi.org/10.1002/pola.23851>
- [109] K. Morita; T. Hashimoto; M. Urushisaki; T. Sakaguchi, Cationic cyclopolymerization of divinyl ethers with norbornane-, norbornene-, or adamantane-containing substituents: Synthesis of cyclopoly(divinyl ether)s with bulky rigid side chains leading to high glass transition temperature, *J. Polym. Sci., Part A: Polym. Chem.*, 51 (2013) 2445-2454. <https://doi.org/10.1002/pola.26630>
- [110] T. Hashimoto; H. Matsui; M. Urushisaki; T. Sakaguchi, Star-shaped cyclopolymers: A new category of star polymer with rigid cyclized arms prepared by controlled cationic cyclopolymerization and subsequent microgel formation of divinyl ethers, *J. Polym. Sci., Part A: Polym. Chem.*, 53 (2015) 1094-1102. <https://doi.org/10.1002/pola.27540>
- [111] S. Kigoshi; A. Kanazawa; S. Kanaoka; S. Aoshima, In situ and readily prepared metal catalysts and initiators for living cationic polymerization of isobutyl vinyl ether: dual-purpose salphen as a ligand framework for ZrCl₄ and an initiating proton source, *Polymer Chemistry*, 6 (2015) 30-34. <https://doi.org/10.1039/C4PY01012D>
- [112] S. Kigoshi; A. Kanazawa; S. Kanaoka; S. Aoshima, Tetradentate schiff base ligand/MCl_n initiating systems for the controlled cationic polymerization of isobutyl vinyl ether: Effects of the ligand framework, *J. Polym. Sci., Part A: Polym. Chem.*, 57 (2019) 989-996. <https://doi.org/10.1002/pola.29354>
- [113] I. M. Zaleska; M. Kitagawa; S. Sugihara; I. Ikeda, Synthesis of biocompatible and biodegradable block copolymers of polyvinyl alcohol-block-poly(ϵ -caprolactone) using metal-free living cationic polymerization, *J. Polym. Sci., Part A: Polym. Chem.*, 47 (2009) 5169-5179. <https://doi.org/10.1002/pola.23569>
- [114] S. Sugihara; M. Kitagawa; Y. Inagawa; I. M. Zaleska; I. Ikeda, Effects of monomer and ether structure on metal-free living cationic polymerization of various vinyl ethers using hydrogen chloride with ether, *Polym. Bull.*, 64 (2009) 209-220. <https://doi.org/10.1007/s00289-009-0137-9>
- [115] J. Song; J. Xu; D. Tang, Rapid living cationic polymerization of vinyl ethers by a single-molecular initiating system, *J. Polym. Sci., Part A: Polym. Chem.*, 54 (2016) 1373-1377. <https://doi.org/10.1002/pola.27986>
- [116] P. W. Siu; K. Hazin; D. P. Gates, H(OEt₂)₂[P(1,2-O₂C₆Cl₄)₃]: synthesis, characterization, and application as a single-component initiator for the carbocationic polymerization of olefins, *Chemistry*, 19 (2013) 9005-9014. <https://doi.org/10.1002/chem.201204288>
- [117] K. Hazin; S. C. Serin; B. O. Patrick; M. B. Ezhova; D. P. Gates, [HL₂][P(1,2-O₂C₆Cl₄)₃] (L = THF, DMF): Bronsted acid initiators for the polymerization of n-butyl vinyl ether and p-methoxystyrene, *Dalton Trans*, 46 (2017) 5901-5910. <https://doi.org/10.1039/c6dt04820j>
- [118] D. R. Dreyer; C. W. Bielawski, Graphite Oxide as an Olefin Polymerization Carbocatalyst: Applications in Electrochemical Double Layer Capacitors, *Adv. Funct. Mater.*, 22 (2012) 3247-3253. <https://doi.org/10.1002/adfm.201103152>
- [119] K. Nagata; T. Kawahara; K. Hashimoto; K. Fujiki; S. Tamesue; T. Yamauchi; N. Tsubokawa, Grafting of polymers onto graphene oxide by cationic and anionic polymerization initiated by the surface-initiating groups, *Compos. Interfaces*, 22 (2014) 25-37. <https://doi.org/10.1080/15685543.2015.982482>

- [120] K. Takagi; K. Yamachi; H. Murakata, Halogen-Bonding-Mediated and Controlled Cationic Polymerization of Isobutyl Vinyl Ether: Expanding the Catalytic Scope of 2-Iodoimidazolium Salts, *Chemistry*, 23 (2017) 9495-9500. <https://doi.org/10.1002/chem.201702455>
- [121] H. Kammiyada; A. Konishi; M. Ouchi; M. Sawamoto, Ring-Expansion Living Cationic Polymerization via Reversible Activation of a Hemiacetal Ester Bond, *ACS Macro Letters*, 2 (2013) 531-534. <https://doi.org/10.1021/mz400191t>
- [122] H. Kammiyada; M. Ouchi; M. Sawamoto, A Study on Physical Properties of Cyclic Poly(vinyl ether)s Synthesized via Ring-Expansion Cationic Polymerization, *Macromolecules*, 50 (2017) 841-848. <https://doi.org/10.1021/acs.macromol.6b02704>
- [123] H. Kammiyada; M. Ouchi; M. Sawamoto, A convergent approach to ring polymers with narrow molecular weight distributions through post dilution in ring expansion cationic polymerization, *Polymer Chemistry*, 7 (2016) 6911-6917. <https://doi.org/10.1039/c6py01683a>
- [124] H. Kammiyada; M. Ouchi; M. Sawamoto, Expanding vinyl ether monomer repertoire for ring-expansion cationic polymerization: Various cyclic polymers with tailored pendant groups, *J. Polym. Sci., Part A: Polym. Chem.*, 55 (2017) 3082-3089. <https://doi.org/10.1002/pola.28648>
- [125] A. Nagaki; M. Takumi; Y. Tani; J.-i. Yoshida, Polymerization of vinyl ethers initiated by dendritic cations using flow microreactors, *Tetrahedron*, 71 (2015) 5973-5978. <http://dx.doi.org/10.1016/j.tet.2015.05.096>
- [126] Y. Tani; M. Takumi; S. Moronaga; A. Nagaki; J.-i. Yoshida, Flash cationic polymerization followed by bis-end-functionalization. A new approach to linear-dendritic hybrid polymers, *Eur. Polym. J.*, 80 (2016) 227-233. <https://doi.org/10.1016/j.eurpolymj.2016.02.021>
- [127] D. Xie; Y. Lu, Achieving Low-Cost and Accelerated Living Cationic Polymerization of Isobutyl Vinyl Ether in Microflow System, *Ind. Eng. Chem. Res.*, 57 (2018) 7441-7449. <https://doi.org/10.1021/acs.iecr.8b01256>
- [128] D. Xie; Y. Lu, Fast living cationic polymerization of isobutyl vinyl ether tailored by single nucleophile in microflow system, *Eur. Polym. J.*, 113 (2019) 220-228. <https://doi.org/10.1016/j.eurpolymj.2019.01.046>
- [129] S. Kumagai; K. Nagai; K. Satoh; M. Kamigaito, In-Situ Direct Mechanistic Transformation from RAFT to Living Cationic Polymerization for (Meth)acrylate-Vinyl Ether Block Copolymers, *Macromolecules*, 43 (2010) 7523-7531. <https://doi.org/10.1021/ma101420u>
- [130] M. Uchiyama; K. Satoh; M. Kamigaito, Diversifying Cationic RAFT Polymerization with Various Counteranions: Generation of Cationic Species from Organic Halides and Various Metal Salts, *ACS Macro Letters*, 5 (2016) 1157-1161. <https://doi.org/10.1021/acsmacrolett.6b00541>
- [131] M. Uchiyama; K. Satoh; M. Kamigaito, Cationic RAFT polymerization using ppm concentrations of organic acid, *Angew. Chem. Int. Ed. Engl.*, 54 (2015) 1924-1928. <https://doi.org/10.1002/anie.201410858>
- [132] M. Uchiyama; K. Satoh; M. Kamigaito, Thioether-Mediated Degenerative Chain-Transfer Cationic Polymerization: A Simple Metal-Free System for Living Cationic Polymerization, *Macromolecules*, 48 (2015) 5533-5542. <https://doi.org/10.1021/acs.macromol.5b01341>
- [133] M. Uchiyama; K. Satoh; M. Kamigaito, A phosphonium intermediate for cationic RAFT polymerization, *Polymer Chemistry*, 7 (2016) 1387-1396. <https://doi.org/10.1039/C5PY01879J>
- [134] S. Sugihara; K. Yamashita; K. Matsuzuka; I. Ikeda; Y. Maeda, Transformation of Living Cationic Polymerization of Vinyl Ethers to RAFT Polymerization Mediated by a Carboxylic RAFT Agent, *Macromolecules*, 45 (2011) 794-804. <https://doi.org/10.1021/ma201988n>
- [135] H. Aoshima; M. Uchiyama; K. Satoh; M. Kamigaito, Interconvertible living radical and cationic polymerization through reversible activation of dormant species with dual activity, *Angew. Chem. Int. Ed. Engl.*, 53 (2014) 10932-10936. <https://doi.org/10.1002/anie.201406590>
- [136] S. Sugihara; Y. Sakamoto; M. Nakayama; K. Michishita; Y. Maeda, Transformation from xanthate-type cationogen mediated metal-free RAFT cationic polymerization with "HCl-Et₂O" into RAFT radical polymerization to form poly(alkyl vinyl ether)-b-polyvinyl alcohol amphiphiles, *Polymer*, 154 (2018) 153-163. <https://doi.org/10.1016/j.polymer.2018.09.002>
- [137] Y. Yağci; I. Reetz, Externally stimulated initiator systems for cationic polymerization, *Prog. Polym. Sci.*, 23 (1998) 1485-1538. [https://doi.org/10.1016/S0079-6700\(98\)00010-0](https://doi.org/10.1016/S0079-6700(98)00010-0)
- [138] M. U. Kahveci; M. Uygun; M. A. Tasdelen; W. Schnabel; W. D. Cook; Y. Yagci, Photoinitiated Cationic Polymerization of Vinyl Ethers Using Substituted Vinyl Halides, *Macromolecules*, 42 (2009) 4443-4448. <https://doi.org/10.1021/ma900359c>
- [139] M. U. Kahveci; Y. Yagci, Photoinitiated Cationic Polymerization of Vinyl Ethers Using Substituted Vinyl Halides in the Presence of Metallic Zinc, *Macromolecules*, 44 (2011) 5569-5572. <https://doi.org/10.1021/ma200783x>

- [140] M. U. Kariveci, F. Oytun, Y. Yagci, Influence of type of zinc salts on photoinitiated living cationic polymerization of vinyl ethers, *Polymer*, 54 (2013) 4798-4801. <https://doi.org/10.1016/j.polymer.2013.07.037>
- [141] D. Tunc; Y. Yagci, Thioxanthone-ethylcarbazole as a soluble visible light photoinitiator for free radical and free radical promoted cationic polymerizations, *Polymer Chemistry*, 2 (2011) <https://doi.org/10.1039/C1PY00269D>
- [142] G. Yilmaz; S. Beyazit; Y. Yagci, Visible light induced free radical promoted cationic polymerization using thioxanthone derivatives, *J. Polym. Sci., Part A: Polym. Chem.*, 49 (2011) 1591-1596. <https://doi.org/10.1002/pola.24582>
- [143] M.-A. Tehfe; F. Dumur; E. Contal; B. Graff; F. Morlet-Savary; D. Gigmes; J.-P. Fouassier; J. Lalevée, New insights into radical and cationic polymerizations upon visible light exposure: role of novel photoinitiator systems based on the pyrene chromophore, *Polymer Chemistry*, 4 (2013) 1625-1634. <http://dx.doi.org/10.1039/C2PY20950K>
- [144] B. Aydogan; G. E. Gunbas; A. Durmus; L. Toppare; Y. Yagci, Highly Conjugated Thiophene Derivatives as New Visible Light Sensitive Photoinitiators for Cationic Polymerization, *Macromolecules*, 43 (2010) 101-106. <https://doi.org/10.1021/ma901858p>
- [145] H. Chen; J. Yang; D. Guo; L. Wang; J. Nie, Photopolymerization kinetics of α -disulfone cationic photoinitiator, *Journal of Photochemistry and Photobiology A: Chemistry*, 232 (2012) 57-63. <https://doi.org/10.1016/j.jphotochem.2012.02.005>
- [146] G. Yilmaz; B. Iskin; F. Yilmaz; Y. Yagci, Visible Light-Induced Cationic Polymerization Using Fullerenes, *ACS Macro Letters*, 1 (2012) 1212-1215. <https://doi.org/10.1021/mz3004743>
- [147] M. K. Gupta; R. P. Singh, Novel allylic phosphonium salts in free radical accelerated cationic polymerization, *Polym. Bull.*, 62 (2008) 271-280. <https://doi.org/10.1007/s00289-008-0014-y>
- [148] M. K. Gupta; R. Mehare; R. P. Singh, Novel addition-fragmentation agent in cationic photopolymerization, *Polym. Bull.*, 65 (2009) 25-34. <https://doi.org/10.1007/s00289-009-0182-4>
- [149] B. Aydogan; Y. Y. Durmaz; M. U. Kahveci; M. Uygun; M. A. Tasdelen; Y. Yagci, New Photoinitiating Systems for Cationic Polymerization Acting at Near UV and Visible Range, *Macromolecular Symposia*, 308 (2011) 25-34. <https://doi.org/10.1002/masy.201151005>
- [150] S. Chen; W. D. Cook; F. Chen, Photopolymerization of Vinyl Ether Networks Using an Iodonium Initiator: Effect of Radiation Intensity and Iodonium Concentration, *Macromolecules*, 42 (2009) 5965-5975. <https://doi.org/10.1021/ma9006297>
- [151] P. Xiao; F. Dumur; T. T. Bui; F. Goubard; B. Graff; F. Morlet-Savary; J. P. Fouassier; D. Gigmes; J. Lalevée, Panchromatic Photopolymerizable Cationic Films Using Indoline and Squaraine Dye Based Photoinitiating Systems, *ACS Macro Letters*, 2 (2013) 736-740. <https://doi.org/10.1021/mz400316y>
- [152] C. Son; A. Inagaki, Synthesis and photocatalytic activity of a naphthyl-substituted photosensitizing BINAP-palladium complex, *Dalton Trans*, 45 (2016) 1331-1334. <https://doi.org/10.1039/c5dt04228c>
- [153] J. V. Crivello; M. F. Aldersley, Supramolecular diaryliodonium salt-crown ether complexes as cationic photoinitiators, *J. Polym. Sci., Part A: Polym. Chem.*, 51 (2013) 801-814. <https://doi.org/10.1002/pola.26452>
- [154] A. Kocaarslan; S. Tabanlı; G. Eryurek; Y. Yagci, Near-Infrared Free-Radical and Free-Radical-Promoted Cationic Photopolymerizations by In-Source Lighting Using Upconverting Glass, *Angew. Chem. Int. Ed. Engl.*, 56 (2017) 14507-14510. <https://doi.org/10.1002/anie.201707944>
- [155] Z. Li; J. Zhu; X. Guan; R. Liu; Y. Yagci, Near-Infrared-Induced Cationic Polymerization Initiated by Using Upconverting Nanoparticles and Titanocene, *Macromol. Rapid Commun.*, 40 (2019) e1900047. <https://doi.org/10.1002/marc.201900047>
- [156] V. Kottisch; Q. Michaudel; B. P. Fors, Cationic Polymerization of Vinyl Ethers Controlled by Visible Light, *J. Am. Chem. Soc.*, 138 (2016) 15535-15538. <https://doi.org/10.1021/jacs.6b10150>
- [157] Q. Michaudel; T. Chauvire; V. Kottisch; M. J. Supej; K. J. Stawiasz; L. Shen; W. R. Zipfel; H. D. Abruna; J. H. Freed; B. P. Fors, Mechanistic Insight into the Photocontrolled Cationic Polymerization of Vinyl Ethers, *J. Am. Chem. Soc.*, 139 (2017) 15530-15538. <https://doi.org/10.1021/jacs.7b09539>
- [158] V. Kottisch; M. J. Supej; B. P. Fors, Enhancing Temporal Control and Enabling Chain-End Modification in Photoregulated Cationic Polymerizations by Using Iridium-Based Catalysts, *Angew. Chem. Int. Ed. Engl.*, 57 (2018) 8260-8264. <https://doi.org/10.1002/anie.201804111>
- [159] E. E. Stache; V. Kottisch; B. P. Fors, Photocontrolled Radical Polymerization from Hydridic C-H Bonds, *J. Am. Chem. Soc.*, (2020) <https://doi.org/10.1021/jacs.0c00287>
- [160] V. Kottisch; Q. Michaudel; B. P. Fors, Photocontrolled Interconversion of Cationic and Radical Polymerizations, *J. Am. Chem. Soc.*, 139 (2017) 10665-10668. <https://doi.org/10.1021/jacs.7b06661>

- [161] B. M. Peterson; V. Kottusch; M. J. Supej; B. P. Fors, On Demand Switching of Polymerization Mechanism and Monomer Selectivity with Orthogonal Stimuli, *ACS Central Science*, 4 (2018) 1228-1234. <https://doi.org/10.1021/acscentsci.8b00401>
- [162] W. Sang; Q. Yan, Electro-Controlled Living Cationic Polymerization, *Angew. Chem. Int. Ed. Engl.*, 57 (2018) 4907-4911. <https://doi.org/10.1002/anie.201712270>
- [163] B. M. Peterson; S. Lin; B. P. Fors, Electrochemically Controlled Cationic Polymerization of Vinyl Ethers, *J. Am. Chem. Soc.*, 140 (2018) 2076-2079. <https://doi.org/10.1021/jacs.8b00173>
- [164] S. Sugihara; Y. Kawamoto; Y. Maeda, Direct Radical Polymerization of Vinyl Ethers: Reversible Addition-Fragmentation Chain Transfer Polymerization of Hydroxy-Functional Vinyl Ethers, *Macromolecules*, 49 (2016) 1563-1574. <https://doi.org/10.1021/acs.macromol.6b00145>
- [165] S. Sugihara; A. Yoshida; S. Fujita; Y. Maeda, Design of Hydroxy-Functionalized Thermoresponsive Copolymers: Improved Direct Radical Polymerization of Hydroxy-Functional Vinyl Ethers, *Macromolecules*, 50 (2017) 8346-8356. <https://doi.org/10.1021/acs.macromol.7b02084>
- [166] S. Sugihara; M. Sudo; K. Hirogaki; S. Irie; Y. Maeda, Synthesis of Various Poly(2-hydroxyethyl vinyl ether)-Stabilized Latex Particles via Surfactant-Free Emulsion Polymerization in Water, *Macromolecules*, 51 (2018) 1260-1271. <https://doi.org/10.1021/acs.macromol.7b02417>
- [167] S. Sugihara; A. Yoshida; T.-a. Kono; T. Takayama; Y. Maeda, Controlled Radical Homopolymerization of Representative Cationically Polymerizable Vinyl Ethers, *J. Am. Chem. Soc.*, 141 (2019) 13954-13961. <https://doi.org/10.1021/jacs.9b06671>
- [168] C. Chen; S. Luo; R. F. Jordan, Cationic Polymerization and Insertion Chemistry in the Reactions of Vinyl Ethers with (α -Diimine)PdMe⁺ Species, *J. Am. Chem. Soc.*, 132 (2010) 5273-5284. <https://doi.org/10.1021/ja100491y>
- [169] C. Chen; R. F. Jordan, Palladium-Catalyzed Dimerization of Vinyl Ethers to Acetals, *J. Am. Chem. Soc.*, 132 (2010) 10254-10255. <https://doi.org/10.1021/ja104523y>
- [170] W. Zhang; P. M. Waddell; M. A. Tiedemann; C. E. Padilla; J. Mei; L. Chen; B. P. Carrow, Electron-Rich Metal Cations Enable Synthesis of High Molecular Weight, Linear Functional Polyethylenes, *J. Am. Chem. Soc.*, 140 (2018) 8841-8850. <https://doi.org/10.1021/jacs.8b04712>
- [171] A. Kanazawa; S. Shibutani; N. Yoshinari; T. Konno; S. Kanaoka; S. Aoshima, Structure Effects of Lewis Acids on the Living Cationic Polymerization of *p*-Methoxystyrene: Distinct Difference in Polymerization Behavior from Vinyl Ethers, *Macromolecules*, 45 (2012) 7749-7757. <https://doi.org/10.1021/ma301505j>
- [172] Z. Jian; S. Mecking, Insertion Polymerization of Divinyl Formal, *Macromolecules*, 49 (2016) 4395-4403. <https://doi.org/10.1021/acs.macromol.6b00983>
- [173] S. Kikuchi; K. Saito; M. Akita; A. Inagaki, Nonradical Light-Controlled Polymerization of Styrene and Vinyl Ethers Catalyzed by an Iridium-Palladium Photocatalyst, *Organometallics*, 37 (2018) 359-366. <https://doi.org/10.1021/acs.organomet.7b00783>
- [174] J. Ye; H. Mu; Z. Wang; Z. Jian, Heteroaryl Backbone Strategy in Bisphosphine Monoxide Palladium-Catalyzed Ethylene Polymerization and Copolymerization with Polar Monomers, *Organometallics*, 38 (2019) 2990-2997. <https://doi.org/10.1021/acs.organomet.9b00340>
- [175] B. P. Carrow; K. Nozaki, Synthesis of Functional Polyolefins Using Cationic Bisphosphine Monoxide-Palladium Complexes, *J. Am. Chem. Soc.*, 134 (2012) 8802-8805. <https://doi.org/10.1021/ja303507t>
- [176] Y. Ota; S. Ito; J.-i. Kuroda; Y. Okumura; K. Nozaki, Quantification of the Steric Influence of Alkylphosphine-Sulfonate Ligands on Polymerization, Leading to High-Molecular-Weight Copolymers of Ethylene and Polar Monomers, *J. Am. Chem. Soc.*, 136 (2014) 11898-11901. <https://doi.org/10.1021/ja505558e>
- [177] R. Nakano; K. Nozaki, Copolymerization of Propylene and Polar Monomers Using Pd/IzQO Catalysts, *J. Am. Chem. Soc.*, 137 (2015) 10934-10937. <https://doi.org/10.1021/jacs.5b06948>
- [178] Y. Mitsushige; H. Yasuda; B. P. Carrow; S. Ito; M. Kobayashi; T. Tayano; Y. Watanabe; Y. Okuno; S. Hayashi; J. Kuroda; Y. Okumura; K. Nozaki, Methylene-Bridged Bisphosphine Monoxide Ligands for Palladium-Catalyzed Copolymerization of Ethylene and Polar Monomers, *ACS Macro Letters*, 7 (2018) 305-311. <https://doi.org/10.1021/acsmacrolett.8b00034>
- [179] S. Dai; C. Chen, Direct Synthesis of Functionalized High-Molecular-Weight Polyethylene by Copolymerization of Ethylene with Polar Monomers, *Angew. Chem. Int. Ed.*, 55 (2016) 13281-13285. <https://doi.org/10.1002/anie.201607152>
- [180] T. Imaeda; T. Hashimoto; S. Irie; M. Urushisaki; T. Sakaguchi, Synthesis of ABA-triblock and star-diblock copolymers with poly(2-adamantyl vinyl ether) and poly(*n*-butyl vinyl ether) segments: New thermoplastic elastomers composed solely of poly(vinyl ether) backbones, *J. Polym. Sci., Part A: Polym. Chem.*, 51 (2013) 1796-1807. <https://doi.org/10.1002/pola.26561>

- [181] N. Bouček, A. T. Sumathi, K. D. Aignamuri, Y. Ghanou, N. Hajichristidis, Triblock and pentablock terpolymers by sequential base-assisted living cationic copolymerization of functionalized vinyl ethers, *Polymer Chemistry*, 6 (2015) 1236-1247. <https://doi.org/10.1039/c4py01728e>
- [182] S. Banerjee; T. Maji; T. K. Paira; T. K. Mandal, Diblock Copolymers with Miscible Blocks via One-Pot Sequential Cationic Polymerization and Their Block-Length-Dependent Vesicular Aggregation, *Macromol. Chem. Phys.*, 215 (2014) 440-451. <https://doi.org/10.1002/macp.201300741>
- [183] A. Kanazawa; S. Kanda; S. Kanaoka; S. Aoshima, Alkoxyoxirane, a Unique Cyclic Monomer: Controlled Cationic Homopolymerization Mediated by Long-Lived Species and Copolymerization with Vinyl Ether via Alkoxy Group Transfer, *Macromolecules*, 47 (2014) 8531-8540. <https://doi.org/10.1021/ma502151g>
- [184] T. Shirouchi; A. Kanazawa; S. Kanaoka; S. Aoshima, Controlled Cationic Copolymerization of Vinyl Monomers and Cyclic Acetals via Concurrent Vinyl-Addition and Ring-Opening Mechanisms, *Macromolecules*, 49 (2016) 7184-7195. <https://doi.org/10.1021/acs.macromol.6b01565>
- [185] N. Yokoyama; H. Yoshida; A. Kanazawa; S. Kanaoka; S. Aoshima, Synthesis of block or graft copolymers containing poly(styrene derivative) segments by living cationic polymerization using acetal moieties as latent initiating sites, *Polymer Chemistry*, 6 (2015) 6316-6324. <https://doi.org/10.1039/c5py00736d>
- [186] A. Kanazawa; S. Aoshima, Cationic Terpolymerization of Vinyl Ethers, Oxetane, and Ketones via Concurrent Vinyl-Addition, Ring-Opening, and Carbonyl-Addition Mechanisms: Multiblock Polymer Synthesis and Mechanistic Investigation, *Macromolecules*, 50 (2017) 6595-6605. <https://doi.org/10.1021/acs.macromol.7b01250>
- [187] A. Kanazawa; S. Kanaoka; S. Aoshima, Rational Design of Oxirane Monomers for Efficient Crossover Reactions in Concurrent Cationic Vinyl-Addition and Ring-Opening Copolymerization with Vinyl Ethers, *Macromolecules*, 47 (2014) 6635-6644. <https://doi.org/10.1021/ma501707a>
- [188] D. Hotta; A. Kanazawa; S. Aoshima, Generation of "Living" Species Using Perfluoroalkylsulfonic Acids in Concurrent Cationic Vinyl-Addition and Ring-Opening Copolymerization via Crossover Reactions, *Macromolecules*, 51 (2018) 7983-7992. <https://doi.org/10.1021/acs.macromol.8b01686>
- [189] M. Higuchi; A. Kanazawa; S. Aoshima, Concurrent Cationic Vinyl-Addition and Coordination Ring-Opening Copolymerization via Orthogonal Propagation and Transient Merging at the Propagating Chain End, *ACS Macro Letters*, 6 (2017) 365-369. <https://doi.org/10.1021/acsmacrolett.7b00095>
- [190] M. Higuchi; A. Kanazawa; S. Aoshima, Design of Graft Architectures via Simultaneous Kinetic Control of Cationic Vinyl-Addition Polymerization of Vinyl Ethers, Coordination Ring-Opening Polymerization of Cyclic Esters, and Merging at the Propagating Chain End, *Macromolecules*, 53 (2020) 3822-3831. <https://doi.org/10.1021/acs.macromol.0c00531>
- [191] Y. Seki; A. Kanazawa; S. Kanaoka; T. Fujiwara; S. Aoshima, Precision Synthesis of Polylactide-Based Thermoresponsive Block Copolymers via Successive Living Cationic Polymerization of Vinyl Ether and Ring-Opening Polymerization of Lactide, *Macromolecules*, 51 (2018) 825-835. <https://doi.org/10.1021/acs.macromol.7b02329>
- [192] M. Ciftci; Y. Yagci, Block Copolymers by Mechanistic Transformation from PROAD to Iniferter Process, *Macromol. Rapid Commun.*, 39 (2018) e1800464. <https://doi.org/10.1002/marc.201800464>
- [193] D. Le; T. N. T. Phan; L. Autissier; L. Charles; D. Gigmes, A well-defined block copolymer synthesis via living cationic polymerization and nitroxide-mediated polymerization using carboxylic acid-based alkoxyamines as a dual initiator, *Polymer Chemistry*, 7 (2016) 1659-1667. <https://doi.org/10.1039/c5py01934f>
- [194] M. Minoda; T. Shimizu; S. Miki; J. Motoyanagi, Thermoresponsive NIPAM block copolymers containing densely grafted poly(vinyl ether) brushes synthesized by a combination of living cationic polymerization and RAFT polymerization, *J. Polym. Sci., Part A: Polym. Chem.*, 51 (2013) 786-792. <https://doi.org/10.1002/pola.26421>
- [195] G. Puts; V. Venner; B. Améduri; P. Crouse, Conventional and RAFT Copolymerization of Tetrafluoroethylene with Isobutyl Vinyl Ether, *Macromolecules*, 51 (2018) 6724-6739. <https://doi.org/10.1021/acs.macromol.8b01286>
- [196] K. Jiang; S. Han; M. Ma; L. Zhang; Y. Zhao; M. Chen, Photoorganocatalyzed Reversible-Deactivation Alternating Copolymerization of Chlorotrifluoroethylene and Vinyl Ethers under Ambient Conditions: Facile Access to Main-Chain Fluorinated Copolymers, *J. Am. Chem. Soc.*, 142 (2020) 7108-7115. <https://doi.org/10.1021/jacs.0c01016>
- [197] H. Shimomoto; D. Fukami; S. Kanaoka; S. Aoshima, Fluorinated vinyl ether homopolymers and copolymers: Living cationic polymerization and temperature-induced solubility transitions in various organic solvents including perfluoro solvents, *J. Polym. Sci., Part A: Polym. Chem.*, 49 (2011) 2051-2058. <https://doi.org/10.1002/pola.24634>

- [198] K. Ishige; T. Shimomura; K. L. White; A. Meskimi; M. Kaminari; A. Takahara; B. Armes, Unique Difference in Transition Temperature of Two Similar Fluorinated Side Chain Polymers Forming Hexatic Smectic Phase: Poly{2-(perfluorooctyl)ethyl acrylate} and Poly{2-(perfluorooctyl)ethyl vinyl ether}, *Macromolecules*, 47 (2014) 3860-3870. <https://doi.org/10.1021/ma500503z>
- [199] L. Pichavant; C. Guillermain; X. Coqueret, Reactivity of Vinyl Ethers and Vinyl Ribosides in UV-Initiated Free Radical Copolymerization with Acceptor Monomers, *Biomacromolecules*, 11 (2010) 2415-2421. <https://doi.org/10.1021/bm1005883>
- [200] K. Satoh; H. Hashimoto; S. Kumagai; H. Aoshima; M. Uchiyama; R. Ishibashi; Y. Fujiki; M. Kamigaito, One-shot controlled/living copolymerization for various comonomer sequence distributions via dual radical and cationic active species from RAFT terminals, *Polymer Chemistry*, 8 (2017) 5002-5011. <http://dx.doi.org/10.1039/C7PY00324B>
- [201] A. Tardy; J.-C. Honoré; J. Tran; D. Siri; V. Delplace; I. Bataille; D. Letourneur; J. Perrier; C. Nicoletti; M. Maresca; C. Lefay; D. Gigmes; J. Nicolas; Y. Guillauneuf, Radical Copolymerization of Vinyl Ethers and Cyclic Ketene Acetals as a Versatile Platform to Design Functional Polyesters, *Angew. Chem. Int. Ed.*, 56 (2017) 16515-16520. <https://doi.org/10.1002/anie.201707043>
- [202] E. Mishima; T. Yamada; H. Watanabe; S. Yamago, Precision synthesis of hybrid block copolymers by organotellurium-mediated successive living radical and cationic polymerizations, *Chem Asian J*, 6 (2011) 445-451. <https://doi.org/10.1002/asia.201000402>
- [203] M. Ouchi; A. Konishi; M. Takenaka; M. Sawamoto, Consecutive living polymerization from cationic to radical: a straightforward yet versatile methodology for the precision synthesis of "cleavable" block copolymers with a hemiacetal ester junction, *Polymer Chemistry*, 3 (2012) <https://doi.org/10.1039/c2py20211e>
- [204] A. H. Ma'Radzi; S. Sugihara; S. Miura; N. Konegawa; Y. Maeda, Synthesis of thermoresponsive block and graft copolymers via the combination of living cationic polymerization and RAFT polymerization using a vinyl ether-type RAFT agent, *Polymer*, 55 (2014) 1920-1930. <https://doi.org/10.1016/j.polymer.2014.02.053>
- [205] R. J. Kieber; C. Ozkardes; N. Sanchez; J. G. Kennemur, Cationic copolymerization of isosorbide towards value-added poly(vinyl ethers), *Polymer Chemistry*, 10 (2019) 3514-3524. <http://dx.doi.org/10.1039/C9PY00590K>
- [206] S. Zouganelis; I. Choinopoulos; I. Goulas; M. Pitsikalis, Statistical copolymers of n-Butyl vinyl ether and 2-chloroethyl vinyl ether via metallocene-mediated cationic polymerization. A scaffold for the synthesis of graft copolymers, *Polymers*, 11 (2019) 1510-1533. <https://doi.org/10.3390/polym11091510>
- [207] M.-E. Kourti; E. Fega; M. Pitsikalis, Block copolymers based on 2-methyl- and 2-phenyl-oxazoline by metallocene-mediated cationic ring-opening polymerization: synthesis and characterization, *Polymer Chemistry*, 7 (2016) 2821-2835. <https://doi.org/10.1039/c6py00405a>
- [208] L. Du; J. Y. Kelly; G. W. Roberts; J. M. DeSimone, Fluoropolymer synthesis in supercritical carbon dioxide, *The Journal of Supercritical Fluids*, 47 (2009) 447-457. <https://doi.org/10.1016/j.supflu.2008.11.011>
- [209] T. Irita; K. Imoto; T. Nagai; S. Aoshima, Synthesis of Thermo-Responsive Fluorinated Star-Shaped Polymers by Living Cationic Polymerization, *MRS Proceedings*, 1312 (2011) <https://doi.org/10.1557/opl.2011.130>
- [210] Y. Oda; T. Shibata; H. Tsujimoto; S. Kanaoka; S. Aoshima, Highly efficient synthesis of heteroarm star-shaped polymers using polymer-linking reaction and their characteristic stimuli-responsive behaviors, *Polym. J.*, 44 (2012) 541-549. <https://doi.org/10.1038/pj.2012.23>
- [211] S. Kanaoka; M. Yamada; J. Ashida; A. Kanazawa; S. Aoshima, Domino synthesis of star-shaped polymers based on monomer selective living cationic polymerization: Highly controlled star polymer formation, *J. Polym. Sci., Part A: Polym. Chem.*, 50 (2012) 4594-4598. <https://doi.org/10.1002/pola.26304>
- [212] T. Yoshizaki; A. Kanazawa; S. Kanaoka; S. Aoshima, Quantitative and Ultrafast Synthesis of Well-Defined Star-Shaped Poly(p-methoxystyrene) via One-Pot Living Cationic Polymerization, *Macromolecules*, 49 (2015) 71-79. <https://doi.org/10.1021/acs.macromol.5b02223>
- [213] M. Kawamura; A. Kanazawa; S. Kanaoka; S. Aoshima, Sequence-controlled degradable polymers by controlled cationic copolymerization of vinyl ethers and aldehydes: precise placement of cleavable units at predetermined positions, *Polymer Chemistry*, 6 (2015) 4102-4108. <https://doi.org/10.1039/c5py00493d>
- [214] Y. Ishido; A. Kanazawa; S. Kanaoka; S. Aoshima, Controlled cationic alternating copolymerization of various enol ethers and benzaldehyde derivatives: Effects of enol ether structures, *J. Polym. Sci., Part A: Polym. Chem.*, 52 (2014) 1334-1343. <https://doi.org/10.1002/pola.27122>

- [215] B. W. Greenman; S. Liu; G. Cavalli; E. Alpay; J. H. G. Steinke, Synthesis of beaded poly(vinyl ether) solid supports with unique solvent compatibility, *Polymer*, 51 (2010) 2984-2992. <https://doi.org/10.1016/j.polymer.2010.04.026>
- [216] J. Motoyanagi; K. Higashi; M. Minoda, Synthesis of brush-shaped polymers consisting of a poly(phenylacetylene) backbone and pendant poly(vinyl ether)s via selective reaction of 2-Vinylloxyethyl 4-Ethynylbenzoate, *J. Polym. Sci., Part A: Polym. Chem.*, 52 (2014) 2800-2805. <https://doi.org/10.1002/pola.27304>
- [217] J. vMotoyanagi; T. Ishikawa; M. Minoda, Stimuli-responsive brush-shaped conjugated polymers with pendant well-defined poly(vinyl ether)s, *J. Polym. Sci., Part A: Polym. Chem.*, 54 (2016) 3318-3325. <https://doi.org/10.1002/pola.28220>
- [218] J. Motoyanagi; N. M. Tan; M. Minoda, Synthesis of well-defined poly(vinyl ether)-based macromonomers having pendant glycerols via living cationic polymerization and their application to the preparation of core-shell polymer particles, *Polym. Int.*, 63 (2014) 459-464. <https://doi.org/10.1002/pi.4526>
- [219] H. Kalita; S. Alam; D. Kalita; A. Jayasooriyamu; S. Fernando; S. Samanta; J. Bahr; S. Selvakumar; M. Sibi; J. Vold; C. Ulven; B. J. Chisholm, Novel alkyd-type coating resins produced using cationic polymerization, *Journal of Coatings Technology and Research*, 12 (2015) 633-646. <https://doi.org/10.1007/s11998-015-9667-2>
- [220] H. Kalita; S. Selvakumar; A. Jayasooriyamu; S. Fernando; S. Samanta; J. Bahr; S. Alam; M. Sibi; J. Vold; C. Ulven; B. J. Chisholm, Bio-based poly(vinyl ether)s and their application as alkyd-type surface coatings, *Green Chem.*, 16 (2014) <https://doi.org/10.1039/c3gc41868e>
- [221] S. Samanta; S. Selvakumar; J. Bahr; D. S. Wickramaratne; M. Sibi; B. J. Chisholm, Synthesis and Characterization of Polyurethane Networks Derived from Soybean-Oil-Based Cyclic Carbonates and Bioderivable Diamines, *ACS Sust. Chem. Eng.*, 4 (2016) 6551-6561. <https://doi.org/10.1021/acssuschemeng.6b01409>
- [222] H. Kalita; S. Alam; D. Kalita; A. Chernykh; I. Tarnavchyk; J. Bahr; S. Samanta; A. Jayasooriyama; S. Fernando; S. Selvakumar; A. Popadyuk; D. S. Wickramaratne; M. Sibi; A. Voronov; A. Bezbaruah; B. J. Chisholm, (Eds.). (2014) Synthesis and Characterization of Novel Soybean Oil-Based Polymers and Their Application in Coatings Cured by Autoxidation, In *Soy-Based Chemicals and Materials*, pp. 371-390, American Chemical Society,
- [223] T. Hashimoto; A. Takahashi; M. Urushisaki; T. Sakaguchi, Synthesis of poly(vinyl ether) polyols with pendant oxyethylene chains and properties of hydrophilic, thermo-responsive polyurethanes prepared therefrom, *J. Polym. Sci., Part A: Polym. Chem.*, 48 (2010) 1641-1648. <https://doi.org/10.1002/pola.23930>
- [224] T. Sakaguchi; M. Ohashi; K. Shimada; T. Hashimoto, Synthesis and gas permeability of membranes of Poly(vinyl ether)s bearing oxyethylene segments, *Polymer*, 53 (2012) 1659-1664. <https://doi.org/10.1016/j.polymer.2012.02.036>
- [225] T. Namikoshi; T. Hashimoto; Y. Makino; T. Imaeda; M. Urushisaki; T. Sakaguchi, Synthesis and properties of poly(2-adamantyl vinyl ether)-based optical plastics, *Polym. Bull.*, 71 (2014) 1389-1402. <https://doi.org/10.1007/s00289-014-1130-5>
- [226] T. Sakaguchi; F. Katsura; A. Iwase; T. Hashimoto, CO₂-permselective membranes of crosslinked poly(vinyl ether)s bearing oxyethylene chains, *Polymer*, 55 (2014) 1459-1466. <https://doi.org/10.1016/j.polymer.2014.02.012>
- [227] T. Sakaguchi; S. Yamazaki; T. Hashimoto, Crosslinked membranes of poly(vinyl ether)s having oxyethylene side chains: The effects of the side chain length and the crosslinkable group on CO₂ permeability, *Polymer*, 112 (2017) 278-287. <https://doi.org/10.1016/j.polymer.2017.02.027>
- [228] T. Sakaguchi; S. Yamazaki; T. Hashimoto, Enhancement of CO₂ permeability of poly(vinyl ether)s having oxyethylene chains by the sequence control of crosslinking sites, *RSC Advances*, 7 (2017) 13879-13885. <https://doi.org/10.1039/c7ra01353a>
- [229] T. Sakaguchi; Y. Koide; T. Hashimoto, Synthesis of membranes of poly(vinyl ether)s and their gas permeability, *J. Appl. Polym. Sci.*, 114 (2009) 2339-2343. <https://doi.org/10.1002/app.30834>
- [230] T. Namikoshi; T. Hashimoto; Y. Suzuki; M. Urushisaki; T. Sakaguchi, Synthesis of poly(vinyl ether) optical plastics by cationic copolymerization of tricyclodecane vinyl ether with functionalized vinyl ethers, *J. Appl. Polym. Sci.*, 126 (2012) E307-E314. <https://doi.org/10.1002/app.36973>
- [231] T. Sakaguchi; R. Okunaga; S. Irie; M. Urushisaki; T. Hashimoto, Carbon dioxide-permselective polymer membranes composed of poly(vinyl ether)-based, ABA-type triblock copolymers with pendant oxyethylene chains, *Polym. Bull.*, 74 (2016) 2017-2031. <https://doi.org/10.1007/s00289-016-1820-2>
- [232] Y. Oda; S. Kanaoka; T. Sato; S. Aoshima; K. Kuroda, Block versus random amphiphilic copolymers as antibacterial agents, *Biomacromolecules*, 12 (2011) 3581-3591. <https://doi.org/10.1021/bm200780r>

- [233] Oda Y; Yasunara K; Kanaoka S; Salo T; Aoshima S; K. K., Aggregation of Cationic Amphiphilic Block and Random Copoly(vinyl ether)s with Antimicrobial Activity., *Polymers*, 10 (2018) 93/91-93/11. <https://doi.org/10.3390/polym10010093>
- [234] Y. Oda; C. Zhang; D. Kawaguchi; H. Matsuno; S. Kanaoka; S. Aoshima; K. Tanaka, Design of Blood-Compatible Interfaces with Poly(vinyl ether)s, *Advanced Materials Interfaces*, 3 (2016) <https://doi.org/10.1002/admi.201600034>
- [235] N. Itagaki; Y. Oda; T. Hirata; H. K. Nguyen; D. Kawaguchi; H. Matsuno; K. Tanaka, Surface Characterization and Platelet Adhesion on Thin Hydrogel Films of Poly(vinyl ether), *Langmuir*, 33 (2017) 14332-14339. <https://doi.org/10.1021/acs.langmuir.7b03427>
- [236] H. Matsuno; R. Tsukamoto; Y. Oda; K. Tanaka, Platelet adhesion on the surface of a simple poly(vinyl ether), *Polymer*, 116 (2017) 479-486. <https://doi.org/10.1016/j.polymer.2017.01.036>
- [237] S. Tanaka; H.-K. Kim; A. Sudo; H. Nishida; T. Endo, Anisotropic Photomechanical Response of Stretched Blend Film Made of Polycaprolactone-Polyvinyl Ether with Azobenzene Group as Side Chain, *Macromol. Chem. Phys.*, 209 (2008) 2071-2077. <https://doi.org/10.1002/macp.200800215>
- [238] K. Koshika; N. Sano; K. Oyaizu; H. Nishide, An Aqueous, Electrolyte-Type, Rechargeable Device Utilizing a Hydrophilic Radical Polymer-Cathode, *Macromol. Chem. Phys.*, 210 (2009) 1989-1995. <https://doi.org/10.1002/macp.200900257>
- [239] B. Winther-Jensen; K. Fraser; C. Ong; M. Forsyth; D. R. MacFarlane, Conducting polymer composite materials for hydrogen generation, *Adv. Mater.*, 22 (2010) 1727-1730. <https://doi.org/10.1002/adma.200902934>
- [240] Z. Shervani; Y. Taisuke; S. Ifuku; H. Saimoto; M. Morimoto, Preparation of Gold Nanoparticles Loaded Chitin Nanofiber Composite, *Advances in Nanoparticles*, 01 (2012) 71-78. <https://doi.org/10.4236/anp.2012.13010>
- [241] C. E. Schildknecht; S. T. Gross; H. R. Davidson; J. M. Lambert; A. O. Zoss, Polyvinyl Isobutyl Ethers, *Industrial & Engineering Chemistry*, 40 (1948) 2104-2115. <https://doi.org/10.1021/ie50467a021>
- [242] V. G. Natta, Polymères isotactiques, *Die Makromolekulare Chemie*, 16 (1955) 213-237. <https://doi.org/10.1002/macp.1955.020160124>
- [243] V. G. Natta; I. Bassi; P. Corradini, Über die kettenstruktur des kristallinen polyvinylisobutyläthers, *Die Makromolekulare Chemie*, 18 (1956) 455-462. <https://doi.org/10.1002/macp.1956.020180140>
- [244] J. Lal, Polymerization of vinyl ethers by Ziegler catalysts, *Journal of Polymer Science*, 31 (1958) 179-181. <https://doi.org/10.1002/pol.1958.1203112220>
- [245] M. Ouchi; M. Kamigaito; M. Sawamoto, Stereoregulation in Cationic Polymerization by Designed Lewis Acids. 1. Highly Isotactic Poly(isobutyl vinyl ether) with Titanium-Based Lewis Acids, *Macromolecules*, 32 (1999) 6407-6411. <https://doi.org/10.1021/ma990227i>
- [246] M. Ouchi; M. Sueoka; M. Kamigaito; M. Sawamoto, Stereoregulation in cationic polymerization. III. High isospecificity with the bulky phosphoric acid [(RO)₂PO₂H]/SnCl₄ initiating systems: Design of counteranions via initiators, *J. Polym. Sci., Part A: Polym. Chem.*, 39 (2001) 1067-1074. [https://doi.org/10.1002/1099-0518\(20010401\)39:7<1067::AID-POLA1083>3.0.CO;2-V](https://doi.org/10.1002/1099-0518(20010401)39:7<1067::AID-POLA1083>3.0.CO;2-V)
- [247] K. Satoh; M. Kamigaito; M. Sawamoto, Aromatic Acetals as New Initiators for Cationic Polymerization of Isobutyl Vinyl Ether, *Macromolecules*, 33 (2000) 748-753. <https://doi.org/10.1021/ma991571j>
- [248] T. Kawaguchi; F. Sanda; T. Masuda, Polymerization of vinyl ethers with transition-metal catalysts: An examination of the stereoregularity of the formed polymers, *J. Polym. Sci., Part A: Polym. Chem.*, 40 (2002) 3938-3943. <https://doi.org/10.1002/pola.10483>
- [249] P. Sudhakar; K. Vijayakrishna, Isospecific polymerization of vinyl ethers with titanium catalysts containing modified tridentate anionic donor ligands, *Polym. Int.*, 58 (2009) 1362-1365. <https://doi.org/10.1002/pi.2667>
- [250] P. Sudhakar; K. Vijayakrishna, Highly Stereoselective Living Polymerization of Vinyl Ethers at Ambient Temperature Mediated by Chiral Titanium Complexes, *ChemCatChem*, 2 (2010) 649-652. <https://doi.org/10.1002/cctc.201000012>
- [251] P. Sudhakar; K. Vijayakrishna, Polymerization of vinyl ethers using titanium catalysts containing tridentate triamine ligand of the type N[CH₂CH(Ph)(Ts)N]₂⁻, *Polymer*, 50 (2009) 783-788. <https://doi.org/10.1016/j.polymer.2008.12.017>
- [252] A. Kanazawa; S. Kanaoka; S. Aoshima, A stepping stone to stereospecific living cationic polymerization: Cationic polymerization of vinyl ethers using iron(II) sulfate, *J. Polym. Sci., Part A: Polym. Chem.*, 48 (2010) 3702-3708. <https://doi.org/10.1002/pola.24144>
- [253] A. J. Teator; F. A. Leibfarth, Catalyst-controlled stereoselective cationic polymerization of vinyl ethers, *Science*, 363 (2019) 1439. <https://doi.org/10.1126/science.aaw1703>

