

Thiol-Ene Cationic and Radical Reactions: Cyclization, Step-Growth, and Concurrent Polymerizations for Thioacetal and Thioether Units

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Abstract: Thiol-ene cationic and radical reactions were conducted not only for 1:1 addition between thiol and vinyl ether but also for cyclization and step-growth polymerization between dithiol and divinyl ether. An organic acid catalyst such as *p*-toluenesulfonic acid (PTSA) induced the cationic thiol-ene reaction to generate the thioacetal as the Markovnikov adduct in high yield, whereas organic radical initiators such as 2,2'-azobisisobutyronitrile (AIBN) caused the radical thiol-ene reaction to give the thioether as the anti-Markovnikov adduct, also in high yield. The cationic and radical addition reactions between dithiol and divinyl ether with oxyethylene units allowed the starting materials to efficiently undergo both cationic step-growth polymerization in the presence of PTSA and radical polymerization in the presence of AIBN or under UV irradiation to yield amorphous poly(thioacetal)s and crystalline poly(thioether)s, respectively. In contrast, under high dilution conditions, the cationic and radical reactions resulted in 16- and 18-membered cyclic thioacetal and thioether products, respectively, which have a structure similar to that of crown ether. Furthermore, concurrent cationic and radical step-growth polymerizations were realized using PTSA under UV irradiation to produce polymers composed of both thioacetal and thioether linkages in the main chains, where the polymer properties are arbitrarily tunable by the concentration of PTSA or the content of the two linkages.

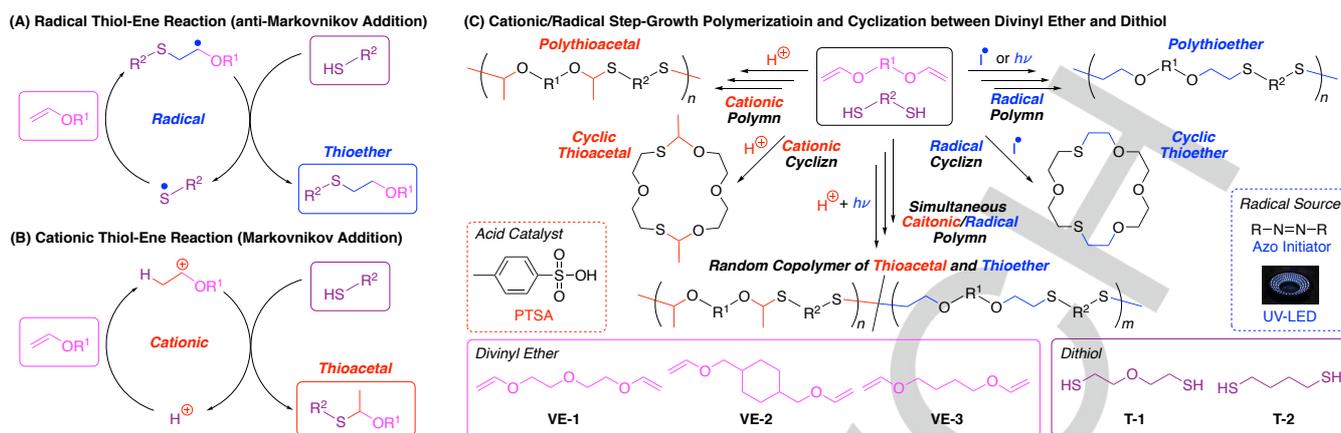
Introduction

Polymerization usually proceeds by repeating a single efficient organic reaction for a monomer or a mixture of monomers to result in a polymer comprising multiple repeating monomer units with the same bonding mode prone to the reaction.¹ Polymer properties are determined not only by the monomer structure but also by the bonding mode, including regio- and stereostructures. If the monomers can be polymerized with different reactions, intermediates, and selectivities, the resulting polymers should have different structures and thus different properties. Furthermore, if those different reactions occur simultaneously, the polymer properties can be arbitrarily tuned by the reactions. Indeed, in chain-growth polymerizations, a single monomer has been polymerized simultaneously by multiple propagating species with

different stereo- or regioselectivity to result in unique polymers, such as random, gradient and block or multiblock structures, which cannot be obtained by repetitive single reactions.²⁻⁹ In addition, concurrently occurring polymerizations of common monomers via different propagating species such as radicals, cations, and anions are attractive because they can dramatically widen the scope of accessible polymer structures with novel and/or tunable properties.¹⁰⁻¹⁸

A thiol and olefin usually undergo radical addition, i.e., thiol-ene reaction, which is one of the most efficient and robust click reactions, in the presence of a radical initiator or under UV irradiation to result in the anti-Markovnikov adduct with high selectivity and high yield.¹⁹⁻²¹ Under the radical conditions, a thiyl radical is generated from thiol and adds to the olefin to form a carbon radical, which then abstracts a hydrogen atom from thiol to result in a thioether as the product, regenerating another thiyl radical (Scheme 1A). A repeated sequence of the radical chain reactions provides the anti-Markovnikov adduct efficiently. Due to the high selectivity and efficiency as well as being a metal-free system, the thiol-ene reaction is now widely used not only in organic chemistry but also in polymer chemistry²²⁻²⁶ and biochemistry.^{27,28} In particular, although the radical thiol-ene reaction was evolved into step-growth polymerization between a dithiol and divinyl compound more than 60 years ago,²⁹ radical thiol-ene step-growth polymerization is being developed again as a highly efficient reaction to yield various poly(thioether)s with relatively high molecular weight in high yield under mild conditions.¹⁹⁻²⁶

In addition to the radical reaction, a thiol and olefin can react via an anionic or Michael mechanism depending on the olefin and conditions, particularly in the presence of basic catalysts.³⁰ Alternatively, we recently found an organic acid-catalyzed cationic thiol-ene reaction for the synthesis of thioacetal, which can be subsequently used as a reversible chain-transfer agent in cationic degenerative chain-transfer polymerization of vinyl ethers.³¹⁻³⁴ In the cationic thiol-ene reaction, a catalytic amount of an organic acid such as *p*-toluenesulfonic acid (PTSA) induces quantitative cationic addition between a thiol and vinyl ether to efficiently form a thioacetal as the Markovnikov adduct. Under the cationic reaction conditions, a proton originating from the acid adds to vinyl ether to generate a carbocation, which then reacts with a thiol to form the thioacetal as the product,



Scheme 1. (A) Radical and (B) cationic thiol-ene reaction between vinyl ether and thiol, and (C) cationic/radical step-growth polymerization and cyclization between divinyl ether and dithiol.

regenerating another proton via the cationic chain reaction (Scheme 1B). The repeated cationic chain reactions thus enable the high-yield synthesis of thioacetal. Although there have been several reports on Markovnikov addition of thiol to electron-rich olefins, including vinyl ether, almost all of the hydrothiolations are catalyzed by metal Lewis acids or transition metal catalysts.^{35–41} PTSA-catalyzed thiol-ene reactions have never been reported despite similar reactions between alcohols and vinyl ethers for the synthesis of acetals.⁴²

We wondered if this efficient cationic thiol-ene reaction could be applicable to cationic step-growth polymerization between dithiol and divinyl ether to synthesize novel polymers constituting thioacetal linkages in the main chain via Markovnikov addition. The resulting poly(thioacetal)s are expected to have different properties from those of poly(thioether)s obtained by radical thiol-ene reaction with the opposite regioselectivity between the same pair of monomers. In addition, if these two step-growth polymerizations proceeding via cationic and radical intermediates with different regioselectivities can be combined and concurrently occur, they can afford polymers comprising thioacetal and thioether linkages and thus have tunable properties.

Recently, Tew and Sarapas have reported the synthesis of functional poly(thioether)s by radical step-growth polymerizations between a functional dithiol and divinyl ether and their application as lithium polymer electrolytes.^{43,44} In addition, various thiols and vinyl ethers have been subjected to radical step-growth polymerizations for other applications.^{45–48} In contrast to the radical polymerizations for poly(thioether)s, Ruckenstein and Hashimoto have independently reported the synthesis of poly(acetal)s via cationic step-growth polymerization between a diol and divinyl ether in the presence of acidic catalysts such as PTSA and then applied the acetal linkages as degradable units.^{49–53} However, there have been no reports on cationic step-growth polymerization between a dithiol and divinyl ether or on concurrent radical and cationic step-growth polymerizations except for a combination of radical thiol-ene step-growth radical polymerization and chain-growth cationic photopolymerization of vinyl ether for preparing cross-linked materials.^{54–56}

In this paper, we demonstrated that cationic and radical step-growth polymerizations between divinyl ethers and dithiols efficiently occur using acid and radical catalysts to selectively generate poly(thioacetal)s and poly(thioether)s, respectively (Scheme 1C). In addition, under high dilution conditions, cyclic 16- and 18-membered thioacetal and thioether, which have a structure similar to that of crown ether, were prepared selectively. Furthermore, concurrent cationic and radical step-growth polymerizations were investigated to construct unique polymer structures consisting of both thioacetal and thioether linkages in the main chain from a single pair of monomers. The effects of the content of the two repeating units on the thermal properties of the resulting polymers were also investigated.

Results and Discussion

1:1 Cationic and Radical Additions between Thiol and Vinyl Ether as Model Reactions.

Prior to working on cationic and radical step-growth polymerizations or polyaddition reactions using dithiols and divinyl ethers, we investigated cationic and radical monoaddition reactions between 1-octanethiol (OctSH) and isobutyl vinyl ether (IBVE) in the presence of acid and radical catalysts, respectively, to demonstrate the high selectivity and efficiency. When an equimolar mixture of OctSH and IBVE was reacted in the presence of a catalytic amount (0.33 mol%) of PTSA in CH_2Cl_2 at -40°C , they quantitatively reacted in 5 min to result in the thioacetal as the Markovnikov adduct with high selectivity ($\geq 99\%$) (Figures 1A), indicating that the organic-acid-catalyzed cationic thiol-ene reaction is highly efficient and selective.

In contrast, when the same equimolar mixture was subjected to radical reaction in the presence of a trace amount (0.2 mol%) of 2,2'-azobisisobutyronitrile (AIBN) in toluene at 60°C , the radical thiol-ene reaction occurred quantitatively in 17 h to result in the thioether as the anti-Markovnikov adduct with high selectivity ($\geq 99\%$) (Figure 1B).

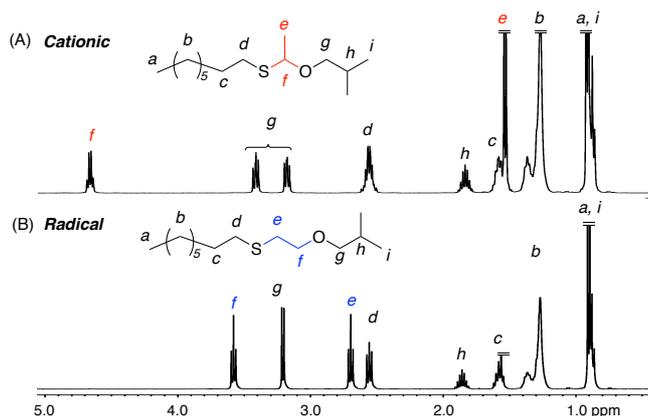


Figure 1. ^1H NMR spectra (CDCl_3 , 25°C) of the adduct obtained in cationic (A) and radical (B) addition: $[\text{OctSH}]_0/[\text{IBVE}]_0 = 1500/1500$ mM, $[\text{PTSA}]_0 = 5.0$ mM in CH_2Cl_2 at -40°C (for cationic), $[\text{AIBN}]_0 = 3.0$ mM in toluene at 60°C (for radical).

Therefore, both the cationic and radical thiol-ene reactions work efficiently with equimolar amounts of thiol and vinyl ether in the presence of appropriate cationic and radical organic catalysts to result in thioacetal and thioether, respectively, with high yield and selectivity.

Cationic and Radical Step-Growth Polymerizations between Dithiol and Divinyl Ether.

Motivated by the quantitative and selective cationic and radical additions between monothiol and monovinyl ether, cationic and radical step-growth polymerizations between dithiol and divinyl ether were examined for bis(2-mercaptoethyl) ether (**T-1**) and diethylene glycol divinyl ether (**VE-1**), both of which possess oxyethylene linkers between the two reactive groups. The cationic polyaddition was similarly conducted using a trace amount (0.067 mol%) of PTSA as the acid catalyst in CH_2Cl_2 at -40°C . Both the $-\text{SH}$ and $\text{C}=\text{C}$ groups were smoothly consumed at almost the same rate and quantitatively (Figure 2A). As the reaction proceeded, size-exclusion chromatography (SEC) curves of the products shifted to the high molecular weight region, although a peak also appeared in the low molecular weight region due to the formation of small cyclic compounds (Figure 2D), which will be clarified later by the reaction under high dilution conditions. The number-average molecular weight (M_n) or number-average degree of polymerization (DP_n) of the obtained polymers progressively increased in the latter stage of the reaction and was close to the theoretical line based on the Flory equation (broken line in Figure 2C), which indicates that the cationic polymerization proceeded via a step-growth mechanism. Thus, the acid-catalyzed cationic thiol-ene reaction is effective for the synthesis of relatively high molecular weight polymers from dithiol and divinyl ether.

Then, the radical step-growth polymerization via radical thiol-ene reaction was examined for the same two monomers, i.e., **T-1** and **VE-1**, using AIBN as the radical catalyst instead of the acid catalyst in toluene at 60°C . Both the thiol ($-\text{SH}$) and alkene groups ($\text{C}=\text{C}$) were consumed at the same rate (Figure 2B) to yield the products, of which the SEC curves shifted to high molecular weights as the functional groups were consumed (Figure 2E). Furthermore, the M_n progressively increased in a

similar way to that of the polymers obtained with PTSA (Figure 2C). Thus, the dithiol and divinyl ether underwent efficient radical step-growth propagation to yield polymers with similar molecular weights.

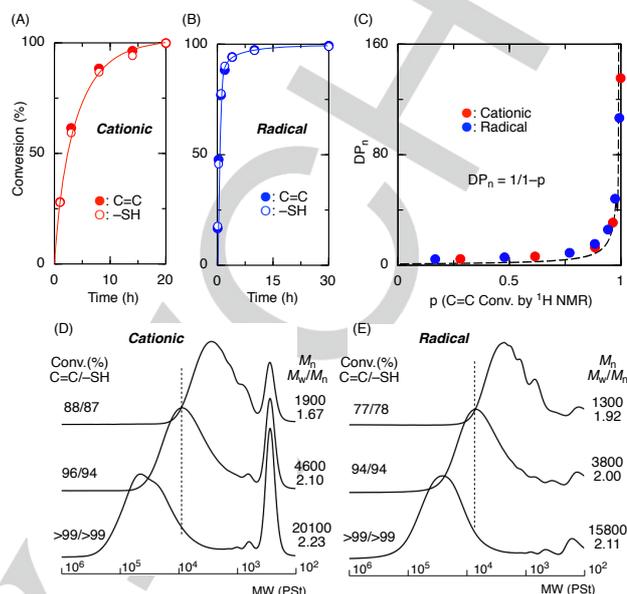


Figure 2. Time-conversion curves for (A) cationic step-growth polymerization and (B) radical step-growth polymerization, number-average polymerization degree (DP_n) as a function of $\text{C}=\text{C}$ conversion (C) for cationic and radical products (the dashed line: theoretical DP_n based on the Flory equation ($\text{DP}_n = 1/(1-p)$), and SEC curves for (D) cationic and (E) radical products: $[\text{T-1}]_0/[\text{VE-1}]_0 = 1500/1500$ mM, $[\text{PTSA}]_0 = 1.0$ mM in CH_2Cl_2 at -40°C (for cationic), $[\text{AIBN}]_0 = 3.0$ mM in toluene at 60°C (for radical).

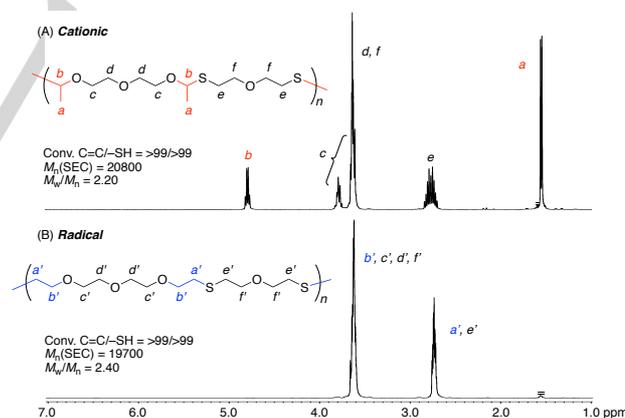


Figure 3. ^1H NMR spectra (CDCl_3 , 55°C) of the polymers obtained in cationic (A) and radical (B) step-growth polymerization.

The polymers obtained from both polymerizations were analyzed by ^1H NMR spectroscopy. In the spectra obtained from radical polymerization, only two simple peaks assignable to methylene protons of ethers (b' , c' , d' , f') and thioethers (a' , e') of the main chain were observed (Figure 3B). On the other hand, the spectrum of the products obtained from cationic polymerization showed slightly complicated peaks, which can be assigned to methyl (a) and methine (b) protons of thioacetal in

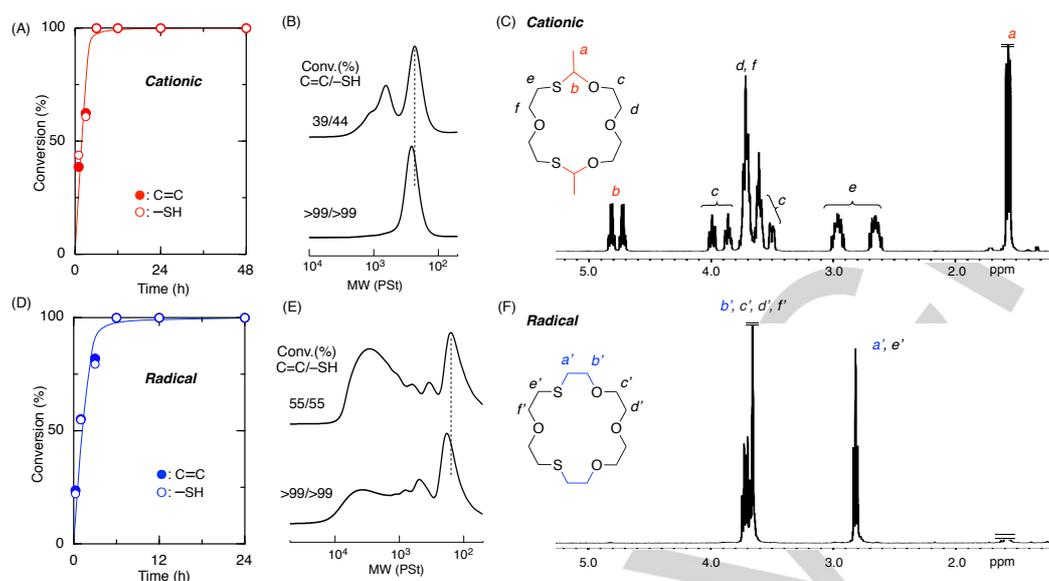


Figure 4. Time-conversion for cationic reaction in high dilution (A), SEC curves of the products (B), and ^1H NMR spectrum (CDCl_3 , 25 °C) of the fractionated cyclic products (C) obtained in the cationic reaction. Time-conversion for radical reaction in high dilution (D), SEC curves of the products (E), and ^1H NMR spectrum (CDCl_3 , 25 °C) of the fractionated cyclic products (F) obtained in the radical reaction. $[\text{VE-1}]_0/[\text{T-1}]_0 = 50/50$ mM, $[\text{PTSA}]_0 = 5.0$ mM in CH_2Cl_2 at -40 °C (for cationic), $[\text{AIBN}]_0 = 3.0$ mM in toluene at 60 °C (for radical).

addition to methylene protons adjacent to oxygen (*d*, *c*, *f*) and sulfur atoms (*e*) in the polymer main chain (Figure 3A). The methylene peaks (*e*) adjacent to thioacetals were slightly different from those adjacent to thioethers obtained in radical polymerization. These results clearly indicate that polymers with different structures were efficiently obtained from the same two monomers via two different step-growth polymerizations. Thus, the cationic and radical step-growth polymerizations of **T-1** and **VE-1** proceeded selectively using organic acid and radical catalysts, which afforded poly(thioacetal) and poly(thioether), respectively.

Although the step-growth polymerizations occurred efficiently both via cationic and radical mechanisms, the conditions such as temperature and solvents used were quite different. To further develop the polymerizations under similar conditions, the cationic polymerizations were conducted at a higher temperature, whereas the radical polymerizations were investigated at a lower temperature (entries 1–5 in Table S1). The cationic polymerization at 0 °C proceeded faster to result in similar poly(thioacetal)s with high molecular weights (Figures S1 and S2). The radical polymerizations occurred not only at 20 °C using a low-temperature radical initiator (V-70) in toluene but also at 0 °C under UV LED irradiation in CH_2Cl_2 to quantitatively afford poly(thioether)s with high molecular weights (Figures S3–S6). These results indicate that both cationic and radical step-growth polymerizations are efficiently achievable under the same conditions, i.e., at 0 °C in CH_2Cl_2 .

1:1 Cationic and Radical Cyclizations between Dithiol and Divinyl Ether under High Dilution Conditions.

The low molecular weight byproducts were expected to be cyclic compounds formed via intramolecular cyclization followed by the 1:1 monoaddition between dithiol and divinyl ether via either cationic or radical mechanisms. The cationic and radical

reactions between **T-1** and **VE-1** were then examined under high dilution conditions to clarify the byproducts and to obtain the expected cyclic compounds in high yield.

Even under the dilution conditions in both the cationic and radical reactions, the thiol and alkene groups were consumed at the same rate and quantitatively (Figures 4A and 4D). The major products observed at the low molecular weight region in the SEC curves were similar to the byproducts obtained under the conditions for the step-growth polymerizations (Figures 4B and 4E). The low molecular weight products were fractionated by preparative SEC and analyzed by ^1H NMR spectroscopy (Figures 4C and 4F). These products were indeed the cyclic thioacetal and thioether obtained via 1:1 cyclization between **T-1** and **VE-1**. In particular, the yield of the 1:1 cyclic thioacetal was very high and almost quantitative due to the reversible formation of thioacetal groups, similar to the degenerative chain-transfer cationic polymerization using thioacetal in the presence of an acid catalyst.³¹ Although the yield of the cyclic product was lower under the radical conditions due to the irreversible reaction, the fraction increased along with the conversion because the concentrations of the starting materials decreased.

These results indicate that the low molecular weight byproducts were the 16- and 18-membered cyclic compounds respectively obtained via 1:1 cationic and radical cyclizations between dithiol and divinyl ether and that they were prepared in relatively high yield under high dilution conditions. The obtained cyclic sulfur compounds with oxyethylene units possibly have special properties or functions. In particular, the 18-membered cyclic molecule (1,4,7,13-tetraoxa-10,16-dithiacyclooctadecane) composed of four oxygen and two sulfur atoms with six methylene units has a structure similar to that of 18-crown-6, a well-known host molecule, but has never been synthesized except for its regioisomers.^{57–61}

Various Dithiols and Divinyl Ethers for Cationic and Radical Step-Growth Polymerizations and Their Thermal Properties.

The versatility of the two step-growth polymerizations was then investigated for other dithiols and divinyl ethers, such as 1,4-butanedithiol (T-2), 1,4-cyclohexanedimethanol divinyl ether (VE-2), and 1,4-butanediol divinyl ether (VE-3), possessing alkyl and cycloalkyl linkers. Despite the monomer structures, both the cationic and radical step-growth polymerizations efficiently proceeded to result in poly(thioacetal)s and poly(thioether)s with high molecular weights and different main-chain structures (Figures S7–S10 and entries 6–9 in Table S1).

Then, the thermal properties of the obtained polymers were evaluated (Figure 5). All the resulting polymers showed low glass transition temperatures (T_g) ($T_g \leq -40$ °C) due to the flexible main-chain structures. Regardless of the combinations of the monomers, the T_g values of the polymers composed of thioacetal linkages with two branched methyl groups in the repeating units were higher than those containing thioether linkages without any branches. Moreover, the linker structure of monomers also affected the T_g values. The cyclohexyl linker (VE-2) gave higher T_g values than did the linear linker. Furthermore, the poly(thioether)s obtained via radical polymerization of the linear monomers, i.e., VE-1/T-1 and VE-3/T-2, showed melting temperatures (T_m) like those of polyethylene oxide and polyethylene, indicating that these polymers were crystalline, whereas no T_m values were observed for poly(thioacetal)s. The degradation temperatures (T_{d5} ; temperature at 5% weight loss) of the obtained polymers were between 220 and 310 °C (Figure S11) under an inert atmosphere with nitrogen flow. Slightly lower T_{d5} values were observed for poly(thioacetal)s than for poly(thioether)s, most likely due to the less stable thioacetal linkages. Thus, various dithiols and divinyl ethers were efficiently polymerized via cationic and radical step-growth polymerizations to provide poly(thioacetal)s and poly(thioether)s with different thermal properties depending on the polymerization catalysts and monomer linkers. In addition, the polymers with oxyethylene units enabled dissolution of a lithium salt ((CF₃SO₂)₂NLi). As the weight fraction of the lithium salt increased, the T_g values of the homogeneous mixtures increased (Figure S12), which suggests that these polymers possibly could function as polymer electrolytes for lithium ion batteries, as previously reported.⁴⁴

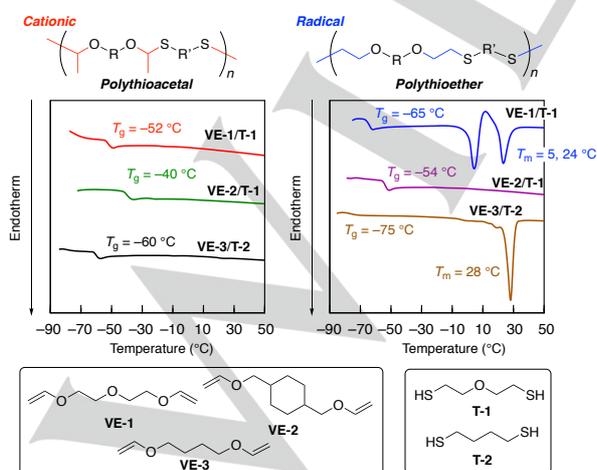


Figure 5. DSC curves of the polymers obtained in cationic and radical step-growth polymerization of various divinyl ethers and dithiols.

Concurrent Cationic and Radical Step-Growth Polymerizations Using an Acid Catalyst under UV Irradiation.

As clarified above, the cationic and radical step-growth polymerizations proceeded under similar conditions in CH₂Cl₂ at 0 °C using PTSA and UV light, respectively. Finally, the concurrent cationic and radical step-growth polymerization of VE-1 and T-1 was investigated using both PTSA and UV light at the same time in CH₂Cl₂ at 0 °C.

When PTSA was used at 0.10 mM under UV light irradiation, both –SH and C=C groups were consumed at the same rate and quantitatively (Figure 6A). As the reactions proceeded, the SEC curves shifted to high molecular weight, and the M_n of the products increased progressively and finally reached over 30,000 (Figure 6B). The ¹H NMR spectrum of the polymer showed peaks assignable to both thioacetal and thioether groups, which were generated by cationic and radical step-growth polymerizations, respectively (Figure 6C). In addition, the ratio of thioacetal and thioether units in the final products was 53/47, indicating that cationic and radical reactions occurred at almost the same probability under the conditions to yield random copolymers of thioacetals and thioethers with almost the same content (Figure 6A). These results demonstrate that a novel simultaneous cationic and radical polymerization was achieved between divinyl ethers and dithiols using the combination of PTSA and UV irradiation.

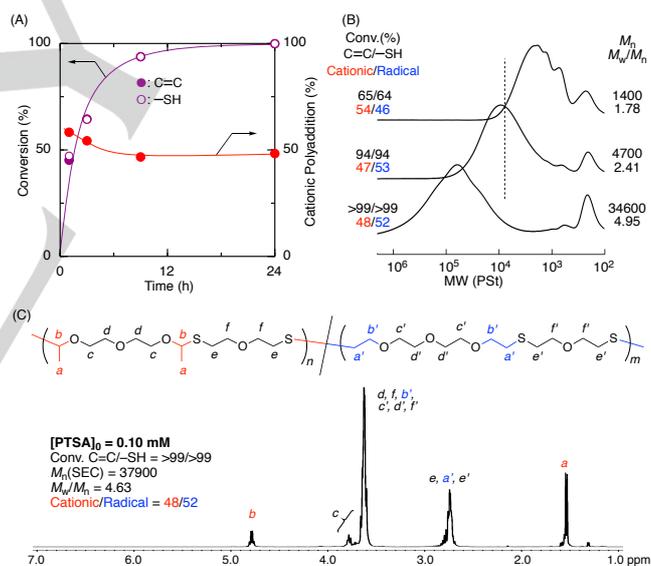


Figure 6. Simultaneous cationic/radical step-growth polymerization of VE-1 and T-1 using PTSA and UV light; [VE-1]₀/[T-1]₀/[PTSA]₀ = 1500/1500/0.10 mM in CH₂Cl₂ at 0 °C.

The simultaneous polymerization was further conducted by changing the concentration of PTSA. Under all the conditions, both thiol and alkene were consumed at the same rate and quantitatively (Figure S13 and Table S2) to yield the polymers, of which the molecular weights increased progressively with the monomer conversions (Figures S14 and S15). The content of thioacetal units or the ratio of the cationic reaction increased as the concentration of PTSA increased (Figures S16 and S17). The unit ratios were thus modulated by the concentration of PTSA. In addition, the T_g values of the obtained polymers increased as the ratio of cationic reactions increased (Figure 7A

and 7B). Thus, the composition of thioacetal and thioether units and the thermal properties of products were arbitrarily tunable by the catalysts during the concurrent cationic and radical step-growth polymerizations.

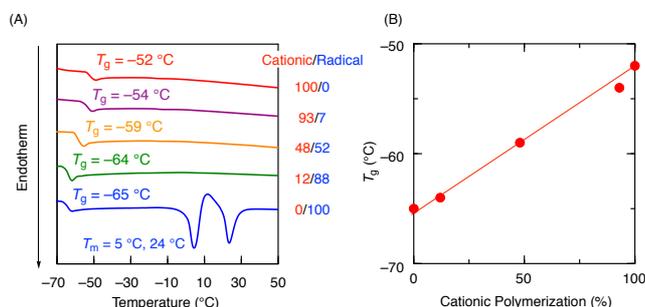


Figure 7. (A) DSC curves of the polymers obtained in simultaneous cationic/radical step-growth polymerization of **VE-1** and **T-1** and (B) effects of the ratio of cationic reaction on T_g values of the obtained polymers; $[\text{VE-1}]_0/[\text{T-1}]_0/[\text{PTSA}]_0 = 1500/1500/0 - 0.20$ mM in CH_2Cl_2 at 0°C .

Conclusion

Thiol and vinyl ether efficiently react under both cationic and radical conditions to result in thioacetal and thioether, respectively, in high yield with high selectivity. The cationic and radical additions are useful not only for 1:1 addition between monothiol and monovinyl ether but also for cyclization and step-growth polymerization between dithiol and divinyl ether, depending on the conditions. Accordingly, the polymers obtained by cationic and radical step-growth polymerizations are poly(thioacetal)s and poly(thioether)s, respectively, which have different properties. In particular, both amorphous poly(thioacetal)s and crystalline poly(thioether)s are accessible from the same pair of monomers just by changing the catalysts. Alternatively, under high dilution conditions, the products obtained by the cationic and radical step-growth polymerizations are 16- and 18-membered cyclic thioacetal and thioether, respectively, which can be used as host or ligand molecules. Concurrent cationic and radical step-growth polymerization is also achievable using organic acid catalysts under UV irradiation to yield polymers linked by both thioacetal and thioether linkages, in which the compositions of the linkages and thermal properties of the polymers can be arbitrarily tuned by the concentration of the acid catalyst. The obtained polymers are supposed to function as polymer electrolytes due to the oxy- and sulfur-ethylene groups and should be degradable polymer materials due to the thioacetal linkages.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201xxxxx>.

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Keywords: polymerization • cyclization • thiol-ene reaction • thioacetal • thioether

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