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A Theoretical Study on the Mechanism of the Cyclopolymerization of Diallyl Monomers

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The cyclization and intermolecular propagation steps of the cyclopolymerization mechanism are studied with density functional theory. In addition to standard cyclization and intermolecular propagation reactions of cyclopolymerization, competing reactions that lead to chain transfer and termination are also discussed. The mechanistic study of the cyclopolymerization reaction of two representative monomers, *N*,*N*-diallylamine (**1**) and *N*,*N*-dimethyl-*N*,*N*-diallylamonium (**2**), was carried out with B3LYP/6-31G* computations. Monomer **1** has almost the same activation barriers for homopolymerization and cyclization. In monomer **2**, cyclization is much more facile than homopolymerization, leading to the higher cyclopolymerization efficiency. In the case of **2**, methyl substituents on nitrogen inhibit hydrogen abstraction, whereas in **1**, hydrogen abstraction reactions from the neutral monomer yield stabilized products leading to chain transfer. Calculations show that facile competing reactions of monomer **1** lower the polymerization efficiency. Monomer **2** displays a stronger preference for cyclization relative to other processes.

Introduction

Allyl monomers are generally considered as poor monomers for radical polymerization, since chain transfer reactions take place readily by abstraction of allylic hydrogens of monomer by the propagating radical.[1] This forms a more stable, resonance-stabilized radical species, decreasing the polymerization efficiency and the molecular weight of the polymer. However, Butler's cyclopolymerization mechanism made it possible to synthesize high molecular weight water-soluble polymers from diallyl monomers.[1−4] The cyclopolymerization of diallyl monomers occurs by the four steps shown in Scheme 1.

Diallyl monomers are employed in various cyclopolymerization and cyclocopolymerization processes, and great effort has been spent on tailor-making of the final products. However, all the factors that control different pathways of cyclopolymerizations are not clear yet.

In previous studies, we have modeled various diallyl monomers to account for the experimentally observed ring sizes in cyclization and explained the origins of regioselectivity based on steric and electronic factors.[5−7] In this work, the cyclization and intermolecular propagation steps of the cyclopolymerization mechanism have been studied from both kinetic and thermodynamic viewpoints. In addition to standard cyclopolymerization

SCHEME 1. Cyclopolymerization Mechanism

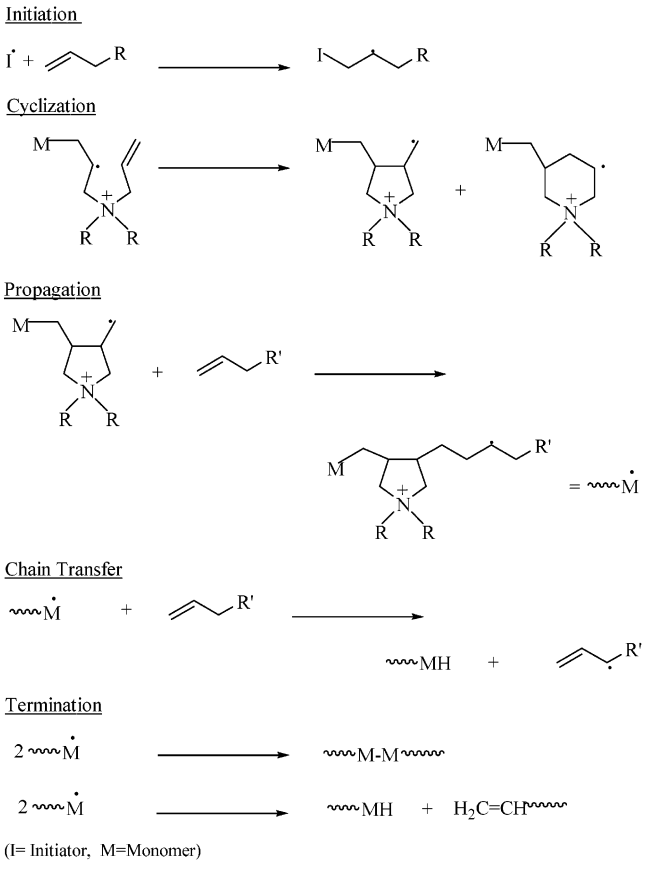

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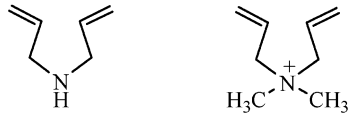
CHART 1. Modeled Monomers



1 **2**

reactions, competing reactions and their efficiencies are also discussed. Two representative monomers, *N*-diallylamine (**1**) and *N*,*N*-dimethyl-*N*,*N*-diallylamonium (**2**) (Chart 1), were studied on the basis of the fact that the monomers are relatively small molecules, and **2** is industrially used in a variety of areas.[8] Additionally, **1** has very low polymerizability while **2** has good polymerization efficiency.[9] In general, cationic monomers polymerize better than neutrals, which has been attributed to the high chain-transfer efficiency of neutral monomers.[1] Thus, the effect of the positively charged allylic substituent in compound **2** is discussed in comparison to the neutral compound **1**.

Methodology

Conformer searches have been performed and structures corresponding to the local minima on the energy hypersurfaces have been located for each compound with the B3LYP functional[10] and the 6-31G* basis set in the Gaussian 98[11] package. Among the conformers located for each compound, the global minimum was chosen, and its nature was confirmed by frequency analysis. The same procedure has been applied to locate the transition structures. In previous studies on the cyclization of diallyl monomers,[5−7] density functional theory[12−15] with the B3LYP[16] functional has been successful for the understanding of the regioselectivity and stereoselectivity of cyclopolymerization. Radom and co-workers have also found that B3LYP/6-31G* geometries are satisfactory in radical reactions, although accurate energetics require more extensive calculations.[17,18]

Single-point calculations in water were performed with the PCM methodology[19] on the geometries obtained from vacuum optimizations. With this methodology, specific solvent−solute interactions are not taken into consideration, and the molecule is placed in a polarizable cavity. However, specific solute−solvent interactions are expected to play a minor role, since Wandrey et al. showed that variations in solvent polarity did not affect the regioselectivity or stereoselectivity of cyclopolymerization of **2**.[8] However, the polar medium is important for overall reaction energies and barriers of reactions of charged species.

The energies listed in the tables are electronic energies for vacuum or electronic energies corrected with free energies of solvation. Differences between ground-state structures and transition structures are labeled as Ea, while the differences in energies of product and reactant are listed as ΔE.

Model compounds used in previous studies have been successful in reproducing the regioselectivity and stereoselectivity in cyclopolymerization.[6,7] Simple alkyl radicals are found to be adequate models of growing polymer radicals for computational efficiencies of radical polymerization reactions.[17] In this study, models are also employed to simplify the long polymer chain. In previous studies of **1** and **2**, the preferential formation of five-membered rings in these cyclization reactions was explained.[6−7,20−22] Consequently, the propagation and hydrogen abstraction reactions of six-membered rings have not been considered further in this work.

Results and Discussion

The cyclopolymerizability of a monomer can be enhanced by suppressing the competing reactions. The effect of monomer structure on the efficiency of cyclopolymerization reactions of monomers **1** and **2** is explored and compared to rates of unproductive side reactions. Once an unreacted monomer is attacked by the initiator or by the propagating polymer chain, the radical formed has mainly three alternative pathways: (1) cyclization as a part of the cyclopolymerization process (Scheme 2, cyclization); (2) attack on another unreacted monomer (Scheme 2, homopolymerization); (3) abstraction of an allylic hydrogen (Scheme 2, intramolecular and intermolecular hydrogen abstraction reactions). Hydrogen abstraction forms resonance-stabilized species that have low reactivity and reinitiation capacity. In a study on allyl acetate, deuteration of the allylic hydrogens resulted in three times faster polymerization of the monomer.[23] Hydrogen abstraction acts as a termination reaction, known as degradative chain transfer.

The model reactions studied here are compared with the actual cyclopolymerization processes. The energy barriers and reaction energies discussed in the text refer to the predicted energetics in water ($\epsilon = 80$) unless otherwise stated.

Cyclization

The cyclization step acts as a driving force for polymerization, since it generates the highly reactive and nucleophilic primary radical. The monofunctional counterparts of **1** and **2** do not have homopolymerization tendencies.[24] For example, allyltrimethylammonium cation ($CH_2CHCH_2N(CH_3)_3^+$) could not be polymerized even under conditions where allylamine can be polymerized to a certain extent.[1] However, **2**, the difunctional ana-

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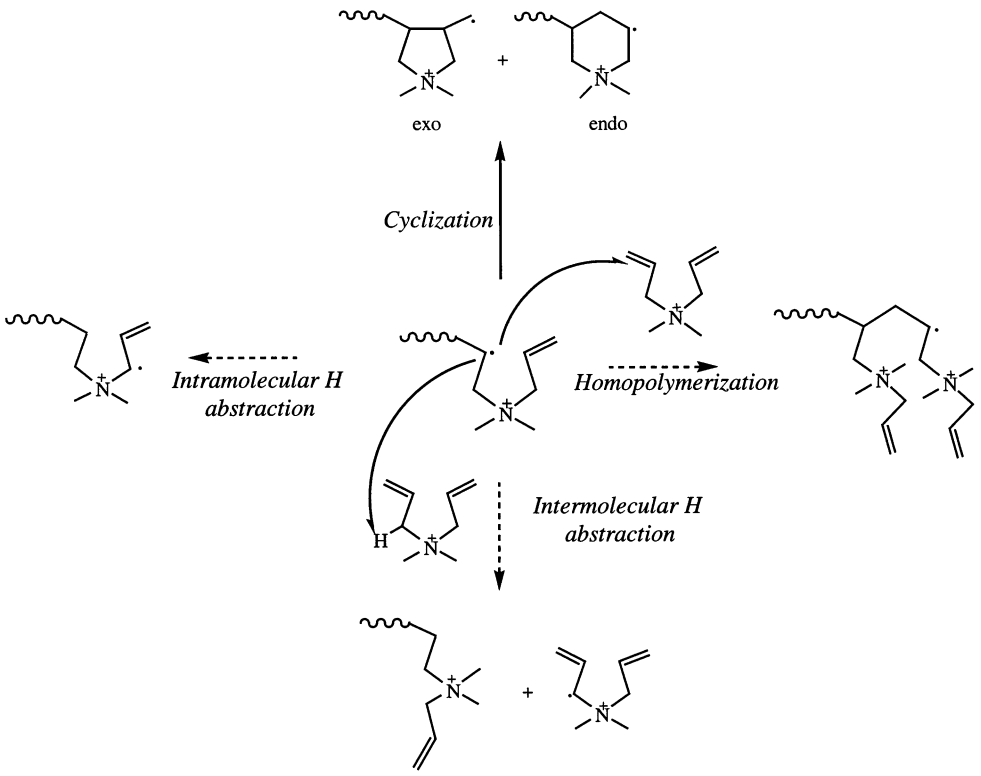
SCHEME 2. Cyclization and the Possible Competing Reactions



logue of the allyltrimethylammonium monomer, could be polymerized to high molecular weights with success.[8]

Previous studies on the cyclization of these monomers exhibited similar properties to the cyclization of hexenyl radicals.[25−32] Although the endo preference might be expected because a secondary radical is more stable than a primary radical,[3] the exo cyclization was found to be favored over the endo by 3.4 kcal/mol in **1** and by 4.2 kcal/mol in **2** (Scheme 3).[6] These results are consistent with the exclusive exo preference of these monomers.[6−9,20−22] As with 1-hexenyl radicals,[25−32] the exo selectivity results from the more favorable overlap of the reacting centers in the transition state.[6,7]

The energy barriers for cyclization show that cyclization is facile with both **1** and **2**, in the gas phase and in solution (Scheme 3). The cation **2** has a lower barrier for cyclization than **1**, which is also consistent with the superior cyclopolymerizability of **2**.

Cyclization vs Homopolymerization. Comparisons of energy barriers for model reactions of homopolymerization and cyclization show that the energy difference is 6.3 kcal/mol for monomer **2** and only 2.1 kcal/mol for monomer **1** in favor of cyclization (Scheme 3). Although the preexponential factors are not considered in this comparison, the trend will be reinforced by their inclusion, because the bimolecular reaction homopolymerization has a more negative activation entropy than the unimolecular cyclization reaction (−40.3 cal/mol K vs −8.9 cal/mol K for **2** in the gas phase). Thus, homopolymerization is much more facile in the neutral monomer than it is in the cationic monomer. Furthermore, only cyclized radicals have been observed by ESR studies on the cyclopolymerization of **2**, indicating the higher rate of cyclization as compared to the intermolecular attack.[33]

The cyclization and homopolymerization reactions show almost the same exothermicities for monomer **2**, but homopolymerization is more exothermic than cyclization for monomer **1**. Tedder et al. have reported that in free-radical reactions, if the exothermicity of a reaction is large and negative, the reaction will be fast and unselective, other factors being less important.[34] In that respect, the homopolymerization of **1** may be enhanced by high exothermicity.

Cyclization vs Hydrogen Abstraction (or Chain Transfer). The high polymerization of monomer **2** is attributed to its low chain-transfer efficiency. In general, cationic monomers are known to have less efficient chain-transfer reactions than neutral ones.[1] This may be due to kinetic or thermodynamic factors. The steric effects around the allylic hydrogen or the inductive effect of neighboring groups may increase the barrier for hydrogen abstraction. It has been proposed that the electron-withdrawing substituents increase the allylic C−H bond strength, thus decreasing degradative chain-transfer reaction.[35]

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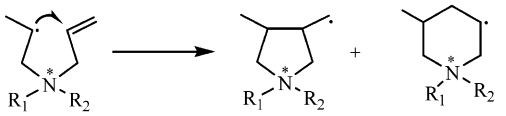
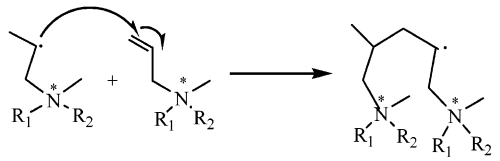
SCHEME 3. Model Reactions and Energetics for Cyclization and Its Competing Reactions

Model Reaction for Cyclization



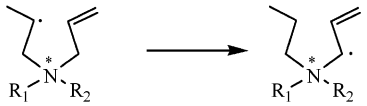
R_1	R_2	Charge (*)	Ea_{exo} (ε=1)	Ea_{exo} (ε=80)	Ea_{endo} (ε=1)	Ea_{endo} (ε=80)	ΔE_{exo} (ε=1)	ΔE_{exo} (ε=80)	ΔE_{endo} (ε=1)	ΔE_{endo} (ε=80)
H	-	0	7.3	6.8	10.9	10.2	-10.9	-11.8	-19.9	-20.9
CH_3	CH_3	1	6.2	3.8	10.3	8.0	-13.1	-14.8	-21.8	-24.1

Model Reaction for Homopolymerization



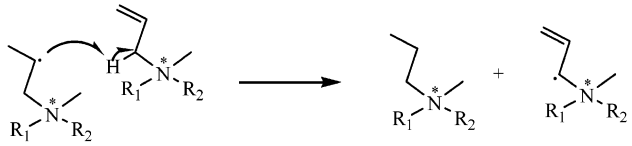
R_1	R_2	Charge (*)	Ea (ε=1)	Ea (ε=80)	ΔE (ε=1)	ΔE (ε=80)
H	-	0	3.9	8.9	-22.3	-18.4
CH_3	CH_3	1	52.6	10.1	29.8	-13.7

Model Reaction for Intramolecular H-abstraction



R_1	R_2	Charge (*)	Ea (ε=1)	Ea (ε=80)	ΔE (ε=1)	ΔE (ε=80)
H	-	0	18.8	19.6	-23.4	-22.7
CH_3	CH_3	1	19.5	22.5	-9.8	-6.4

Model Reaction for Intermolecular H-Abstraction by the Propagating Polymer Chain



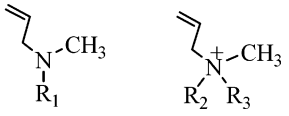
R_1	R_2	Charge (*)	Ea (ε=1)	Ea (ε=80)	ΔE (ε=1)	ΔE (ε=80)
H	-	0	6.4	14.2	-25.1	-23.6
CH_3	CH_3	1	71.1	29.8	-5.8	-2.4

To dissect the factors that control the hydrogen abstraction in monomers **1** and **2**, hydrogen abstraction reactions with methyl radical were modeled for model structures **M1**$_{a-c}$ and **M2**$_{a-c}$ (Chart 2). In these models, the steric effects of both radical and the substrate are relieved to a great extent.

The barrier for hydrogen abstraction from the monofunctional analogues of monomer **2**, **M2**$_c$, is higher than for **M1**$_a$, which is the monofunctional counterpart of **1**. The cation increases the barrier for hydrogen abstraction by strengthening the C−H bond by the inductive effect. To refine the barrier for hydrogen abstraction from the steric effects of methyl groups on nitrogen, **M2**$_a$ and **M2**$_b$ are studied. The barrier is almost unaffected. The −CN group in **M1**$_c$ is another model studied, exhibiting the inductive effect of a cationic center in the absence of the steric effects. The barrier to hydrogen abstraction is almost 2 kcal/mol lower in energy than the cationic, yet higher than models **M1**$_a$ and **M1**$_b$. Thus, the inductive effect of allylic substituents increase the C−H bond strength.

Cyclization vs Intramolecular Hydrogen Abstraction. After initiation, the radical that forms on the secondary carbon may undergo intramolecular hydrogen abstraction, rather than the cyclization (Scheme 2). The activation energies for this reaction in both media are much higher than those for the cyclization of compounds **1** and **2** (Scheme 3). The energy of hydrogen abstraction is −22.7 kcal/mol for the neutral and −6.4 kcal/mol for the cation. This indicates that the intramolecular hydrogen abstraction will not decrease the cyclopolymerization efficiency of monomer **2**, but the high exothermicity may facilitate the intramolecular hydrogen abstraction for the neutral monomer **1**.

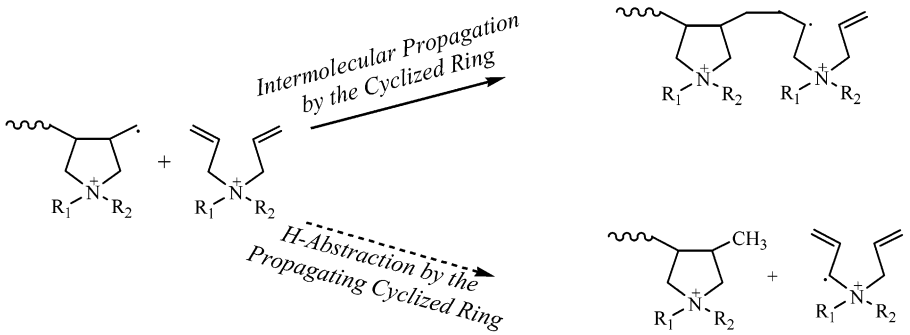
CHART 2. Energetics of Hydrogen Abstraction from Model Structures $M1_{a-c}$ and $M2_{a-c}$ by Methyl Radical



M1 **M2**

Model	R_1	R_2	R_3	Ea (ε=1)	Ea (ε=80)	ΔE (ε=1)	ΔE (ε=80)
$M1_a$	H	-	-	4.5	6.8	-33.7	-32.9
$M1_b$	CH_3	-	-	6.7	8.7	-28.3	-28.0
$M1_c$	CN	-	-	7.1	10.2	-28.8	-26.4
$M2_a$	-	H	H	6.8	12.3	-19.2	-17.8
$M2_b$	-	H	CH_3	7.4	12.0	-20.4	-19.2
$M2_c$	-	CH_3	CH_3	8.3	12.6	-18.9	-18.0

SCHEME 4. Intermolecular Chain Propagation and H-Abstraction by the Cyclized Ring



Cyclization vs Intermolecular Hydrogen Abstraction by the Propagating Polymer Chain. Another conceivable reaction is the intermolecular hydrogen abstraction by the propagating uncyclized radical. For the neutral monomer, **1**, the gas-phase activation energy of intermolecular hydrogen abstraction by the polymer chain is almost the same as the barrier for cyclization, but this trend is reversed in solution (Scheme 3). For monomer **2**, cyclization dominates over the intermolecular hydrogen abstraction.

Hydrogen abstraction reaction by the methyl group is a good indicator of the allylic C−H bond strength, since the reaction involves no significant steric effects. To understand the steric effect of allyl group in the attacking radical, the model reaction of hydrogen abstraction by the uncyclized propagating radical has been studied (Scheme 2, intermolecular hydrogen abstraction). Steric effects, mimicked by the uncyclized propagating radical increase the barrier by 17.2 kcal/mol in **2** and 7.4 kcal/mol in **1** as compared to their hydrogen abstractions by the methyl radical (Scheme 3 and Chart 2). Thus, these values may indicate the steric effects caused by the cationic monomer toward hydrogen abstraction. The intermolecular hydrogen abstraction reaction is exothermic by −23.6 kcal/mol for the neutral monomer (**1**). In the cationic monomer (**2**), the reaction is exothermic by only −2.4 kcal/mol. The stability of the neutral product will facilitate hydrogen abstraction as in the case for intramolecular hydrogen abstraction.

Comparison of activation energies for cyclization versus competing reactions indicates that in **2**, the hydrogen abstractions do not compete with cyclization. The barriers for allylic hydrogen abstraction reactions are relatively high in the cationic monomer, leading to higher polymerization efficiency. In the neutral monomer homopolymerization reaction can compete readily with cyclopolymerization. Furthermore, the hydrogen abstraction reactions are more competitive, and the resulting products are much more stable than the cationic monomers. The product stability may lead to degradative chain transfer and decrease the polymerization efficiency of the neutral monomer.

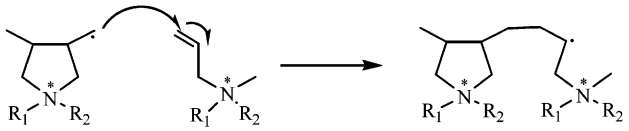
Intermolecular Chain Propagation

After cyclization, the cyclic radical can attack another monomer and lead to cyclopolymerization propagation (Scheme 4, intermolecular propagation by the cyclized ring). The degradative chain transfer reactions may take place by the abstraction of a H from an unreacted monomer by the ring (Scheme 4, hydrogen abstraction by the cyclized ring) and thus decrease the propagation efficiency. These reactions are modeled here by the model reactions in Scheme 5.

For monomer **2**, the activation energy for homopolymerization is 10.1 kcal/mol (Scheme 3) whereas the barrier decreases to 7.1 kcal/mol along the intermolecular propagation reaction by the cyclized ring (Scheme 5). In the case of **1**, these barriers are 8.9 kcal/mol (Scheme 3) and 8.6 kcal/mol (Scheme 5), respectively. Thus, cyclization facilitates the intermolecular propagation of monomer **2** slightly.

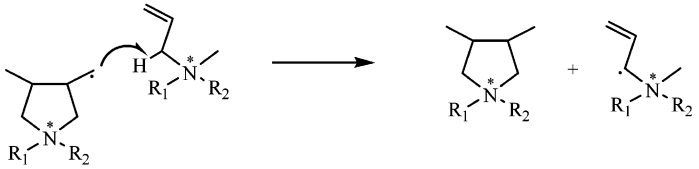
SCHEME 5. Model Reactions and Energetics for Intermolecular Propagation and Hydrogen Abstraction Reactions by the Ring

Model Reaction for Intermolecular Propagation Reaction



R_1	R_2	Charge (*)	Ea (ε=1)	Ea (ε=80)	ΔE (ε=1)	ΔE (ε=80)
H	-	0	4.6	8.6	-24.6	-22.1
CH_3	CH_3	1	44.9	7.1	16.5	-24.0

Model Reaction for Intermolecular H-abstraction by the Propagating Ring



R_1	R_2	Charge (*)	Ea (ε=1)	Ea (ε=80)	ΔE (ε=1)	ΔE (ε=80)
H	-	0	6.6	14.2	-28.3	-26.2
CH_3	CH_3	1	60.3	22.3	-14.7	-11.0

The energy barrier to hydrogen abstraction by the propagating cyclized ring is 22.3 kcal/mol in **2**, while this barrier is 14.2 kcal/mol in **1**. Hydrogen abstraction is more plausible in the neutral monomer **1** such that the barrier is 5.6 kcal/mol higher than the intermolecular propagation reaction while in **2** this difference is 15.2 kcal/mol. Furthermore, the intermolecular propagation reactions by the cyclized ring have almost the same exothermicities (−24.0 kcal/mol for **2** and −22.1 kcal/mol for **1**) (Scheme 5) but hydrogen abstraction reaction by the ring produces a much more stable allylic radical in the neutral monomer ($\Delta E = -26.2$ kcal/mol) whereas this stabilization is not present with monomer **2** ($\Delta E = -11.0$ kcal/mol).

Conclusion

In monomer **1**, homopolymerization and cyclization have almost the same activation barriers. Therefore, homopolymerization competes with cyclopolymerization. In monomer **2**, cyclization is much more facile than homopolymerization leading to higher cyclopolymerization efficiency.

The hydrogen abstraction reactions are found to be less effective in the case of the cationic monomer than in the neutral monomer. This conclusion has been reached by monitoring (i) the allylic C−H bond strength, as shown by model compounds, (ii) the steric effect of the neighboring groups in the vicinity of the allylic position in the case of cationic monomer which decreased the efficiency of hydrogen abstraction, and (iii) the stability of the neutral products formed by hydrogen abstraction as compared to the cationic ones.

Cyclization is found to facilitate the intermolecular propagation in cyclopolymerization by decreasing the barrier for intermolecular attack with respect to homopolymerization.

Overall, the competing reactions are more facile for monomer **1** than for monomer **2**, and the products of competing reactions for the neutral monomer are thermodynamically much more stable than products of the standard cyclopolymerization reactions.

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Supporting Information Available: Coordinates and the total energies of the stationary structures and the transition states discussed in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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