A Computational Study on the Substituent Effect of Diallylamine Monomers in Their Cyclopolymerization Reactions

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The cyclization reactions of *N*-methyl-*N*,*N*-diallylamine (**1**), *N*-methyl-*N*-allyl-2-(methoxycarbonyl)allylamine (**2**), and *N*-methyl-*N*-methallyl-2-(methoxycarbonyl)allylamine (**3**) have been modeled in their cyclopolymerization mechanism. The experimentally observed regioselectivity has been reproduced and explained in terms of steric and electronic factors. The activation energies for the cyclization of the model compounds representing **1**, **2**, and **3** are 5.41, 8.68, and 11.59 kcal/mol, respectively. The ester substituent on **2** and **3** is found to increase the activation energy of the exo transition structure by its steric effect without making a significant effect in the barrier height of endo. The destabilization on the exo transition structure is enhanced by methyl substitution on the double bond. The experimentally determined stereoselectivity for **1** and **2** have also been reproduced. The lower activation energy for **1** despite its low polymerizability is justified by considering the dominance of competing reactions, like H-abstraction and homopolymerization.

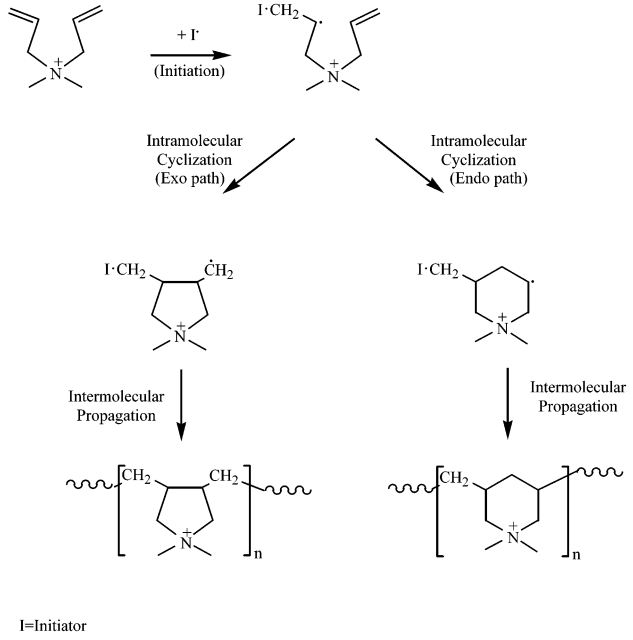
Introduction

Allyl compounds are known as poor monomers for polymerization.They have been polymerized only under special complexing reaction conditions.[1,2] Although monofunctional allyl compounds are not good monomers for polymerization, their difunctional analogues have been found to be polymerized to high molecular weights through cyclopolymerization, as discovered by Butler's pioneering work.[3−5] Since then, several cyclopolymers have been synthesized. These cyclopolymers have found wide usage in industry because of their advantageous physical and chemical properties.

The cyclopolymerization reaction of diallylamines occurs by alternating intramolecular cyclization and intermolecular propagation steps (Scheme 1). In the radical cyclopolymerization, the attack of the initiator produces a radical at the vinylic carbon (initiation, Scheme 1). The secondary radical attacks intramolecularly the other C═C double bond, and produces a five-membered (exo path, Scheme 1) or a six-membered ring (endo path, Scheme 1) on the polymer chain depending on the site of attack. The cyclized monomer reacts with another monomer and the polymerization propagates (intermolecular propagation, Scheme 1).

In cyclopolymerization, usage of monomers whose monofunctional counterparts do not homopolymerize have been found to enhance the cyclization efficiency of the monomer.[6] However, high cyclization efficiency was not always accompanied by an increase in polymerization. Thus, it became important to use monomers that have both high cyclization efficiency and high polymerization capability. In that respect, compounds **1** (*N*-methyl-*N*,*N*-diallylamine), **2** (*N*-methyl-*N*-allyl-2-(methoxycarbonyl)allylamine), and **3** (*N*-methyl-*N*-methallyl-2-(methoxycarbonyl)allylamine) (Figure 1) have drawn considerable attention. Kodaira et al. have reported that **2** has both high cyclization efficiency and high cyclopolymerizability.[7,8] Monomers **1** and **2** have been found to undergo five-membered cyclization whereas **3** formed six-membered rings along with decreased polymerization tendency as compared to **2**.[7−9] These observations were attributed to steric and/or electronic factors due to the ester and methyl substitution on the C═C double bonds.

SCHEME 1: Mechanism of Cyclopolymerization



I=Initiator

In our earlier work, the intramolecular cyclization of a series of diallylamine and diallylammonium monomers has been studied by using quantum chemical methods.[10,11] The steric and electronic factors that influence cylization have been explained and rationalized.[10,11] This paper aims a mechanistic study of the intramolecular cyclization reactions for **1**, **2**, and **3** with the same methodology. The steric and electronic effects of methyl and acetate substitution on the cyclization efficiency of *N*-methyl-*N*,*N*-diallylamine will be discussed. The regioselectivity of ring closure will also be considered. The computational findings will be compared with the experimental polymerizabilities.

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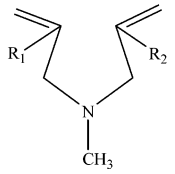


Monomers	R_1	R_2
1	H	H
2	$COOCH_3$	H
3	$COOCH_3$	CH_3

Figure 1. Monomers studied in this work.

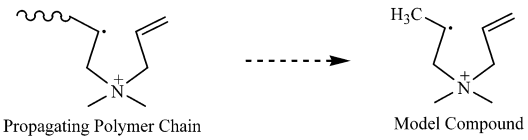


Figure 2. Model for radical intermediates in cyclopolymerization reaction.

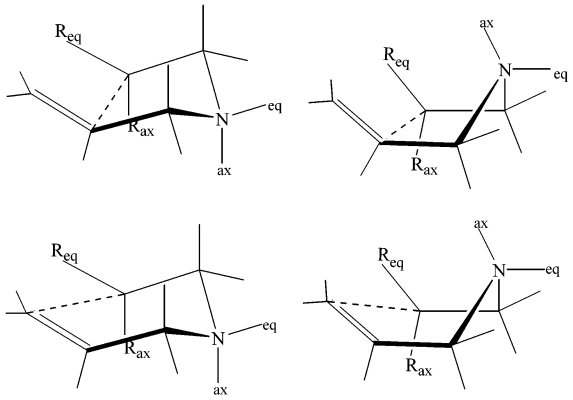


Figure 3. Chair and boat transition structure conformers for five-membered and six-membered ring cyclizations.

Methodology

We have simplified the long polymer chain and have used model compounds for monomers **1**, **2**, and **3** (Figure 2) to reduce the computational cost as in our earlier studies.[10,11] In the models, the long polymer chain is replaced by a hydrogen atom. It has been reported that the monomers behave in the same way in cyclization in their long polymer chains as in their low molecular weight analogues, thus our model can account for the cyclization in the long polymer chains.[7] The model compounds for **1**, **2**, and **3** will be designated by **1′**, **2′**, and **3′**. In the model compounds **1′**, **2′**, and **3′**, initiation has already taken place and the monomer is about to cyclize.

The calculations have been carried out by using the density functional theory,[12−15] with the B3LYP functional[16] and the 6-31G* basis set, using the Gaussian 98 package.[17]

The model compounds of *N*-methyl-*N*,*N*-diallylamine (**1′**), *N*-methyl-*N*-allyl-2-(methoxycarbonyl)allylamine (**2′**), and *N*-methyl-*N*-methallyl-2-(methoxycarbonyl)allylamine (**3′**) were optimized for their global minima. The transition structures for ring formation were modeled for their various conformations depending on the ring size (Figure 3). They will be referred to as chair/boat as in earlier calculations of hex-5-enyl radical.[11,18−25] Frequency calculations have been carried out to confirm the existence of the transition states by verifing for the one imaginary frequency belonging to the reaction coordinate.

IRC[26,27] calculations have been performed on both five- and six-membered transition states for all the models of the monomers and these calculations have led to stationary local minima on both sides. The products and reactants were further optimized for their local minima.

Natural bond orbital[28−32] (NBO) analysis has been carried out on the stationary structures along the cyclization reaction to characterize the stabilizing interactions that may be present in these compounds. CHELP[33] charges for the compounds of interest will also be discussed.

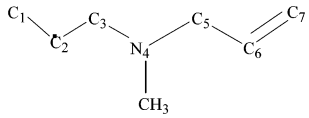
The activation energies, $\Delta E^{\neq}$, free energies of activation, $\Delta G^{\neq}$, entropies of activation, $\Delta S^{\neq}$, heats of reaction, ΔE_{rxn}, and the free energies of reaction, ΔG_{rxn}, are discussed in terms of the cyclization and polymerization efficiencies of the monomers of interest (Table 1).

Throughout the discussion, the numbering system shown in Chart 1 will be used.

TABLE 1: Energetics of 1′, 2′, and 3′ in Their Radical Cyclization Reactions in kcal/mol (Entropy is in cal/mol·K)

energy	**1′**	**2′**	**3′**
reactant	0	0	0
TS_{exo}	5.41	8.68	14.02
TS_{endo}	11.18	12.20	11.59
$product_{exo}$	−11.81	−2.07	3.75
$product_{endo}$	−18.65	−7.88	−8.87
$\Delta S^{\neq}_{exo}$	−9.38	−10.52	−11.92
$\Delta S^{\neq}_{endo}$	−9.98	−11.57	−10.82
$\Delta G^{\neq}_{exo}$	7.26	10.95	16.64
$\Delta G^{\neq}_{endo}$	13.15	14.70	14.00
ΔS_{rxn_exo}	−7.64	−3.61	−11.67
ΔS_{rxn_endo}	−11.91	−10.98	−9.24
ΔG_{rxn_exo}	−10.36	−1.60	6.44
ΔG_{rxn_endo}	−16.29	−5.53	−6.86
$\Delta\Delta E^{\neq}_{endo-exo}$	5.77	3.52	−2.43
$\Delta\Delta S^{\neq}_{endo-exo}$	−0.60	−1.05	1.10
$\Delta\Delta G^{\neq}_{endo-exo}$	5.89	3.75	−2.64

CHART 1: Numbering Scheme Used in This Study



Discussion

Polymerization reactions carried out on compounds **1**, **2**, and **3** have shown that **1** and **2** form exclusively five-membered rings in their polymer backbones whereas **3** forms six-membered ring structures.[7−9] Calculations have been carried out on models for the monomers to understand the factors that affect the regioselectivity in their cyclization reactions. The transition structures corresponding to the cyclizations have shown that **1′** and **2′** have formed exo (five-membered) rings whereas **3′**

prefers the endo (six-membered) ring (Table 1). These results are consistent with the experimental findings.[7−9]

Close inspection of the difference in the activation energies, $\Delta\Delta E^{\neq}$ ($\Delta E^{\neq}_{endo} - \Delta E^{\neq}_{exo}$), for the five- and six-membered transition states of the same monomer, shows that substitution decreases the energy difference between two paths. The $\Delta\Delta G^{\neq}$ ($\Delta G^{\neq}_{endo} - \Delta G^{\neq}_{exo}$) values also reflect the same trend as $\Delta\Delta E^{\neq}$ (Table 1). The energy differences between the exo and the endo transition structures indicate that as substitution on the parent structure, **1′**, increases, the exclusive exo preference decreases either due to destabilization of the exo transition structure with respect to the endo or stabilization of the endo with respect to the exo.

Capon and Rees[34] have interpreted the unexpected exo preference of hexenyl systems in terms of the activation entropy, $\Delta S^{\neq}$. They propose that higher strain energy in the smaller ring is overcome by the more favorable activation entropy of the exo cyclization. $\Delta\Delta S^{\neq}$ ($\Delta S^{\neq}_{endo} - \Delta S^{\neq}_{exo}$) values for **1′**, **2′**, and **3′** are −0.60, −1.0,5 and 1.10 cal/(mol·K), respectively (Table 1). Although the trend is similar to the one observed in the ring size preference, the changes are too small to account for ring preference. For instance, at a very high temperature of 400 K, an energy difference of 1.05 cal/(mol·K) in $\Delta S^{\neq}$, would alter the free energy change only by 0.42 kcal/mol. For compounds **1′**, **2′**, and **3′**, although the numerical values follow the expected trend, the small $\Delta S^{\neq}$ values are far away from behaving as driving force (Table 1).

Julia and co-workers[35] have explained the exo/endo preference of 1,6-ring closures in hex-5-enyl systems by referring to nonbonded interactions that may be present in the six-membered ring. The exo path is favored over the endo for cases where there are unfavorable nonbonded interactions between the pseudoaxial H on C_2 and the syn H on C_6 in the endocylic transition structure of hex-5-enyl system. This distance is 2.62, 2.56, and 2.53 Å for **1′**, **2′**, and **3′**, respectively. Compound **3′** has the shortest C−H distance and yet prefers the endo transition structure. Furthermore, these distances are too long for a significant destabilizing interaction to occur.

In cyclization reactions of the hex-5-enyl radical, Beckwith et al. proposed the conformations of the transition structures to be important in determining the ring size preference.[19] Similarly, in our calculations, the conformations of the transition structures corresponding to the cyclization of **1′**, **2′**, and **3′**, are the key factors in determining the regioselectivity of the cyclization reactions. The three-dimensional orientation of the transition states will be discussed in the following section to account for the regioselectivity observed by both experiments and calculations. The transition states for the cyclization reactions of **1′**, **2′**, and **3′** are similar in many ways to those involved in the cyclization of the hex-5-enyl radical and *N*,*N*-diallylamine and *N*,*N*-diallylammonium monomers considered in our earlier studies as they resemble chair and boat conformations of cyclohexane-like structures (Figure 3).[11]

***N*-Methyl-*N*,*N*-diallylamine (1).** The global minimum for the ground-state structure of **1′**, R1, is in an extended structure with anti conformations about the C−N bonds (Figure 4). There is not a significant delocalization of electrons from the lone pair of nitrogen to the C−N bonds as has been reported to be present in its cationic analogues.[11] The absence of this delocalization can be traced from the C−N bonds being equal to each other (1.465 Å).

The conformation of the transition structure has vital importance in understanding the exo preference of the monomer, which was expected from the Baldwin's rules.[36] The exo

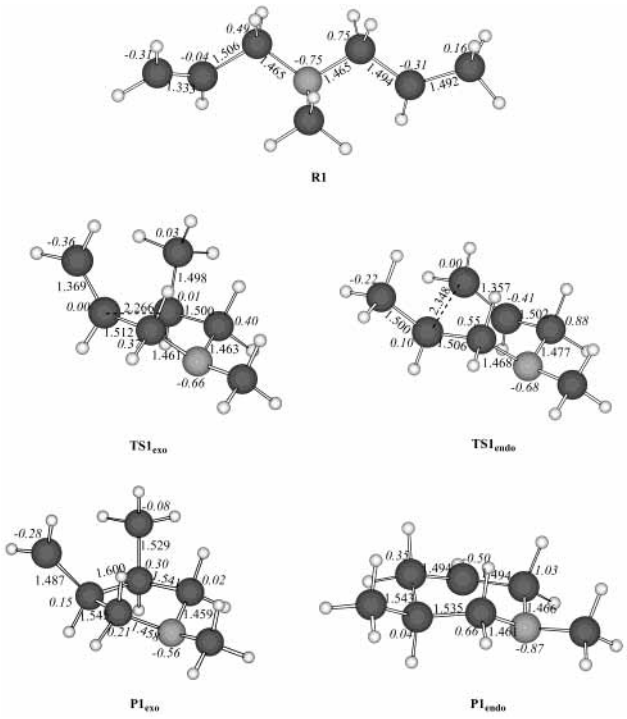


Figure 4. Global minimum, transition structures, and the products for exo and endo cyclization of **1′**.

TABLE 2: Mulliken Bond Orders in the Transition Structures

MBA	1	2	3
$TS_{exo}(C_2-C_6)$	0.105	0.145	0.163
$TS_{endo}(C_2-C_7)$	0.069	0.103	0.098

transition structure ($TS1_{exo}$) is chairlike with the methyl substituent on nitrogen in the equatorial position (Figure 4). In the six-membered transition structure, $TS1_{endo}$, the skeleton of the ring is chairlike and equatorial substitution is favored, as observed in five-membered transition structure (Figure 4). Axial orientation of the methyl group on nitrogen and the axial methyl group on the radical center destabilize the endo less than the exo because a six-membered ring has a more extended structure and it can accommodate the axial substituents more easily. Overall, the predominant factor that determines the stability of the transition structures $TS1_{exo}$ and $TS1_{endo}$ over all the other transition state conformations is based on the equatorial preference of the substituent on the cyclohexane ring.

In $TS1_{exo}$ and $TS1_{endo,}$ the C═C distances have elongated but yet the distances are more reactant-like than product-like. The carbons at the reacting centers have only partial sp^3 character in the transition state. Thus, the geometrical parameters show that both the endo and the exo transition states are early.

The Mulliken bonding analysis (MBA), NBO results, and CHelp charges also confirm the preference for $TS1_{exo}$ versus $TS1_{endo}$. Mulliken bond orders indicate the bond order of the forming C−C bond to be stronger in the case of $TS1_{exo}$ (Table 2). CHelp electrostatic charges (Figure 4) show that the radical center attacks the more electrophilic site (−0.31 vs −0.04) of the C═C double bond and leads to a five-membered ring. The NBO delocalization energy of molecular orbitals involved in bond formation is higher in the exo transition structure than in the endo (Table 3). The stabilizing interactions for five-membered ring formation are 55.79 kcal/mol in $TS1_{exo}$ and 41.47 kcal/mol for $TS1_{endo}$ (Table 3). These analyses show that steric effects as well as electrostatic effects favor exo cyclization.

TABLE 3: Natural Bond Orbital Analysis on the Exo and Endo Transition Structures (Energies in kcal/mol)

$TS1_{exo}$	energy	$TS1_{endo}$	energy
α		α	
$LP(C_2^{\bullet}) \rightarrow BD^*(C_6{=}C_7)$	24.23	$LP(C_2^{\bullet}) \rightarrow BD^*(C_6{=}C_7)$	17.59
$LP(C_2^{\bullet}) \rightarrow BD^*(C_6{=}C_7)$	0.28		
β		*β*	
$BD(C_6{=}C_7) \rightarrow LP^*(C_2^{\bullet})$	0.77	$BD(C_6{=}C_7) \rightarrow LP^*(C_2^{\bullet})$	20.93
$BD(C_6{=}C_7) \rightarrow LP^*(C_2^{\bullet})$	25.05	$LP^*(C_2^{\bullet}) \rightarrow BD^*(C_6{=}C_7)$	2.95
$LP^*(C_2^{\bullet}) \rightarrow BD^*(C_6{=}C_7)$	5.46		
sum	55.79	sum	41.47

$TS2_{exo}$	energy	$TS2_{endo}$	energy
α		α	
$LP(C_2^{\bullet}) \rightarrow BD^*(C_6{=}C_7)$	30.05	$LP(C_2^{\bullet}) \rightarrow BD^*(C_6{=}C_7)$	25.60
$LP(C_2^{\bullet}) \rightarrow BD^*(C_6{=}C_7)$	0.66		
β		*β*	
$BD(C_6{=}C_7) \rightarrow LP^*(C_2^{\bullet})$	1.14		
$LP(C_6) \rightarrow LP^*(C_2^{\bullet})$	143.97	$BD(C_6{=}C_7) \rightarrow LP^*(C_2^{\bullet})$	39.22
sum	175.82	sum	64.82

$TS3_{exo}$	energy	$TS3_{endo}$	energy
α		α	
$LP(C_2^{\bullet}) \rightarrow BD^*(C_6{=}C_7)$	44.44	$LP(C_2^{\bullet}) \rightarrow BD^*(C_6{=}C_7)$	24.36
β		*β*	
$LP(C_6) \rightarrow LP^*(C_2^{\bullet})$	171.78	$LP(C_7) \rightarrow LP^*(C_2^{\bullet})$	110.42
sum	216.22	sum	134.78

In earlier reports on cyclopolymerization of diallyl monomers, the endo preference was expected because a secondary radical that forms at the endo attack is considered to be more stable than the primary radical at the exo attack.[4] Furthermore, a six-membered ring is expected to be more stable than a five-membered one. We have performed calculations on both five- and six-membered products, $P1_{exo}$ and $P1_{endo}$, and have observed this expectation to hold (Table 1). The endo product is lower in energy than the exo product by 6.84 kcal/mol, but the experimental observation and our calculations of activation energy indicate that the stability of the product has no effect on the regioselectivity.

Although the Mulliken bonding analysis and the NBO analysis can be used to rationalize the preference of $TS1_{exo}$ vs $TS1_{endo}$, the three-dimensional structure of the transition state is the key factor in explaining the observed regioselectivity. As explained earlier,[5,6] in the exo transition state, the p-orbital of the radical center and the π orbital of C−C double bond provide an efficient overlap geometry. On the other hand, in the 6-endo transition state, the reacting centers do not have an efficient overlap. This enhanced overlap efficiency of the 5-exo transition state overcomes the stability of the six-membered ring structure and all other effects that may favor an endo product. The atom−atom overlap weighted natural atomic orbital analysis reveals the bond order for the forming bond to be higher in exo than in endo transition state (0.2539 in $TS1_{exo}$ and 0.2087 in $TS1_{endo}$). Thus, our findings indicate both the electronic and steric effects to favor the formation of the exo structure.

In a ^{13}C NMR study on polymerization of **1**,[9] the cis:trans ratio is found to be 5:1, whereas the calculated ratio is 1.6:1 at 25 °C. In our calculations, the qualitative trend is obeyed. The C═C bond, being anti with C−N bonds provides a chairlike geometry to the system. The pseudoequatorial substitution on C_1 is preferred because equatorial substitution is preferred for the cyclohexane ring. In the trans transition structure, the methyl group is in pseudoaxial orientation and this destabilizes the system by only 0.27 kcal/mol. In the real polymerization process, the long polymer chain is on C_1 and, hence, this causes much more destabilization than in the model system. Thus, the calculated cis:trans ratio is lower than expected.

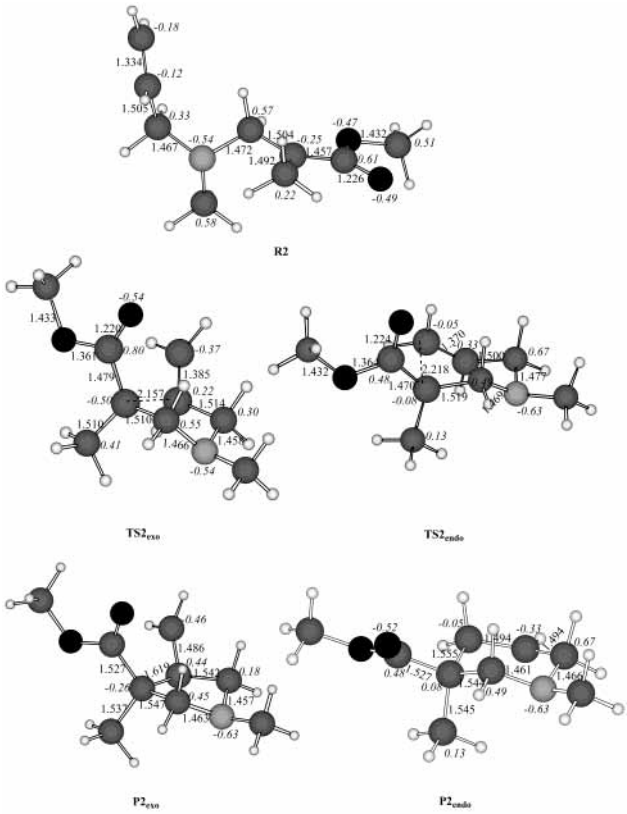


Figure 5. Global minimum, transition structures, and the products for exo and endo cyclization of **2′**.

***N*-Methyl-*N*-allyl-2-(methoxycarbonyl)allylamine (2).** The initiation reaction of the ester-substituted diallyl compounds has been found to start from the ester side.[7,8] This assumption has been tested by modeling the radicals formed after the initiation from both the allyl and the ester sides. The radical that formed by initiation from the ester side is found to be 7.40 kcal/mol more stable than the radical that formed by initiation from the allyl side. The stability of the radical formed by initiation from the ester side, **2′**, is obviously due to the conjugation between the C═O bond and the radical.

The structure corresponding to the global minimum of compound **2′**, R2, does not adopt an all anti orientation in its backbone as in the case of R1 (Figure 5). The radical center, C═O and the oxygen of ester group are all coplanar, as expected for maximum delocalization. The methyl group on the ester is syn with the C═O group. Due to the lack of symmetry in R2, the C−N bonds are not equal to each other as in R1.

Methyl ester substitution on *N*-methyl-*N*-*N*-diallylamine, **1**, did not alter the regioselectivity for the cyclization reaction and the exo cyclization is preferred over the endo (Table 1). In $TS2_{exo}$, the skeleton of the transition state is chairlike (Figure 5). The ester group, being bulkier than methyl, occupies the pseudoequatorial orientation. The methyl group on nitrogen is also in the equatorial position. **2′** has a chairlike transition structure in its six-membered transition state, $TS2_{endo}$, as in **1′** (Figure 5). The methyl on nitrogen and the ester substituent prefer the equatorial position as in $TS2_{exo}$. As in the case of $TS1_{exo}$, the axial methyl group on nitrogen destabilizes the transition state less in its endo analogue because the six-membered ring, being more flexible than the five-membered ring can accommodate the axial group much better.

Both the endo and the exo paths have early transition states and $TS2_{endo}$ is earlier than $TS2_{exo}$ such that the C═C bond is longer and the carbons at the reacting centers have more sp^3 character in $TS2_{endo}$. The geometrical changes in $TS2_{exo}$ and $TS2_{endo}$ indicate that **2′** has a later transition state than **1′**.

The Mulliken bonding analysis, NBO results, and the CHelp charges also confirm the experimental regioselectivity as in the case of **1′**. The Mulliken bonding analysis for exo and endo transition states showed stronger bonding for the five-membered transition structure than for the six-membered (Table 2). NBO results show that there is a greater donor−acceptor interaction in $TS2_{exo}$ than in $TS2_{endo}$ (Table 3). CHelp charges indicate that the ester group provides conjugation between the radical center and the C−O bonds. The electron density on C_2 is smaller in R2 as compared to R1. As in the case of **1**, the preferred site of attack on the C_6═C_7 double bond is C_6, which is slightly more electrophilic than C_7.

Compound **2** is reported to produce dominantly the trans product in its polymers.[7] Our calculations account for the experimentally observed stereoselectivity. The experimentally observed activation energy difference for the trans−cis cyclization is determined to be 1.07 kcal/mol.[7] We have calculated this energy difference as 1.51 kcal/mol. The cis:trans ratio is reported to vary from 10:90 to 34:66 by changing the temperature in the range −78 to +180 °C.[7] The cis:trans ratio is calculated to be 27:73 at 180 °C. Decreasing the temperature to 25 °C increases the trans content to 13:87. Thus, our calculations produce the experimental trend qualitatively.

Steric Effect of the Ester Group in Cyclization. The ester group behaves as a bulky substituent on a cyclohexane ring. In its endo and exo transition states, it acquires the most stable orientation with respect to the ring, i.e., the equatorial orientation on C_2. This causes a change in the skeleton of the ring, such that in **1**, the cis conformation is the preferred geometry but in **2** the trans orientation is preferred.

The bulky group causes steric hindrance in both exo and endo ring closures and steric crowding at the reacting sites. This increases the activation energy of cyclization because the reacting centers have to undergo more conformational change in trying to attain the suitable geometry for cyclization reaction at the expense of energy cost. This effect is more pronounced in the exo transition structure because a five-membered ring is less extended than a six-membered ring and can accommodate the ester group less easily. Thus, as a result of inclusion of the ester group in the parent structure, the activation energy for exo cyclization of **2′** is higher by 3.27 kcal/mol than that of **1′** whereas, this increase is only 1.02 kcal/mol in the case of endo cyclization.

Furthermore, if there is extended delocalization involving the radical center in radical addition reactions, the radical center is reported to resist pyramidalization.[37] This effect may lead to an increase in the activation energy of **2′** with respect to **1′**.

Electronic Effect of the Ester Group in Cyclization. According to NBO analysis, the radical on C_2 has more stabilizing interactions with the ester side of the molecule than the nitrogen. The NBO energies for the interaction of the lone pair on C_2, $LP(C_2)$, with the antibonding lone-pair on C of C═O (LP*) is 128.08 kcal/mol, whereas interaction of $LP(C_2)$ with the antibonding orbital of the C_3—N_4 bond ($BD^*(C_3—N_4)$), is 3.52 kcal/mol and the interaction of $LP(N_4)$ with $BD^*(C_2—C_3)$ is only 0.88 kcal/mol. The radical on C_2 is delocalized with the ester group as expected. Due to these interactions and the decreased electron density on C_2 (−0.25 vs −0.31), the radical is reluctant to attack the C═C double bond.

Effect of the Ester Group in Polymerization. In the real polymerization reaction, there are a number of reactions other than cyclopolymerization, like homopolymerization or chain transfer reactions by H-abstraction from the allylic C. In our calculations, these reactions are not taken into account. The monofunctional counterpart of diallyl compounds, the allyl monomers, have low polymerization and this was attributed to chain transfer reaction by hydrogen. The secondary radical that forms by H-abstraction in chain transfer reactions is stabilized by resonance and is reluctant to polymerize. In that respect, the chain transfer reaction acts as a termination reaction. In the diallyl monomers, the cyclopolymerization takes place, overcoming the competing reactions such as H-abstraction and homopolymerization.

Although the diallylamine monomer **1** has a low barrier for cyclization, it is less polymerizable with respect to **2** because it still suffers from H-abstraction. The ester group may have steric and electronic effects in diminishing the H-abstraction and, thus, enhances cyclopolymerization. The secondary radical that forms at C_2 before cyclization is stabilized by the conjugation of the ester group and abstracts the H less readily. This is verified by the NBO delocalization energies and decreased electron density on the radical center. Second, the ester group may cause bulkiness in the vicinity of the hydrogens to be abstracted and this may decrease H-abstraction efficiency. Thus, chain transfer reaction by H-abstraction plays an important role and is more dominant in **1** than in **2**, although the cyclization reaction is more facile with **1**. This is also conformed by the allyl C−H bond lengths in the global minimum which are 1.112, 1.106, 1.109, and 1.100 Å in R1′ and 1.101, 1.102, 1.099, and 1.107 Å in their analogues in R2′. Comparison of allylic C−H bond lengths in **1′** and **2′** shows that the C−H bonds are stronger in **2′** than in **1′**, diminishing chain transfer reaction by H-abstraction.

In addition, the ester group may suppress homopolymerization. It is known that the monomers whose monofunctional part do not have polymerization tendency increase cyclopolymerizability.[6] The functional counterparts of **2** are known to undergo poor polymerization.[7,8] Thus, the monomer with the ester group has an enhanced cyclopolymerization tendency than homopolymerization, which is another competing reaction for cyclopolymerization.

***N*-Methyl-N-methallyl-2-(methoxycarbonyl)allylamine (3).** Initiation in **3** can produce a secondary radical on both sides of the diallyl compound, and our calculations have shown that initiation takes place from the ester site as in the case of **2**. The secondary radical that forms upon initiation from the ester side (C_2) is found to be 7.06 kcal/mol more stable than the structure with a secondary radical at C_6. Thus, our calculations account for the presence of the methallyl pendant unsaturation encountered in polymers of *N*-methyl-*N*-allyl-2-(methoxycarbonyl)-allylamine.[8]

The global minimum for the model of *N*-methyl-*N*-methallyl-2-(methoxycarbonyl)allylamine (R3) has almost the same three-dimensional structure as the global minimum for *N*-methyl-*N*-allyl-2-(methoxycarbonyl)allylamine (R2) (Figure 6). The methyl group on the double bond does not make any significant structural change in the conformation of the reactant. However, it alters the regioselectivity of the cyclization reaction in **3′**. The energy barriers on the model structure of **3** have showed endo preference, which is in accordance with the experimental results.[8]

The Mulliken bonding analysis indicates a stronger bonding for the exo transition structure than the endo (0.163 vs 0.098),

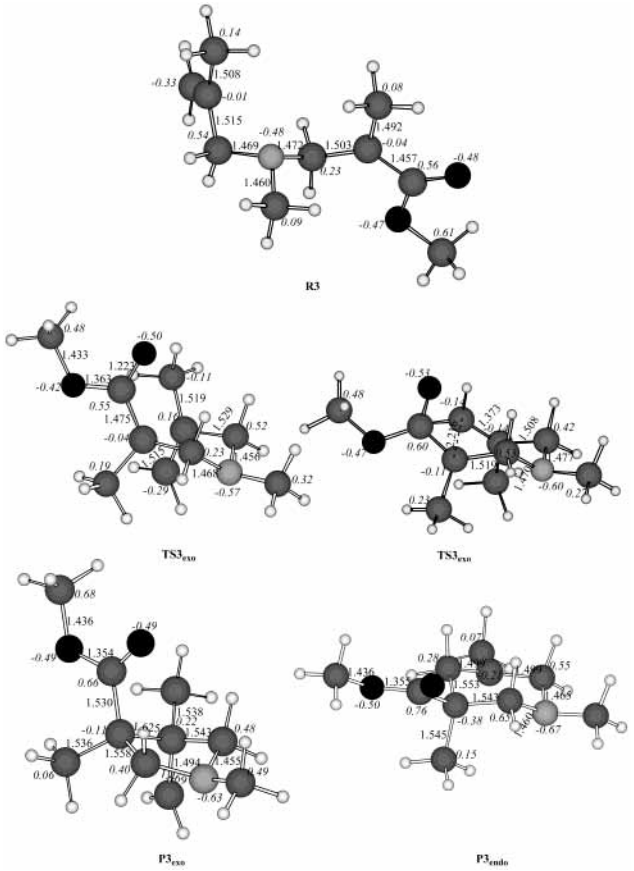


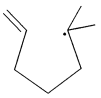
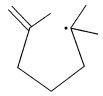
Figure 6. Global minimum, transition structures, and the products for exo and endo cyclization of **3′**.

and likewise, the NBO stabilization energy is higher for $TS3_{exo}$ (216.22 kcal/mol) than for $TS3_{endo}$ (134.78 kcal/mol). These findings support the formation of stronger bonding in exo rather than in the endo transition state, contrary to our expectations and the experimentally observed regioselectivity.[8] However, CHelp charges show that the radical prefers to attack the more nucleophilic site (C_7) of the C═C double bonds. These analyses indicate that the observed regioselectivity is not purely directed by electronic effects. In $TS3_{exo}$ the reacting centers may form the C−C bond more effectively, but at a higher energy cost due to the steric effect of substituents on the C═C double bond. Hence, the transition structures and their energies are much better indicators of regioselectivity.

The geometry of the transition state, $TS3_{endo}$, is similar to $TS2_{endo}$. The methyl substituent on nitrogen is in the equatorial orientation, and the C═C bond is directed such that the ring has a chairlike geometry. As in the case of $TS2_{endo}$, the bulkier ester group occupies the equatorial position at C_2. Methyl substitution on the C═C bond does not alter its axial vs equatorial preference and the chairlike geometries of $TS1_{endo}$ and $TS2_{endo}$ are preserved in $TS3_{endo}$.

In $TS3_{exo}$, the geometry of the ring is boatlike, contrary to **1** and **2**. Methyl substitution on nitrogen is in the equatorial position as seen in $TS1_{exo}$, $TS1_{endo}$, $TS2_{exo}$, and $TS2_{endo}$. The ester group occupies the pseudoequatorial position as in $TS2_{exo}$. In $TS3_{exo}$, the favored conformation of the C═O group is due to a stabilizing interaction between the oxygen of C═O and the H on C_3 at a distance of 2.391 Å. C_7 is in an axial-like orientation. In $TS1_{exo}$ and $TS2_{exo}$, the pseudoequatorial orientation of C═C was preferred, but in the case of $TS3_{exo}$, the methyl substituent on the C═C bond occupies the equatorial position

TABLE 4: Relative Rates for Cyclization of Hexenyl Analogues[19]

	k_{exo}	k_{endo}
	1	0.02
	1.4	0.02
	0.022	0.04
	< 0.0002	0.02

because it is slightly bulkier. This has caused a boatlike transition structure for $TS3_{exo}$.

Effect of Methyl Substitution in Cyclization. We have explained the exo preference of diallylamine compounds mainly by the more favorable overlap efficiency of the reacting centers in the exo transition structure. In the literature, there are examples of compounds that undergo six-membered ring formation as substitution on double bonds increases.[19] The five-membered ring formation is explained by kinetic control of the reaction and the six-membered ring formation by taking steric factors and stabilization of six-membered radical into consideration as in experimental studies on **2** and **3**. However, our calculations show that in the case of **1′**, **2′**, and **3′**, the experimentally observed regioselectivity is due to a lower activation barrier of the cyclization reaction. Also, the six-membered product of **3′** is 12.62 kcal/mol lower in energy than the five-membered product. Although the six-membered products are lower in energy than the five-membered in **1′** and **2′**, the observed regioselectivity is exo and the kinetic factors dominate in the ring size preference.

The geometry of $TS3_{exo}$ is different than the transition structures located for hex-5-enyl[19] and diallylamine analogues modeled in our previous work.[10,11] In those cases, the reacting centers have optimum overlap efficiency in exo geometry. The favorable overlap efficiency of the exo cyclization overcomes the factors favoring the endo path, such as the stability of the six-membered ring, the strain in the five-membered product, and the less stable primary radical that forms in the exo cyclization. However, as substituents are introduced to the parent system, as in the case of **2** and **3**, the five-membered ring can hardly form, because the substituents at the reacting centers interfere and prevent cyclization. Thus, in **3**, as in radical addition reactions to alkenes, the radical prefers the unsubstituted site for attack.[38] The relative rates of cyclization in hexenyl analogues show that as substituents on the C═C bond or the radical center increases, the relative rate of endo cyclization remains almost unaffected (Table 4). However, the rate of exo cyclization is affected much more than endo cyclization. In this study, we observe a similar effect. The geometries of the transition states $TS3_{exo}$ and $TS3_{endo}$ show that the methyl group on the double bond promotes steric interaction. In $TS3_{exo}$, the five-membered ring can hardly accommodate the two substituents; methyl at C_6 and ester at C_2; thus, the destabilization is brought to the exo transition structures rather than to the more extended endo. As a result, the activation energy for the exo

cyclization of **3′** is much higher than that of **1′** and **2′**, whereas the activation energy of **1′**, **2′**, and **3′** in the endo cyclization is almost the same in all (Table 1).

Effect of Methyl Substitution in Polymerizability. In the cyclopolymerization of **2** the cyclization step is reported to be rate-determining by ESR studies,[39] so the activation energies related to the cyclization step are crucial in comparing the cyclopolymerizabilities of the monomers. The polymerization of **3** is reported to be slower than **2**.[7,8] In accordance with the experimental observations, the activation energy of cyclization for **3′** is higher than **2′**. This is explained and demonstrated by the increased steric effect of the methyl group in cylization.

Conclusion

In this study, the cyclization reactions of **1′**, **2′**, and **3′** are studied as models for the cyclization reaction that takes place in the cyclopolymerization of monomers **1**, **2**, and **3**. The calculated activation energies for cyclization have been used with success in explaining the experimental regioselectivities. The exo vs endo preferences of the models are rationalized by taking into account different factors such as steric, electrostatic effects, and entropy. The favorable entropy difference is shown to be insufficient in explaining the regioselectivity, and steric effects seem to dominate the electrostatic effects.

The regioselectivity is governed mostly by the steric effects of methyl and ester substituents. Conclusively, the observed regioselectivity is mainly due to factors that cause destabilization in the exo transition states and that do not favor the exo cyclization. This conclusion is drawn by almost unchanged reaction barrier in endo cyclization and increased activation energy in exo cyclization by substitution. The experimental stereoselectivity has also been reproduced by considering the transition state geometries.

The methodology and the models used have enabled us to reproduce the experimental results whose mechanistic details had not been clarified earlier. We have been able to rationalize the substituent effect on the regioselectivity of the cyclization of diallyl derivatives. Finally, the fact that the cyclization barriers are not in agreement with the rates of the cyclopolymerization has led us to consider the expected side reactions. The strength of the α C−H bonds has been considered. It is shown that the α C−H bonds are stronger for ester-substituted monomers. This prevents the effective H-abstraction, thus decreasing the efficiency of degradative chain transfer, which acts as a termination reaction in cyclopolymerization. The intermolecular reactions constitute the scope of our next study where the homopolymerization and H-abstraction reactions of diallyl monomers will be discussed.

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