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Effect of Lewis acids on the stereoregularity of N,N-dimethyl acrylamide: A computational approach

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ABSTRACT

In this study, the effect of Lewis acid coordination ($ScCl_3$) in controlling the stereoregularity during the free radical polymerization of N,N-dimethyl acrylamide (DMAM) has been investigated by Density Functional Theory (DFT). Experimentally, $ScCl_3$, $Sc(OTf)_3$ and $Yb(OTf)_3$ have been used to increase the isotactic percentage in the polymerization of another acrylamide derivative, N-isopropyl acrylamide (NIPAM) (Habaue et al., 2002). The relative orientation of the terminal and penultimate side chains is expected to determine the stereoregularity in free radical polymerization reactions (Noble et al., 2014). We have analyzed the mechanistic details of the propagation reaction by considering all coordination types of the Lewis acid to the propagating species. Calculations have shown the bridging of the Lewis acid between the terminal side chain and the monomer to be the most probable pathway, which is in favor of the pro-*meso* propagation during the free radical polymerization of DMAM. In this case, it is the bridging capacity of the catalyst along the less crowded direction that dictates the preference for isotacticity. Overall, the strategy suggested in this study can be easily used by experimentalists in their endeavour of choosing the catalysts in order to end-up with the desired stereoregulation of the polymer chain.

1. Introduction

Living/controlled radical polymerization has gained great attention because the control of highly active radical species is very difficult, since they undergo very fast propagation and termination steps and generate dead chains [1]. However, well-defined polymers with controlled molecular weights can be obtained with living/controlled radical polymerization [2]. The tacticity of the growing chain should also be controlled during the free radical polymerization since it affects the physical properties of the final product. For instance, crystallinity leads to high physical strength and to an increased solvent and chemical resistance and is significantly affected by stereoregularity of the polymer chain. While *atactic* polymers are amorphous (noncrystalline), the corresponding *isotactic* and *syndiotactic* polymers are usually highly crystalline materials [3]. The glass transition temperature, T_g, [4–6] the association behavior [7], and the chain conformation [8] are affected by the tacticity of the growing chain. It was also observed that the tacticity influences the hydrophobicity, and thus the phase transition behavior, of poly (N-isopropylacrylamide) (PNIPAM). The hydrophobicity has been observed to increase as the *meso* content increases [9–11].

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Many attempts to produce stereospecific or stereoregular polymers have been made in confined media, such as the solid state, inclusion compounds, porous materials, and templates [12]. In solution polymerization, it is more difficult to provide a stereospecific environment around the growing radical center, because the monomer and the growing radical species move freely and diffuse in the reaction media. Therefore, vinyl monomers usually produce polymers with an inherent tacticity specific to their chemical structures. In view of production cost, solvent or additive-mediated systems might be the most promising solutions to obtain stereospecific polymers. Recently, enzymes have been demonstrated to be viable for the catalysis of a wide variety of organic transformations, they often achieve outstanding activities and selectivities [13,14].

Lewis acids have been widely used in the regulation of tacticity in the polymerization reactions over the last few decades. In 1963, Imoto et al. [15,16] reported the acceleration of the polymerization and copolymerization of methylmethacrylate (MMA) in the presence of zinc chloride ($ZnCl_2$), but no stereoregularity was obtained at the concentrations used. However, in 1966 Otsu et al. investigated the slight increase in the isotacticity of poly (MMA) with high concentrations of $ZnCl_2$ [17]. Magnesium bromide ($MgBr_2$), which has a poor solubility, is used as Lewis acid in the polymerization of MMA. A bidentate complex between the carbonyl oxygens of the propagating chain and the solid surface of the catalyst is reported to form [18]. In this study, as the amount of soluble $MgBr_2$ increases, the syndiotactic stereospecificity increases, whereas with the solid Lewis acid, isotacticity is preferred. In the radical polymerization of α-alkoxymethacrylates, zinc bromide ($ZnBr_2$) increases the syndiotacticity. On the other hand, around 70% isotacticity is obtained in the presence of scandium (III) triflate ($Sc(OTf)_3$, $OTf = CF_3SO_3^-$) in the same polymerization [19]. Isobe et al. have gained great success in obtaining isotactic products in the polymerization of methacrylates by using $Sc(OTf)_3$ among various metal triflates [20]. In the atom transfer radical polymerization (ATRP) of acrylamide, the Lewis acids yttrium (III) triflate ($Y(OTf)_3$) and aluminium chloride ($AlCl_3$) have led to increased isotacticity with increased polymerization rate [21]. Okamoto and coworkers have carried out a stereocontrolled radical polymerization of acrylamides; the isotactic specific radical polymerization of various acrylamides [22,23] and methacrylamides [24,25] was achieved in the presence of a catalytic amount of Lewis acids such as $Y(OTf)_3$ and ytterbium (III) triflate ($Yb(OTf)_3$). Methacrylamides and their N-monosubstituted derivatives can be polymerized only by the free radical method because of the acidic amide proton; thus the development of an effective and facile stereocontrol method is very important. In the living anionic propagation of N,N-dimethyl acrylamide (DMAM), the effect of triethylaluminum (Et_3Al) on the relative stabilities of chain end structures with different tacticities has been investigated by Density Functional Theory (DFT) calculations where complexation of Lewis acid with monomer leads to its activation [26]. Experimentally, the interaction between the monomer and Lewis acids was investigated as the basis of stereocontrol in favor of isotactic specificity in the radical polymerization of (*S*)-N-(2-hydroxy-1-phenylethyl) methacrylamide ((*S*)-HPEMA) [27]. In addition to stereoregulation, rate acceleration with the Lewis acid catalysis in radical polymerizations was also observed [20,28–31]. Some Li^+ salts were shown to be effective in catalyzing both initiation and propagation steps in the radical polymerization of simple terminal alkenes [30]. Also, lithium bis(trifluoromethanesulfonyl)imide ($LiNTf_2$) enhanced isotactic propagation while accelerating the reaction during the free radical polymerization of MMA [28]. Recently, the dual role of $LiNTf_2$ in the radical polymerization of DMAM has been investigated experimentally and computationally; in this study Li^+ was stabilizing the propagating radical species and also activating the incoming monomer [32].

Acrylamides are very important monomers and are used in daily life in pesticide formulations, cosmetics and packaging. DMAM, has been recognized as a co-monomer for the conformational control of polypeptides, as well as an anti-aging agent [33,34]. DMAM was also used as a co-monomer for pH-responsive photoluminescent polymer [35] and as a non-thermoresponsive reference co-monomer [36].

Habaue et al. reported the effect of various Lewis acids on the stereochemical control during the radical polymerizations of some acrylamides and methacrylamides (Table 1) [23]. In the absence of a Lewis acid, both monomers in the table yield slightly syndiotactic polymers. However, in the presence of Lewis acids, isospecificity increases. Although the rare earth metal chloride $ScCl_3$ was slightly less effective than its triflate salt in enhancing the isotactic products, $ScCl_3$ is used in this study since it will decrease the computational cost.

This study aims to examine the control of stereoregulation by Lewis acids during the free radical polymerization of DMAM making use of computational tools. Our previous studies on modeling the tacticity of N-isopropylacrylamide (NIPAM) [37] and MMA [38] in H-bonding solvents have given a solid basis for modeling free radical polymerization in a complex molecular environment.

Table 1
Experimental findings for stereocontrol in the presence of Lewis acids in methanol [23].

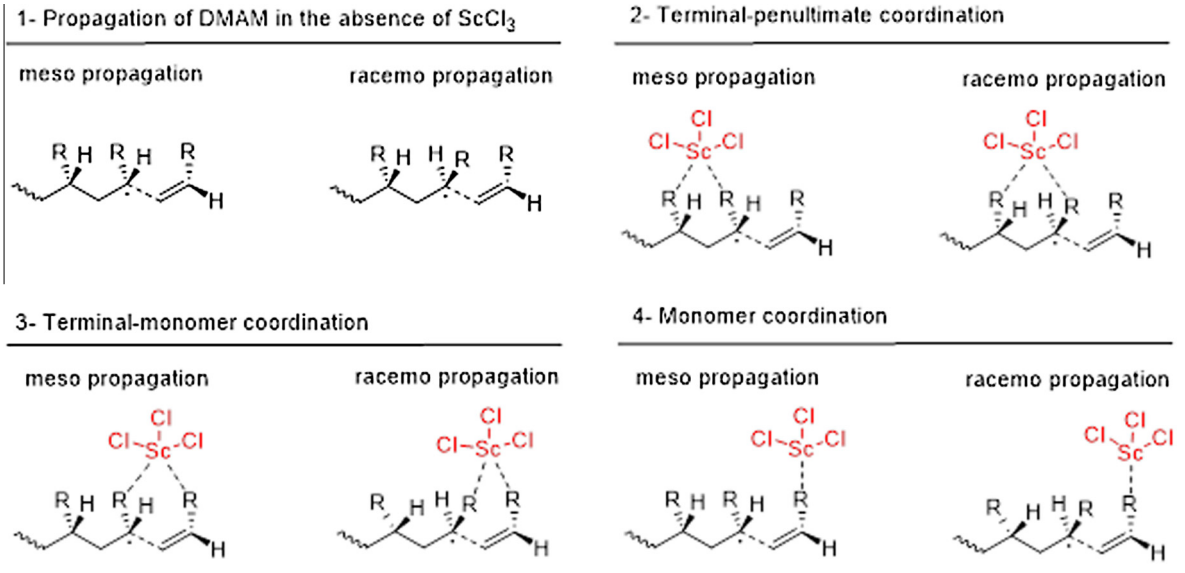
Monomer	Lewis acid	Tacticity (m/r)
NIPAM	–	45/55
NIPAM	$Sc(OTf)_3$	62/38
NIPAM	$ScCl_3$	57/43
NIPAM	$Yb(OTf)_3$	82/18
DMAM	–	46/54
DMAM	$Yb(OTf)_3$	84/16

The relative orientation of the terminal and penultimate side chains is expected to determine the stereoregularity in the free radical polymerization reaction. The *meso* and *racemo* propagation of DMAM in the absence and the presence of $ScCl_3$ is depicted in Scheme 1. In part 1, where no acid is present in the medium, the probability of having both *meso* and *racemo* propagation should be equal since the radicalic chain end and the incoming monomer are free to rotate. In the presence of Lewis acid, more than one way of coordination is possible. Coordination with the terminal and the penultimate units (Scheme 1, part 2) is proposed as the isotactic regulating route [18,28]. However, the reaction in part 3 of Scheme 1 can also provide stereoregulation since in this case Lewis acid interacts with both the terminal side-chain and the incoming monomer. It is also possible that the catalyst only interacts with the terminal group (Scheme 1, part 4); this type of complexation is not expected to assist stereoregulation. Herein we will investigate each of these possibilities to unravel the molecular origin of the observed stereoselectivity.

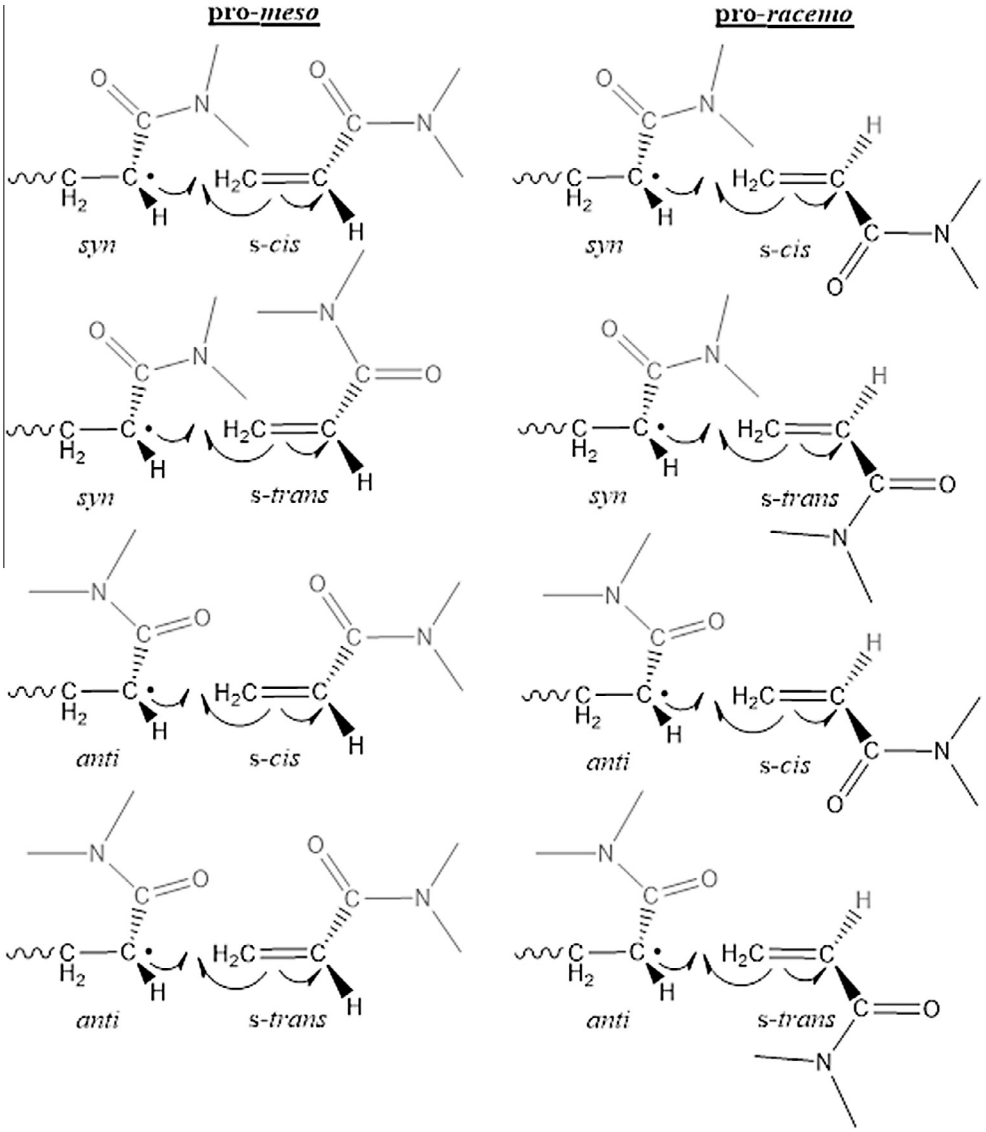
2. Methodology

In order to understand the role of Lewis acids in controlling the stereoregularity in the propagation of DMAM, structures along the reaction paths depicted in Scheme 1 have been constructed, and optimized with M06-2X/6-311+G(d,p) since this functional is recommended for thermochemistry, kinetics, and description of noncovalent interactions [39]. Recently, this functional has been used successfully to calculate the activation energy of MMA homopropagation [40]. All geometry optimizations have been performed in methanol with the Polarizable Continuum Model (PCM) [41,42]. For each stationary point a conformational search has been carried out with the same methodology. The calculated free energy of solvation was corrected with the term RT ln (24.46) in order to take into account the unit transformation from 1 mol L^{-1} (g) to 1 mol L^{-1} (solution) [43]. The Gaussian 09 program package [44] has been used throughout the study. The Gibbs free energy barriers of the propagation steps were calculated as the Gibbs free energy difference of transition states and the separated reactants in the absence of Lewis acid coordination. The same strategy has been used for the terminal-penultimate model propagation where the separated reactants are the dimeric radical complexed with the Lewis acid and the monomer itself. In the terminal-monomer type of propagation the Gibbs free energy barriers were calculated as the Gibbs free energy difference of transition states and the most stable pre-reactive complexes. Finally, the Gibbs stabilization energies of the complexes were calculated as the differences of the Gibbs free energies between the propagating radical complex with the Lewis acid (dimer or trimer), the propagating radical (dimer or trimer) and the Lewis acid.

In the free radical polymerization, the relative orientation of the terminal and the penultimate side-chains of the polymer terminus determines the stereochemistry. Thus, the direction of approach of the incoming monomer to the pro-chiral center is important. In this paper, we want to model all possible coordination modes of the Lewis acid to the propagating species as schematically depicted in Scheme 1. Since the system may be subjected to a lot of attack modes and conformational changes, we first performed an in depth analysis of the propagation step in the absence of the Lewis acid. At second instance, $ScCl_3$ is systematically added to the system. The propagating radical may attack the double bond of the monomer to yield either the pro-*meso* or the pro-*racemo* radical chains. The attack of *syn*- and *anti*-DMAM radicals to s-*cis* and s-*trans* DMAM monomers during the propagation step is depicted in Scheme 2. A *syn*-DMAM radical, can approach the DMAM monomer from 4 different directions. Similarly, there are 4 possible ways for an *anti*-DMAM radical to attack a monomer. Overall, 8 different



Scheme 1. Stereoselectivity during radical polymerization of DMAM in the absence (1) and the presence (2–4) of $ScCl_3$ as Lewis acid.



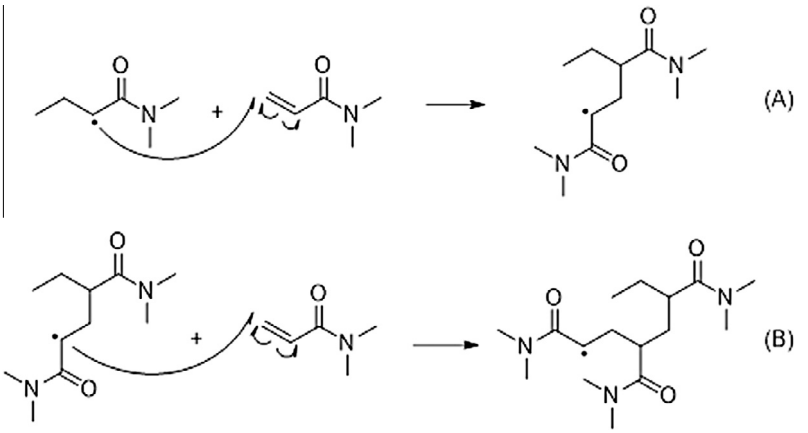
Scheme 2. Stereoselective radical (*syn* and *anti*) addition to DMAM (s-*cis* and s-*trans*).

transition states displayed in Scheme 2 have been located for the dimeric propagation step (Part A in Scheme 3) of the DMAM polymerization. This is followed by a full conformational search around the forming bond. The stationary points located in this manner were used for further analysis. IRC calculations [45,46] were carried out in order to justify the nature of the transition states. Dimeric radicalic chains obtained from the IRC calculations were used in modeling the next step of the propagation (Part B in Scheme 3) where a dimeric radical attacks the incoming monomer. After locating the global minima and their corresponding transition states for the first and the second propagation steps, the Lewis acid coordination scenarios depicted in Scheme 1 have been investigated. Dimeric and trimeric radicalic chains obtained from the IRC calculations are shown in Figs. S3 and S4 and the enthalpies of the reaction are tabulated in Table S1 of the Supporting Information. All the reactions are found as exothermic.

3. Results and discussion

3.1. Unimeric reactants

The conformational study in methanol revealed that the s-*cis* conformation of the DMAM monomer and the *syn* conformation of the DMAM radical are preferred over the s-*trans* and the *anti* conformations of the monomer and the radical by



Scheme 3. First (A) and second (B) propagation steps for the polymerization of DMAM.

2.05 kcal mol^{-1} and 3.12 kcal mol^{-1}, respectively (Fig. S1). Similarly, in the previous computational studies on the radical polymerization of acrylamide (AM), methacrylamide (MAM) [47], and N-isopropylacrylamide (NIPAM) [37], the s-*cis* monomer and the *syn*-radical were more stable than their s-*trans* and *anti* counterparts.

In the presence of the Lewis acid the optimized structures of all conformations of both the monomer and radical are displayed in Fig. S1 of the SI. The reactant complexes where the $ScCl_3$ catalyst interacts with the carbonyl oxygen are clearly preferred over the complexes where the catalyst interacts with the nitrogen with an energy gain of more than 25 kcal mol^{-1}. In addition the s-*cis* conformer of the monomer and the *syn* conformer of the radical are the most stable structures as was the case without catalyst. The most stable conformations are displayed in Fig. 1.

Notice that the Lewis acid destabilizes the monomer s-*cis*-N-$ScCl_3$ by 5.99 kcal mol^{-1} Gibbs energy. Monomer (O)$\cdots$$ScCl_3$ and Radical (O)$\cdots$$ScCl_3$ complexes have stabilization energies of −19.59 and −24.08 kcal mol^{-1}, respectively. Whereas Sc–N distances are shorter than 2 Å for the Monomer (O)$\cdots$$ScCl_3$ and Radical (O)$\cdots$$ScCl_3$ complexes, Sc–N distances are longer than 2 Å in the case of Monomer (N)$\cdots$$ScCl_3$ and Radical (N)$\cdots$$ScCl_3$ complexes. Steric repulsions between the dimethyl groups and the catalyst may be the cause for this elongation and the destabilization of these species. Therefore, for the remainder of this article, only coordination on the carbonyl oxygens of the monomers and the radicals will be considered.

3.2. Dimeric transition states

For the construction of the dimeric transition states, all combinations of s-*cis* and s-*trans* conformations of the monomer with *syn* and *anti* conformations of the radicalic species yielding pro-*meso* and pro-*racemo* configurations have been considered (Scheme 2). All prestructures of possible transition states are then optimized following the standard procedure in searching transition states. It is not surprising that a combination of the most stable reactant pairs (s-*cis* monomer and *syn* radical) has the largest potential to generate the transition state with the lowest barrier. Indeed, *di*-TS-pro-*meso* is the lowest energy isotactic structure and *di*-TS-pro-*racemo* is the lowest energy syndiotactic structure (Fig. 2). However, the energy difference between these two is negligible.

To understand the effect of the catalyst on the tacticity, transition states with $ScCl_3$ have been located starting from the transition state structures without a Lewis acid (Fig. 2). Transition states in which the Lewis acid is interacting with the radical (LA-on radical), the monomer (LA-on monomer) and both (LA-bridged) have been modeled. In these structures, the coordination number of the Lewis acid seems to be the determining factor for the stability of the transition states. The most stable transition state that has only one Lewis acid/Lewis base interaction is *di*-TS-S1-pro-*meso*, which has a relative Gibbs free energy (RGFE) of 15.32 kcal mol^{-1} with respect to the most stable LA-bridged transition state, *di*-TS-S12-pro-*meso*. This can be explained by the fact that $ScCl_3$ prefers penta-coordination rather than tetra-coordination. $ScCl_3$ can have six-membered chelation with the polar groups of the monomers or the solvent in the medium due to its high coordination number [19,48]. However, due to the complexity of the transition state structures, a consistent coordination number of five will be used for $ScCl_3$ in the bridging position in the remainder of this article. Structures of all pro-*meso* and pro-*racemo* dimeric transition states in the presence of $ScCl_3$ are shown in Fig. S2, of which a selection of LA-bridged, LA-on radical and LA-on monomer cases is displayed in Fig. 2. Pro-*meso* transition state with $ScCl_3$ at bridging position, *di*-TS-S12-pro-*meso*, has an interaction between the chlorine (Cl) atom of the $ScCl_3$ and methyl proton of the monomer, which may cause extra stabilization compared to the pro-*racemo* transition state *di*-TS-S12-pro-*racemo*. The Gibbs free energy differences of pro-*meso* and pro-*racemo* transition states are negligible at dimeric transition state level.

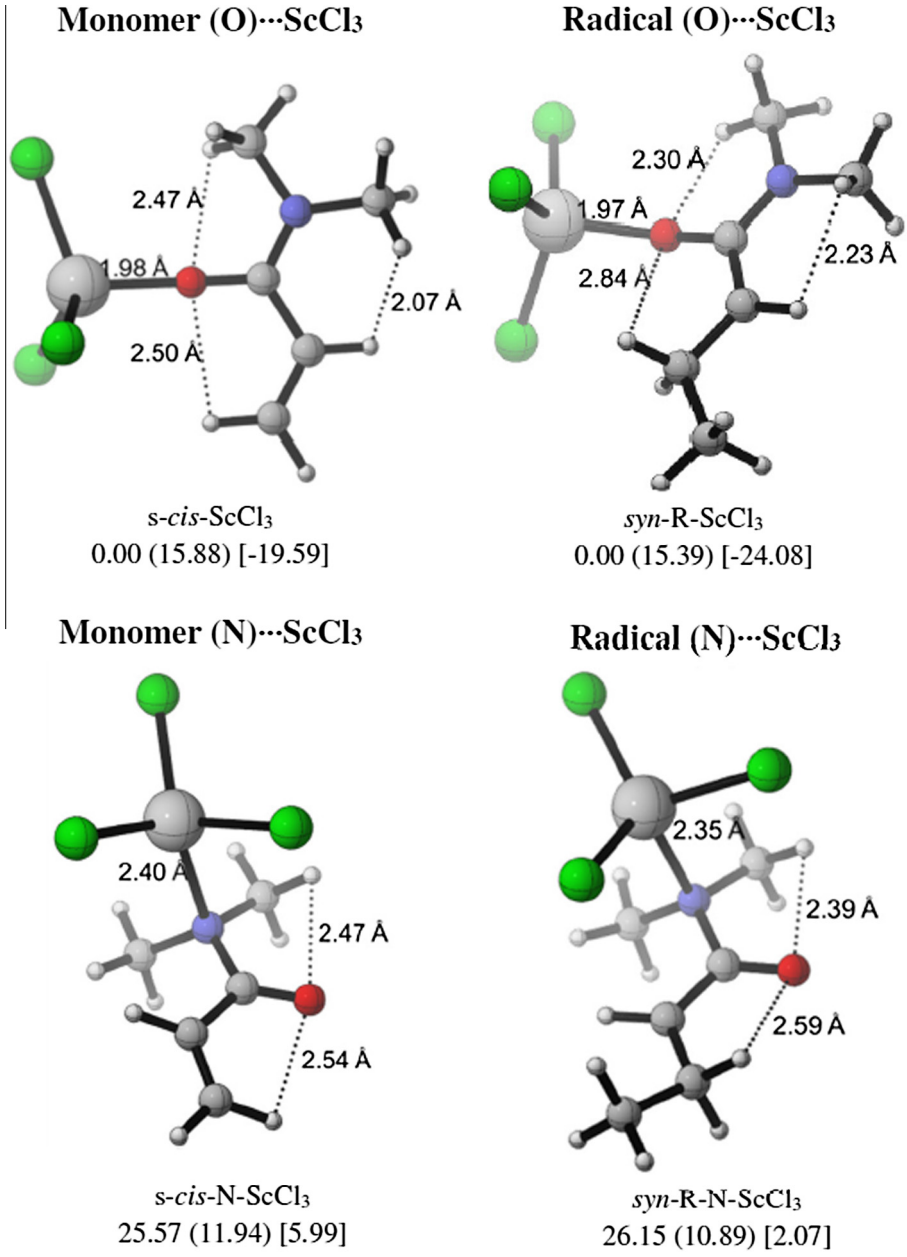


Fig. 1. Relative Gibbs free energies (kcal mol^{-1}), dipole moments (D) in parentheses, and Gibbs stabilization energies (kcal mol^{-1}) in square brackets for the reactants in the presence of $ScCl_3$ in methanol (M06-2X/6-311+G(d,p)).

3.3. Trimeric transition states

To better understand the role of Lewis acids in enhancing the stereoregulation during the free radical polymerization of DMAM, the study has been extended to trimers. The optimized dimeric radicalic chains and more specifically transition states resulting from combining an s-*cis* monomer and a *syn*-radical as most stable reactant pair, have been used as initial structures for the trimeric propagation (Scheme 3, part B). In a next step their attack to the s-*cis* monomer is considered since it was previously found to be the most stable unimeric reactant (Fig. 3). Like in the dimeric case, pro-*meso* and pro-*racemo* transition states have comparable energies. Both structures (*tri*-TS-pro-*meso* and *tri*-TS-pro-*racemo*) have a curling pattern along the propagating chain, which could be expected in the absence of a Lewis acid.

In the presence of a Lewis acid, the monomer-coordination scenario in Scheme 1 (part 4) is omitted since it was already investigated in the dimeric case (Fig. 2), where $ScCl_3$ was found to prefer the bridging position in order to have penta-

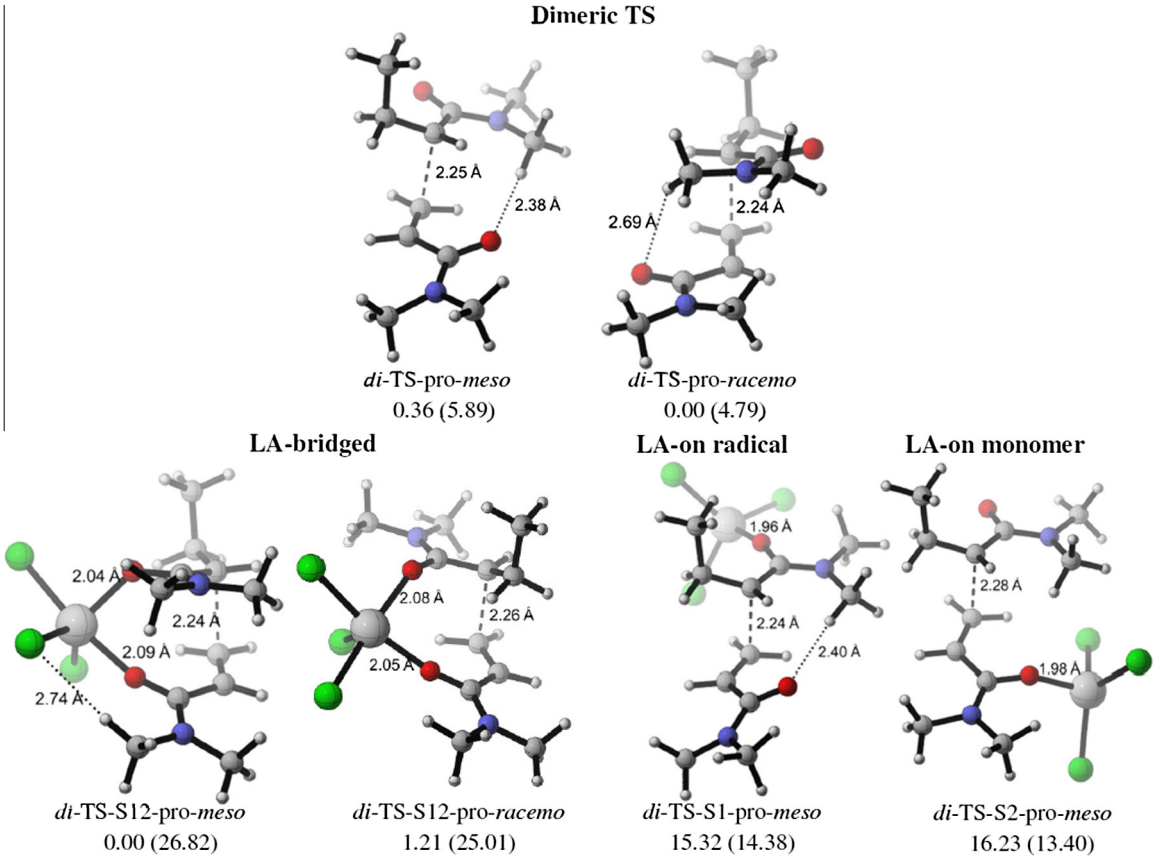


Fig. 2. Relative Gibbs free energies (kcal mol^{-1}), and dipole moments (D) in parentheses for the dimeric transition states in methanol (M06-2X/6-311+G(d,p)).

coordination. So, the cases where $ScCl_3$ molecules are bonded to the transition states in terminal-penultimate coordination (Scheme 1, part 2) and terminal-monomer coordination manner (Scheme 1, part 3) have been modeled (Fig. 3).

In both terminal-penultimate and terminal-monomer cases the pro-*meso* propagation is favored over the pro-*racemo* propagation. Pro-*meso* transition states have extra stabilizing hydrogen bonds between the Cl of the Lewis acid and the methyl protons of the DMAM monomer which are absent in the pro-*racemo* cases. The Gibbs free energy difference between the terminal-monomer coordinated transition state *tri*-TS-S23-pro-*meso* and its terminal-penultimate coordinated counter-part *tri*-TS-S12-pro-*meso* was negligible. Also, *tri*-TS-S23-pro-*racemo*, which has a relative Gibbs free energy of 2.74 kcal mol^{-1}, is slightly less stable than *tri*-TS-S12-pro-*racemo*. Steric crowding in the *tri*-TS-S12-pro-*meso* and *tri*-TS-S23-pro-*racemo* makes these transition states slightly less stable than their counter-parts. In the terminal-monomer coordination transition states, the Lewis acid interacts with both the incoming monomer and the rotatable radicalic chain end. It can be suggested that the catalyst travels to the radicalic site as the chain grows, accepting the new monomer in a new terminal-monomer transition state.

3.4. How does the Lewis acid affect the kinetics and the stereoselectivity?

Table 2 reports the kinetic results for the dimeric and the trimeric propagation steps of DMAM. In the absence of Lewis acid coordination, the pro-*racemo* propagation is favored in the dimeric case, this was also proposed in the experimental study by Habaue et al. [23] Furthermore, the difference between the Gibbs free energy barriers of the *meso* and *racemo* propagations in the trimeric case is negligible. Since the radical end of the propagating chain and the incoming monomer are easily rotatable, no stereoselectivity was expected in the absence of $ScCl_3$.

In the presence of a Lewis acid, bridging to the carbonyl oxygens at the end of the propagating chain and incoming monomer in dimeric case, there is pro-*meso* selectivity. In the presence of $ScCl_3$ a linear propagation is observed for pro-*meso* case, that is why lower activation barriers and higher propagation rate constants are observed for these dimeric transition states. In the trimeric propagation case in the presence of Lewis acid coordination, Boltzmann distributions of pro-*meso* and pro-*racemo* transition states based on Gibbs free energies of activation revealed that 90.87% and 99.02% of the products will be in *meso* configuration both in the case of terminal-penultimate coordination and terminal-monomer coordination,

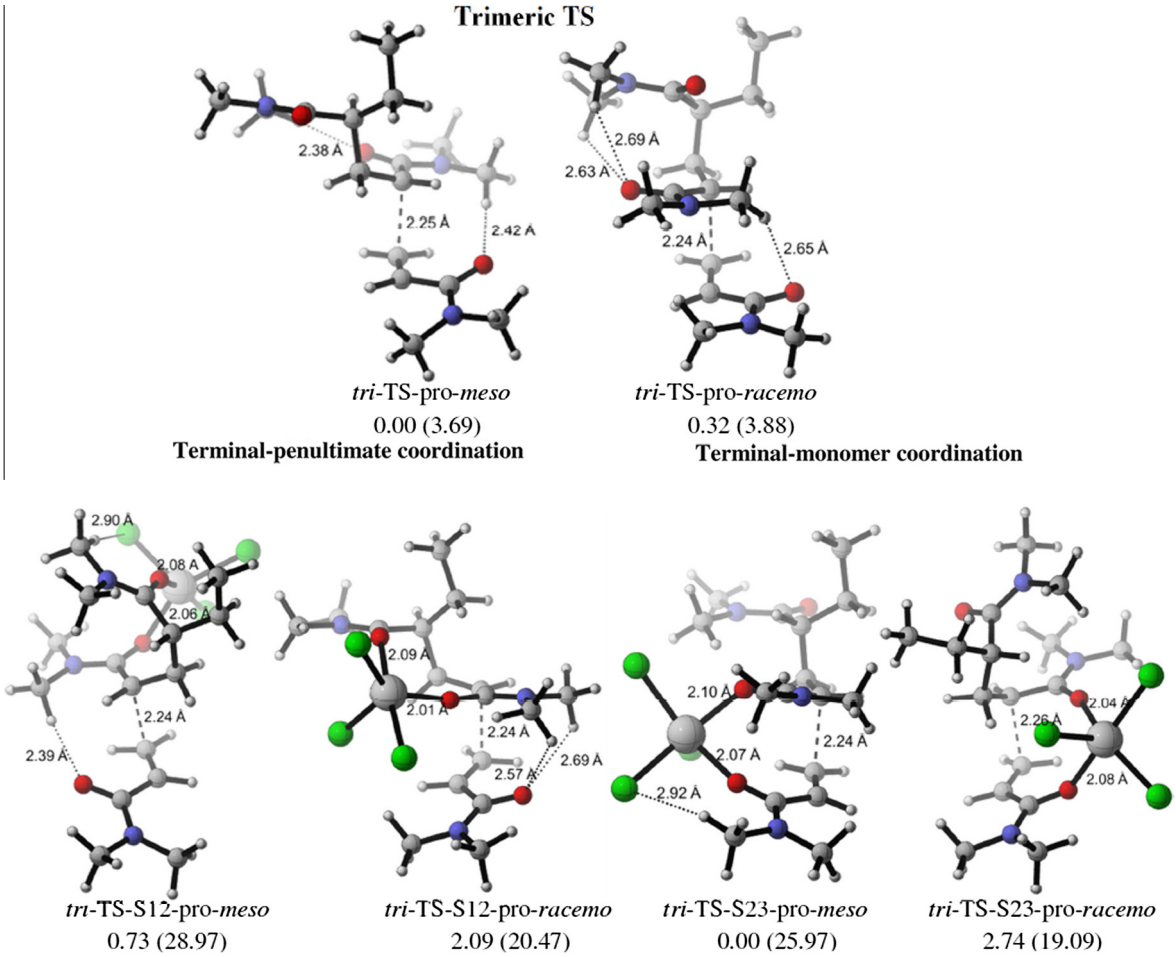


Fig. 3. Relative Gibbs free energies (kcal mol^{-1}), and dipole moments (D) in parentheses for the trimeric transition states in methanol (M06-2X/6-311+G(d,p)).

Table 2
Gibbs free energy barriers, ($\Delta G^{\#}$, kcal mol^{-1}), activation energy barriers, (E_a, kcal mol^{-1}), propagation rate constants, (k_p, L mol^{-1} s^{-1}), and tacticity percentages of the best dimeric and trimeric transition state pathways at 298.15 K (M06-2X/6-311+G(d,p)).

	TS	Name	$\Delta G^{\#}$	E_a	k_p	%
No $ScCl_3$	Dimeric	*di*-TS-pro-*meso*	13.80	2.23	1.18E+04	35.44
		di-TS-pro-*racemo*	13.45	1.36	2.15E+04	64.56
	Trimeric	*tri*-TS-pro-*meso*	14.42	2.11	4.14E+03	63.07
		tri-TS-pro-*racemo*	14.74	1.34	2.42E+03	36.93
With $ScCl_3$	Dimeric[a]	*di*-TS-S12-pro-*meso*	7.31	7.49	6.70E+08	88.45
		di-TS-S12-pro-*racemo*	8.52	9.40	8.73E+07	11.55
	Trimeric[b]	*tri*-TS-S12-pro-*meso*	12.27	1.56	1.57E+05	90.87
		tri-TS-S12-pro-*racemo*	13.63	0.99	1.57E+04	9.13
		tri-TS-S23-pro-*meso*	7.00	6.90	1.14E+09	99.02
		tri-TS-S23-pro-*racemo*	9.73	9.69	1.13E+07	0.98

[a] "S12" refers to transition states having $ScCl_3$ in the bridging position between the radical and the incoming monomer.
[b] "S12" and "S23" refer to the terminal-penultimate and terminal-monomer coordinated transition states, respectively.

respectively. These tacticity percentages are much higher than the experimental values reported in Table 1. The catalyst in the experimental medium is very low in concentration, every propagating chain may not encounter the catalyst. However a one-to-one interaction between the catalyst and the monomer has been modeled in this study; this may be the cause of the higher tacticity percentages obtained in this study. Gibbs free energy barriers for terminal-monomer coordination (7.00 kcal mol^{-1} for *tri*-TS-S23-pro-*meso* and 9.73 kcal mol^{-1} for *tri*-TS-S23-pro-*racemo*) are lower than the terminal-

penultimate case (12.27 kcal mol^{-1} for *tri*-TS-S12-pro-*meso* and 13.63 kcal mol^{-1} for *tri*-TS-S12-pro-*racemo*) which indicates that the terminal-monomer complexation of the $ScCl_3$ is more favorable stereocontroling the path during the polymerization of DMAM. The propagation rate constants obtained both in the dimeric and the trimeric cases revealed that Lewis acid has a dual role in the propagation of DMAM by accelerating and stereocontroling the polymerization in favor of pro-*meso* selectivity. In a pulsed-laser polymerization (PLP) in conjunction with size-exclusion chromatography (SEC) study, the propagation rate coefficient of DMAM in aqueous solution (0.20 g g^{-1} monomer mass fraction) and in bulk were measured as 43,489 and 10,479 l mol^{-1} s^{-1}, respectively [49]. The calculated rate coefficients in the absence of Lewis acid in Table 2 are in the same range with these values.

4. Conclusion

The mechanism of the free radical polymerization of DMAM in the absence and presence of the Lewis acid $ScCl_3$ and the effect of the latter on stereoselectivity have been modeled. Kinetic calculations with M06-2X/6-311+G(d,p) have shown that $ScCl_3$ increases the isotactic specificity for the pro-*meso* propagation both in the dimeric and the trimeric models. $ScCl_3$ interacts with the carbonyl oxygens of the side chains in a bridging manner, in this way the pro-*meso* propagation is favored sterically. In the presence of Lewis acid, the terminal-monomer coordination scenario was preferred over the terminal-penultimate coordination. Also, the propagation in the presence of $ScCl_3$ is catalytic. Such molecular level insight into the factors controlling the stereoselectivity may be obtained from detailed computational kinetic studies. Our results clearly show the catalytic function of the $ScCl_3$ species, as the propagation kinetics is faster in the presence of the Lewis acid. In further studies, the behavior of other Lewis acids in the polymerization of acrylamide derivatives can be investigated. On the basis of this work we suggest that strategies for effective stereocontrol need to be re-considered, our observation is such that reagents that simultaneously activate the monomer while binding to the terminal and penultimate groups are promising. A detailed DFT modeling of the propagation reaction, when carried out as demonstrated above, has the potential to guide experimentalists towards devising strategies to improve and control the stereoselectivity.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.eurpolymj.2016.08.010.

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