



## Role of Initiator Structure on Thiol-Ene Polymerization: A Comprehensive Theoretical Study

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**Abstract:** The effect of initiator nature on thiol-ene polymerization was elaborated in this work with two initiators, four thiols, and eight monomers by utilizing the M06-2X/6-31++G(d,p) level of theory. For this purpose, a comparative investigation was carried out by modeling hydrogen abstraction from thiols ( $k_{HA}$ ) and addition reaction to monomers ( $k_i$ ), which is considered a side reaction. It was confirmed that the 2,2-dimethoxy-2-phenylacetophenone (DMPA) initiator is a suitable thiol-ene initiator except for the polymerization of electron-deficient or conjugated monomers. It was determined that the azobis(isobutyronitrile) (AIBN) initiator could not give a homogeneous thiol-ene product regardless of the monomer structure. However, it has been found that aromatic thiols should be used to obtain relatively better results with this initiator.

**Keywords:** Thiol-ene polymerization; density functional theory; reaction kinetics; structure-reactivity relationships.

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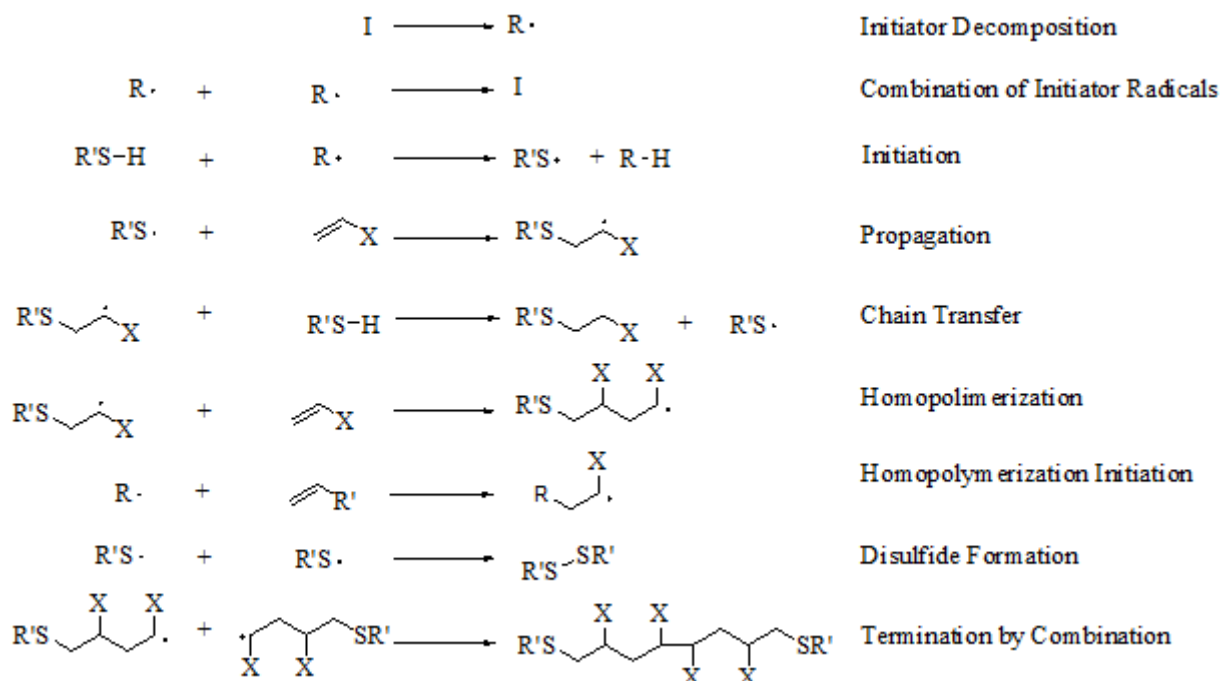
### INTRODUCTION

Thiol-ene reaction has attracted attention in the polymer field due to its unique mechanism, which combines the advantages of classical radical and step-growth polymerizations as a radical step-growth procedure (1-3). It also has a "click chemistry" feature (3) as it exhibits properties such as being fast, solvent-free, insensitive to oxygen, showing late gel points, with a high yield (4), not forming by-products, forming a uniform polymer structure, and giving products with a narrow glassy transition temperature (3). Thiol-ene polymerization was first used on surface coatings and films by photo-curable polymers and resins (5). Today, there are many applications from electro-optical materials (6) to dendrimers (7) and from drug carriers (8) to microfluidic devices (9-11).

Many experimental and theoretical studies have focused on the elaboration of steps of thiol-ene polymerization and factors affecting the process (12), such as the effect of solvent medium (13-15), the influence of substrate (12,16), or thiol reactivity (17-19). It was demonstrated that the main driving force for the thiol-ene polymerization is the rate ratios for propagation and chain transfer reactions ( $k_p/k_{ct}$ )(12). However, the literature studies have shown that one of the factors affecting the polymerization processes is the electronic structure of the initiator. Experimental and theoretical studies on this subject are limited (20,21). As depicted in Scheme 1, one of the side reactions is radical initiator addition to alkene functionality, leading to classical free radical initiation of homopolymerization. Recombination of initiator radicals, disulfide formations, and

termination by the combination of carbon-centered radicals are other possible side reactions. This study basically focused on the initiation of homopolymerization since this side reaction can consume one of the thiol-ene polymerization reactants. Our previous study has given clues

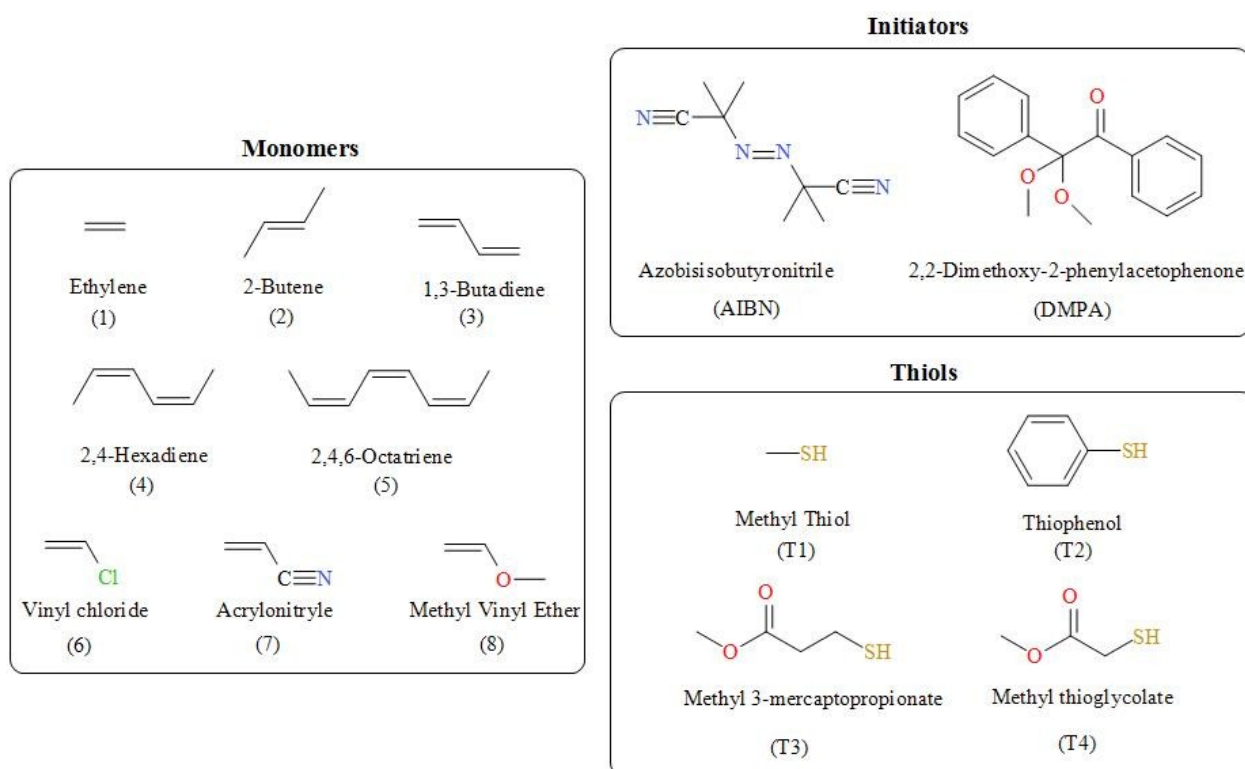
about this point by investigating a limited number of thiol and alkene functionality (21). In this study, elaboration of initiator performance was extended a larger reaction sets with eight alkenes, four thiols, and two different initiators.



**Scheme 1:** List of possible reactions during thiol-ene polymerization (22).

Hydrogen abstraction from thiols by initiator radicals is the critical step for initiating thiol-ene polymerization. However, initiator radicals can also attack alkene C=C double bond, which initiates classical radical polymerization and is considered a side reaction. Therefore, the reactivity analysis of

radicals generated from azobis(isobutyronitrile) (AIBN) as a classical radical polymerization initiator and 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a thiol-ene polymerization initiator has a crucial role in investigating the efficiency of an initiator for an effective thiol-ene polymerization.



**Scheme 2:** Chemical structures of monomers, thiols, and initiators investigated in this study.

Methyl thiol (T1), thiophenol (T2), methyl 3-mercaptopropionate (T3), and methyl thioglycolate (T4) were used to analyze the effect of thiol functionality. Moreover, eight alkenes were tested due to their different electronic natures, from electron-deficient to electron-rich or conjugated structures, to investigate thiol radical attacks to monomers, which gives by-products.

## METHODOLOGY

Quantum chemical calculations were carried out by using the Gaussian 16 program package (23). All geometry optimizations, frequencies, and energies were calculated by using M06-2X functional (24). M06-2X/6-31++G(d,p) level of theory has been performed successfully to model thiol-ene polymerization (15,17). Therefore, this level of theory is preferred to model the performance of initiators. The rate constants were predicted using the transition state theory mentioned in the literature (25). The tunneling ( $\kappa$ ) coefficient was calculated based on the Wigner approximation, given in the following equation (26,27).

$$\kappa(T) = 1 + \frac{1}{24} \left| \frac{h\omega^\ddagger}{k_B T} \right|^2$$

Where,  $h$  is Planck's constant ( $6.6260755 \times 10^{-34}$  J.s),  $\omega^\ddagger$  is the imaginary frequency,  $k_B$  is the

Boltzmann's constant ( $1.380658 \times 10^{-23}$  J.K<sup>-1</sup>), and  $T$  is the temperature (298.15 K). Moreover, the stability of concerned radicals was expressed by the standard radical stabilization energies (RSE) (28, 29).

## RESULTS AND DISCUSSION

Thiol-ene reaction has appeared in literature since 1905 (30). Many experimental (12,31-36) or theoretical (15-17,19,21) studies have been carried out to elucidate the mechanism of thiol-ene polymerization. However, limited studies have focused on the role of the initiator on polymerization involving thiol-ene reactions (20-22,37,38). For the first time, a comprehensive investigation was carried out by application of quantum chemical tools in this study.

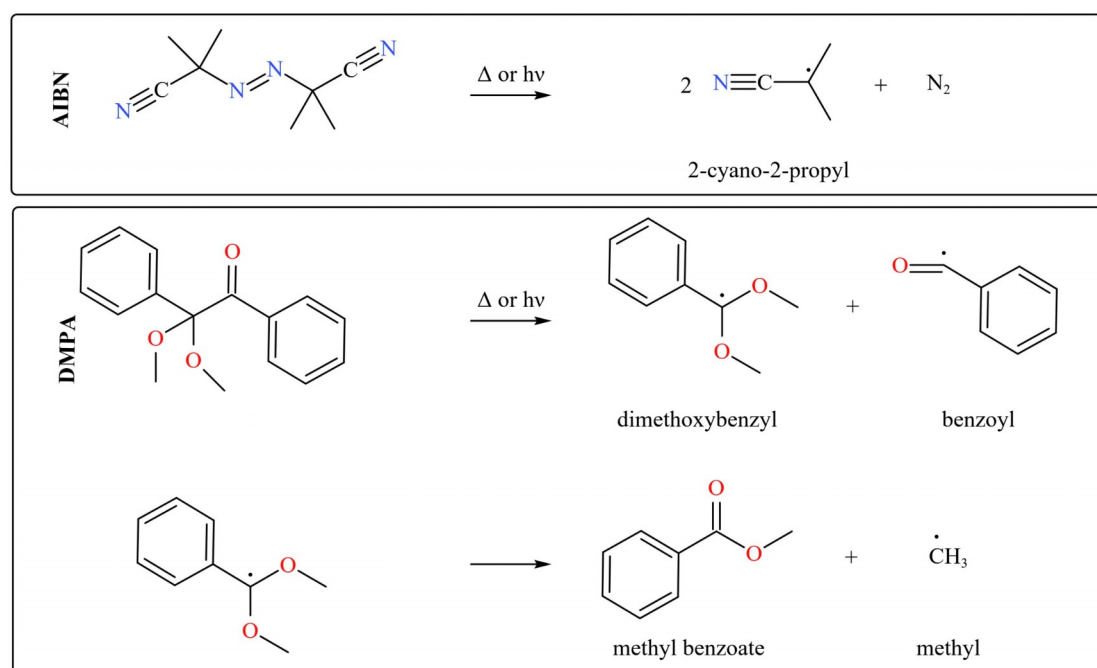
It was elaborated that whether azobis(isobutyronitrile) (AIBN) and 2,2-dimethoxy-2-phenylacetophenone (DMPA) give side reactions in thiol-ene polymerization. Exposure to light or heat leads to the decomposition of these initiators to form radicalic species. Since the polymerization reactions are performed as based on the reactivity of the radicals formed, the decomposition step of the initiators was not modeled by quantum chemical methods. What is expected from the radicals formed is that they initiate thiol-ene polymerization by abstracting the hydrogen atom

from thiols. Otherwise, the initiator radical can give a side reaction by attacking the monomer effectively. This possibility reduces the efficiency of the thiol-ene polymerization.

### Hydrogen Abstraction from Thiols

Application of AIBN as the initiator produces 2-cyano-2-propyl radical ( $\text{NC}(\text{CH}_3)_2\text{C}\cdot$ ). On the other hand, when DMPA is used as the initiator, two

different radicals are formed in the first place, the benzoyl and dimethoxy radicals. While the benzoyl radical ( $\text{C}_6\text{H}_5\text{CO}\cdot$ ) is stable, the other radical is unstable and undergoes further decomposition to yield methyl radical ( $\text{CH}_3\cdot$ ) and methyl benzoate (39). For this reason, when examining the reactivity of DMPA, the reactions of  $\text{CH}_3\cdot$  and  $\text{C}_6\text{H}_5\text{CO}\cdot$  radicals have to be taken into account.



**Scheme 3:** Radicals formed from the initiators.

Hydrogen abstraction reactions of the  $\text{NC}(\text{CH}_3)_2\text{C}\cdot$  radical are significantly less exothermic than the reaction of the other radicals (Table S1). This is because  $\text{NC}(\text{CH}_3)_2\text{C}\cdot$  radical is much more stable than the others (21). For example, while the enthalpy of the reaction with thiophenol is  $-45.90$  kJ/mol, it is  $-110.84$  kJ/mol when the  $\text{CH}_3\cdot$  radical reacts with the same thiol,  $-54.13$  kJ/mol when the  $\text{C}_6\text{H}_5\text{CO}\cdot$  radical reacts. Reactions with other thiols have a similar tendency. The fact that the enthalpies of the reactions carried out with T3 and T4 thiols are similar is due to almost the same stability of the sulfur-centered radicals (Table S1). The order of stability for considered thiol radicals is  $\text{T2-r} > \text{T1-r} > \text{T3-r} \approx \text{T4-r}$  (Figure S2), causing the reaction enthalpies to have the same order in terms of exothermicity (Table S1). All exothermic reactions can be interpreted as breaking the weak H-S sigma bond and forming a relatively stronger C-H sigma bond instead.

The stability of the attacking radical has a critical role in both the reaction enthalpies and the size of the activation energies. For example, when the

most stable  $\text{NC}(\text{CH}_3)_2\text{C}\cdot$  radical reacts with the T4 thiol, the reaction enthalpy is  $-15.56$  kJ/mol, and the reaction barrier in Gibbs free energy is  $67.72$  kJ/mol. When the most unstable  $\text{CH}_3\cdot$  radical attacks the same thiol, the reaction enthalpy is  $-80.49$  kJ/mol, and the reaction barrier in Gibbs free energy is  $38.84$  kJ/mol. It is a fact that when the thiol structure changes, the reaction barriers and enthalpies change accordingly. However, it is seen that the barriers of the reactions with the  $\text{NC}(\text{CH}_3)_2\text{C}\cdot$  radical are larger than  $55.00$  kJ/mol, while the barriers in the reactions of other radicals are smaller than  $45.00$  kJ/mol. These results show that the radical formed from AIBN performs a much slower hydrogen abstraction reaction than the radicals formed from DMPA. Another remarkable point is that the reaction barrier is significantly reduced when the hydrogen scavenging reaction is carried out with thiophenol. It means that the reaction with the thiol takes place faster than the others.

### Addition Reactions

The radicals generated from AIBN and DMPA initiators have the potential to react with monomers as a side reaction. The conformational analysis for this reaction of radicals is given in Figure S4. The located activated complex geometries found out from this study are shown in Figures S5-S7, and all reaction energetics and kinetics are given in Tables S2-S4.

Based on the quantum chemically calculated results, the exothermicity of the reactions with the AIBN radical is less than the reactions of the other radicals. Even, it is endergonic for 2-butene and vinyl ether (1.25 kJ/mol and 5.13 kJ/mol, respectively). All reactions of other radicals ( $\text{CH}_3\bullet$  and  $\text{C}_6\text{H}_5\text{CO}\bullet$ ) are relatively exothermic. For example, when the  $\text{CH}_3\bullet$  radical is added to vinyl ether, the reaction enthalpy is -106.42 kJ/mol, and when  $\text{C}_6\text{H}_5\text{CO}\bullet$  is added to the same monomer, it is -80.44 kJ/mol.

It was observed that there was a direct relationship between the stability of the attacking radicals to the monomers and the activation Gibbs energies. The more stable  $\text{NC}(\text{CH}_3)_2\text{C}\bullet$  radical has higher reaction barriers, while the less stable  $\text{CH}_3\bullet$  and  $\text{C}_6\text{H}_5\text{CO}\bullet$  radicals have lower activation energies (Table S2). If the reactivity of  $\text{CH}_3\bullet$  and  $\text{C}_6\text{H}_5\text{CO}\bullet$  radicals are compared among themselves, interestingly, it is seen that the barriers to the reactions of the more unstable  $\text{CH}_3\bullet$  radical are relatively higher. The SOMO energies of the radicals can explain this. It was calculated -0.28407 Hartree for  $\text{CH}_3\bullet$ , while SOMO energy is relatively higher (-0.26103 Hartree) for  $\text{C}_6\text{H}_5\text{CO}\bullet$ . Therefore, SOMO of  $\text{C}_6\text{H}_5\text{CO}\bullet$  has the potential to more stabilizing the transition state structure by effective interaction with  $\pi^*$  orbital of the substrate. In addition, the interaction of the monomer with the  $n$  orbitals in the pi bond system of the  $\text{C}_6\text{H}_5\text{CO}\bullet$  radical leads to more stable transition state geometries (Figure S7).

### Reaction Kinetics

In this study, what is expected from a good initiator candidate is that the generated radical should prefer to react with thiol instead of monomer. This preference is presented by a large difference between the rate constants ( $k_{\text{HA}} \gg k_i$ ). More favored hydrogen abstraction from thiol can result in more homogeneous thiol-ene polymerization. If there is a competition between these two reactions, the initiator radical reduces the monomer concentration, increasing the heterogeneity of polymerization product. The mentioned rate constants are given in Table 1, and the logarithms of the ratios of these calculated rate constants,  $\log(k_{\text{HA}}/k_i)$ , are given in Table 2.

The addition reaction of alkyl thiyl radicals to electron-deficient monomers occur relatively faster (1,3-butadiene, 2,4-hexadiene, 2,4,6-octatriene, and acrylonitrile) than the electron-rich monomers (2-butene, vinyl chloride, and methyl vinyl ether). If the rate constants of the hydrogen abstraction reactions from thiols are evaluated, it is seen that they are greater than  $10^7 \text{ M}^{-1}\cdot\text{s}^{-1}$  for the radicals  $\text{CH}_3\bullet$  and  $\text{C}_6\text{H}_5\text{CO}\bullet$ . When the radical formed from AIBN is used in the hydrogen abstraction reaction, this value is lowered below  $10^5 \text{ M}^{-1}\cdot\text{s}^{-1}$ .

When the hydrogen abstraction reaction rate is closer to the addition reaction rate for the AIBN, the initiator enhances the side reaction. However, it was calculated that the hydrogen abstraction ( $1.82\text{E}+04 \text{ M}^{-1}\cdot\text{s}^{-1}$ ) from  $\text{C}_6\text{H}_5\text{-SH}$  by the formed radicals from AIBN occurred faster than other thiols. It means that using the AIBN initiator, the best thiol-ene polymerization is possible with the preference of aromatic thiols. In the case of using the DMPA initiator, better results are obtained as a general tendency of initiators. However, by-product formation is possible for electron-deficient monomers (1,3-butadiene, 2,4-hexadiene, 2,4,6-octatriene, and acrylonitrile) since they have relatively fast addition reactions. Especially for acrylonitrile, the rate constant in the addition reaction with  $\text{C}_6\text{H}_5\text{CO}\bullet$  is very large ( $1.03\text{E}+06 \text{ M}^{-1}\cdot\text{s}^{-1}$ ).

**Table 1:** Addition ( $k_i$ ) and hydrogen abstraction reaction ( $k_{HA}$ ) kinetics ( $M^{-1}.s^{-1}$ ) for  $NC(CH_3)_2C\bullet$ ,  $CH_3\bullet$ , and  $C_6H_5CO\bullet$  radicals.

	$NC(CH_3)_2C\bullet$	$CH_3\bullet$	$C_6H_5CO\bullet$
Addition to monomers ( $k_i$ )			
ethylene (1)	2.57E-01	1.24E+02	4.04E+02
2-butene (2)	5.69E-02	3.92E+00	3.76E+02
1,3-butadiene (3)	1.78E+02	3.49E+04	2.86E+04
2,4-hexadiene (4)	6.46E+00	2.99E+02	2.44E+04
2,4,6-octatriene (5)	2.20E+02	2.16E+03	8.22E+04
vinyl chloride (6)	2.78E+00	7.17E+02	1.55E+03
acrylonitrile (7)	6.04E+01	4.59E+04	1.03E+06
methyl vinyl ether (8)	1.27E+00	9.13E+00	3.63E+02
Hydrogen abstraction from thiols ( $k_{HA}$ )*			
T1**	1.50E+02	4.66E+07	3.01E+08
T2	1.82E+04	1.36E+08	3.62E+08
T3**	2.18E+03	2.32E+07	5.25E+07
T4	4.73E+02	4.41E+07	2.37E+08

\* Wigner's tunneling correction was performed. \*\* Reference (21)

The hydrogen abstraction rate constants of  $NC(CH_3)_2C\bullet$  radical vary between  $1.50E+02 M^{-1}.s^{-1}$  and  $1.82E+04 M^{-1}.s^{-1}$  (Table 1). Moreover, rate constants of its addition to alkenes vary between  $5.69E-02 M^{-1}.s^{-1}$  (2-butene (2)) and  $2.20E+02 M^{-1}.s^{-1}$  (2,4,6-octatriene (A5)). These results show that the rates of the specific reactions are very close to each other when the AIBN initiator is used. Especially in conjugated monomers, such as 1,3-butadiene or 2,4,6-octatriene, the addition reaction rate constants are in the order of  $10^2 M^{-1}.s^{-1}$ . Therefore, the possibility of desired thiol-ene polymer product cannot be obtained due to this side reaction. Furthermore, an increase in the initiator concentration also leads to an increase in the probability of side reaction. These findings explain why AIBN is not a good initiator for the polymerization. When DMPA is used as the initiator, kinetic data for the hydrogen abstraction rate constants of the radical  $CH_3\bullet$  vary between  $2.32E+07 M^{-1}.s^{-1}$  and  $1.36E+08 M^{-1}.s^{-1}$  (Table 1). For the addition reaction of the same radical, kinetic data changes from  $3.92E+00 M^{-1}.s^{-1}$  (2-butene (2)) to  $4.59E+04 M^{-1}.s^{-1}$  (acrylonitrile (7)). The kinetic data addition reaction for the commercial monomers, especially 1,3-butadiene and acrylonitrile, are in the order of  $10^4 M^{-1}.s^{-1}$ . Compared to the AIBN radical ( $NC(CH_3)_2C\bullet$ ), a larger difference is obtained between the rate constants. The hydrogen abstraction by the benzoyl ( $C_6H_5CO\bullet$ ) radical, another radical formed from DMPA, is significantly fast and its rate coefficient changes from  $5.25E+07 M^{-1}.s^{-1}$  to  $3.62E+08 M^{-1}.s^{-1}$ . As a side reaction, attacking the same radical to the alkenes is relatively slow, and rate coefficients of this reaction change from  $3.63E+02 M^{-1}.s^{-1}$  (methyl vinyl ether) to  $1.03E+06 M^{-1}.s^{-1}$  (acrylonitrile). Again, the difference between

the rate constants is better compared to the AIBN radical ( $NC(CH_3)_2C\bullet$ ). Nevertheless, the rate constant of the addition to commercial monomers, especially acrylonitrile, is above the order of  $10^5 M^{-1}.s^{-1}$ . As a result, electron-poor monomers have a great possibility to give heterogeneous thiol-ene polymerization products with both radicals formed from DMPA. This probability decreases as the initiator concentration decreases, or better results can be obtained without using an initiator.

Table 2 makes kinetic evaluation more understandable and straightforward. The data in the table were obtained by taking the logarithm of the  $k_{HA}/k_i$  ratio for the reactions. In this way, it is made visible to what extent the rates of both reactions compete with each other. The  $\log(k_{HA}/k_i)$  data colors were determined according to the following definition; red for values less than two, yellow for values between two and three, and blue for values greater than three. The red color symbolizes that the presence of side reactions is significant, the yellow color symbolizes that the by-product may show itself, albeit partially, and the blue color symbolizes that the presence of the by-product is negligible. As a result, it was demonstrated that the AIBN initiator is not a good option for the polymerization since it has a high probability of forming by-products. The applicability of the DMPA initiator for thiol-ene polymerization is well known and has also been proven by quantum chemical calculations. It was predicted that the heterogeneity of the polymerization product resulting from side reactions would increase when initiator concentration is kept high. These findings are also well correlated with a kinetic modeling investigation in the previous literature study (38).

**Table 2:** Ratios for the reaction rate constants of hydrogen abstraction from thiols and addition reactions of  $\text{NC}(\text{CH}_3)_2\text{C}\cdot$ ,  $\text{CH}_3\cdot$ , and  $\text{C}_6\text{H}_5\text{CO}\cdot$  radicals to monomers on a logarithmic scale,  $\log(k_{\text{HA}}/k_i)$ .

Monomers	$\text{NC}(\text{CH}_3)_2\text{C}\cdot$				$\text{CH}_3\cdot$				$\text{C}_6\text{H}_5\text{CO}\cdot$			
	T1	T2	T3	T4	T1	T2	T3	T4	T1	T2	T3	T4
ethylene (1)	2.8	4.9	3.9	3.3	5.6	6.0	5.3	5.6	5.9	6.0	5.1	5.8
2-butene (2)	3.4	5.5	4.6	3.9	7.1	7.5	6.8	7.1	5.9	6.0	5.1	5.8
1,3-butadiene (3)	-0.1	2.0	1.1	0.4	3.1	3.6	2.8	3.1	4.0	4.1	3.3	3.9
2,4-hexadiene (4)	1.4	3.4	2.5	1.9	5.2	5.7	4.9	5.2	4.1	4.2	3.3	4.0
2,4,6-octatriene (5)	-0.2	1.9	1.0	0.3	4.3	4.8	4.0	4.3	3.6	3.6	2.8	3.5
vinyl chloride (6)	1.7	3.8	2.9	2.2	4.8	5.3	4.5	4.8	5.3	5.4	4.5	5.2
acrylonitrile (7)	0.4	2.5	1.6	0.9	3.0	3.5	2.7	3.0	2.5	2.5	1.7	2.4
methyl vinyl ether (8)	2.1	4.2	3.2	2.6	6.7	7.2	6.4	6.7	5.9	6.0	5.2	5.8

The colored values defined as red is  $x < 2$ , yellow is  $2 < x < 3$ , and blue is  $x > 3$  ( $x = k_{\text{HA}}/k_i$ ).

## CONCLUSION

This comprehensive quantum chemical study demonstrates the importance of initiator selection for thiol-ene polymerization. It was found out that aromatic thiols (such as thiophenol) were more prone to thiol-ene polymerization when AIBN is preferred as the initiator. Best results with this combination were obtained with 2-butene and methyl vinyl ether. Regardless of the type of initiator, 2-butene has a high affinity for the thiol-ene reaction. It is worth noting that initiators have a high tendency to initiate classical radical polymerization as a side polymerization with electron-deficient or conjugated monomers. As a general assessment, the performance of AIBN is not satisfactory compared to the application of DMPA.

Radicals formed from DMPA have been found to initiate the thiol-ene reaction without any problems, regardless of the thiol structure, except for electron-poor or conjugated monomers. Especially 2-butene, vinyl chloride, methyl vinyl ether have a low tendency to give by-products with this initiator. Even conjugated 2,4-hexadiene monomer can effectively initiate thiol-ene reaction instead of classical radical polymerization initiation. Another finding is that the  $\text{C}_6\text{H}_5\text{CO}\cdot$  radical is more likely to form by-products than the  $\text{CH}_3\cdot$  radical for the DMPA initiator. In any case, it was calculated that radicals formed from DMPA had a lower tendency to side-reactions than radicals formed from AIBN.

It is worth noting that these results only provide some information about the initiation step of the thiol-ene polymerization. A good initiation does not always mean that it results in a good

polymerization; other reactions in the thiol-ene polymerization mechanism, such as propagation and chain transfer, strongly depend on the chemical structures of monomers and thiols, as mentioned in the introduction. On the other hand, a poor initiation performance always results in a heterogeneous product.

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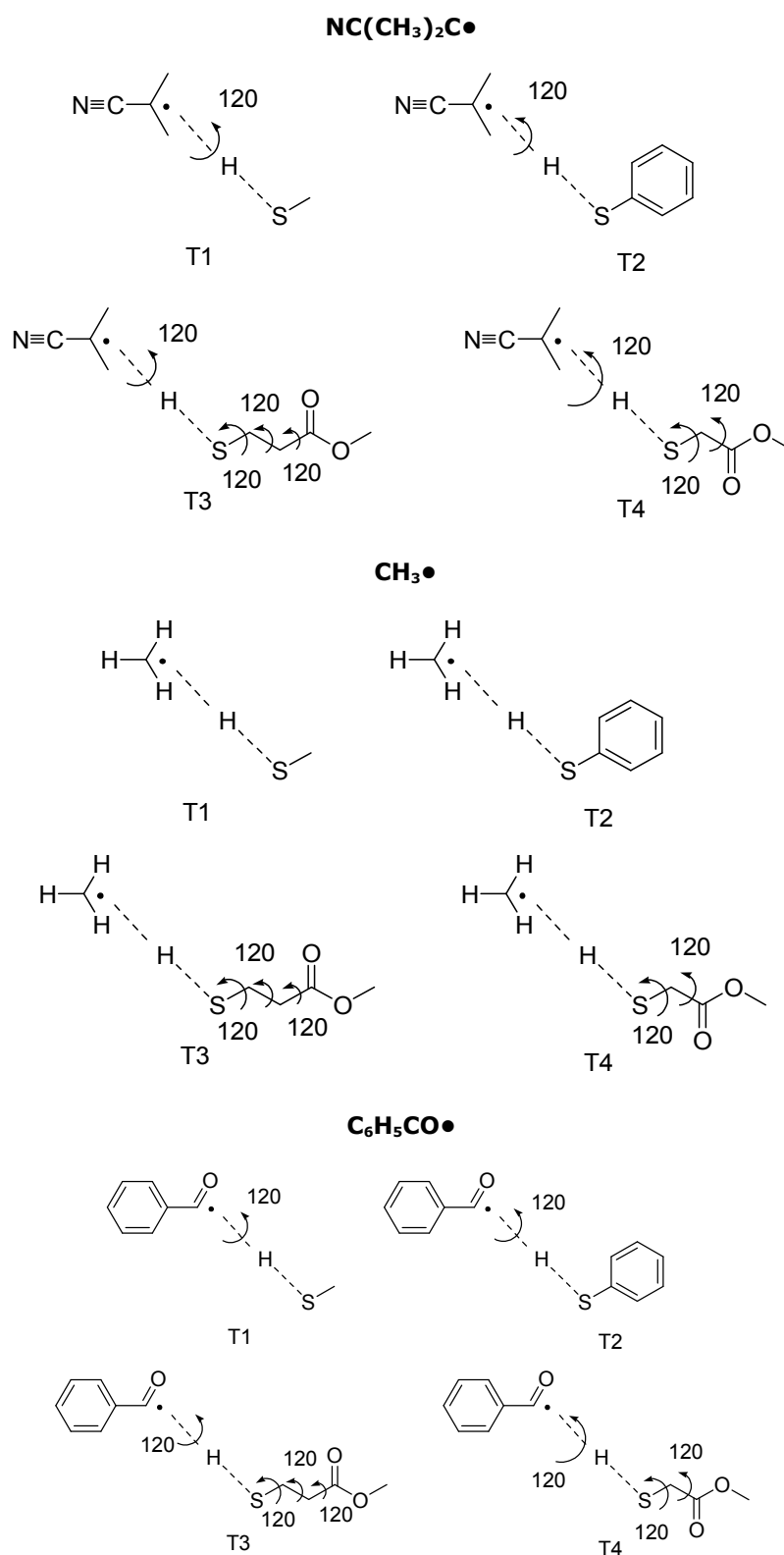
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## **Role of Initiator Structure on Thiol-Ene Polymerization: A Comprehensive Theoretical Study**

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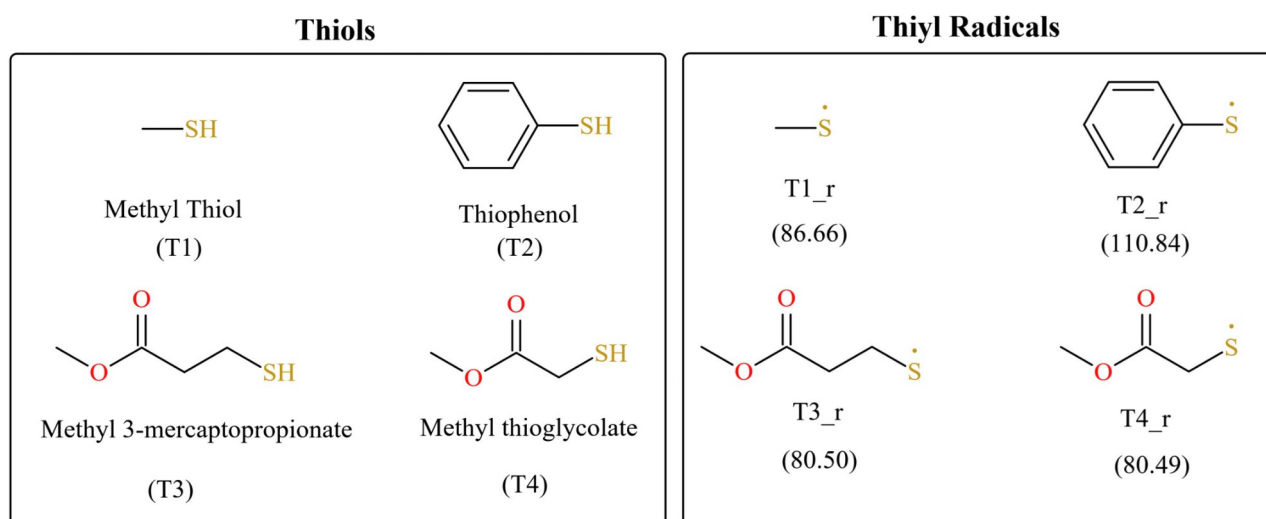
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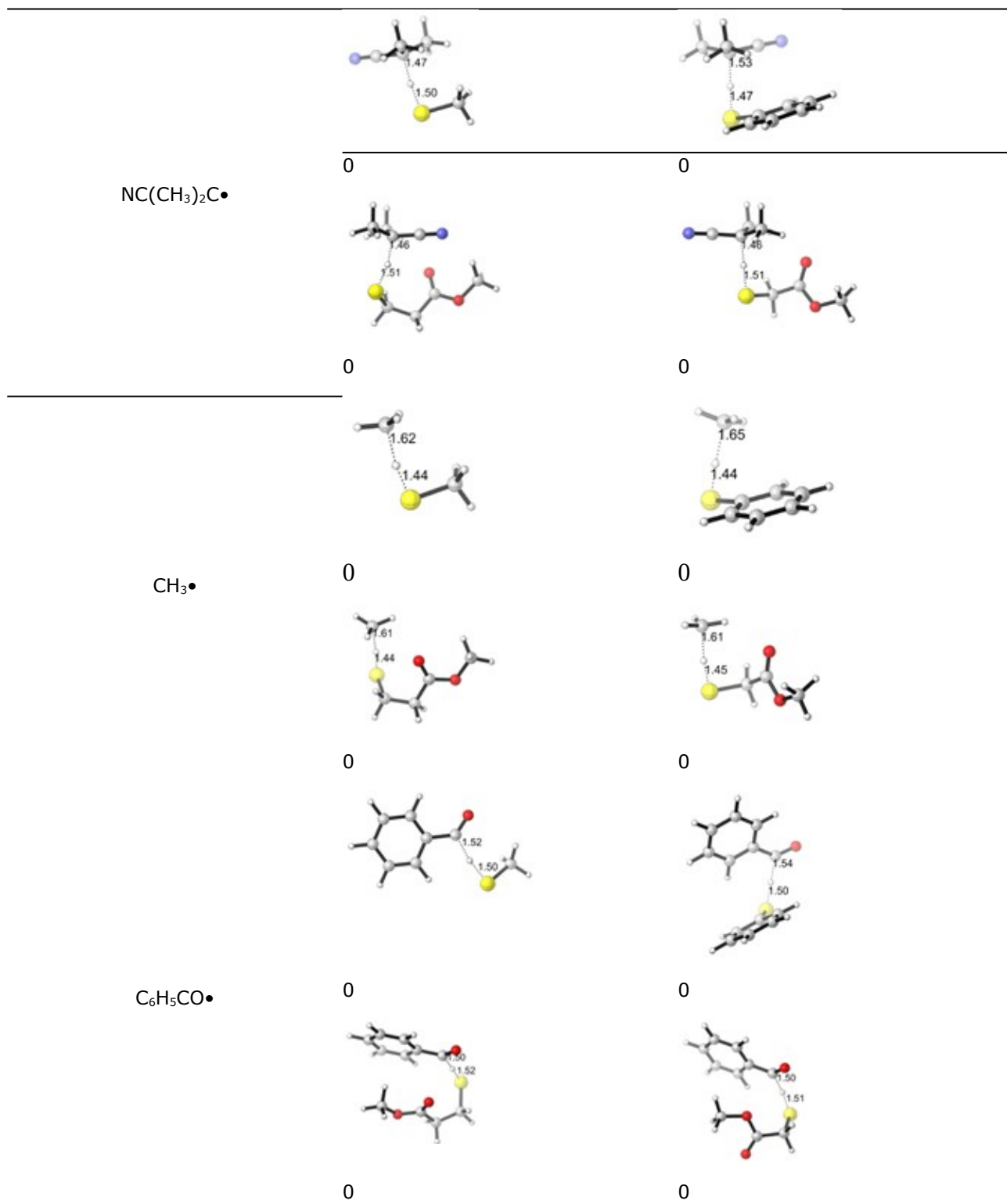
**Figure S1:** Schematic representation of conformational analysis at the transition states for hydrogen abstraction reaction of  $\text{NC}(\text{CH}_3)_2\text{C}\bullet$ ,  $\text{CH}_3\bullet$ , and  $\text{C}_6\text{H}_5\text{CO}\bullet$  radicals from T1, T2, T3, and T4 thiols.

**Table S1:** Energetics (kJ/mol) and kinetics ( $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ ) for the hydrogen abstraction reaction from T1, T2, T3, and T4 thiols by  $\text{NC}(\text{CH}_3)_2\text{C}\cdot$ ,  $\text{CH}_3\cdot$ , and  $\text{C}_6\text{H}_5\text{CO}\cdot$  radicals.

	Thiol	$\Delta H_{\text{rxn}}$	$\Delta G_{\text{rxn}}$	$\Delta H^\ddagger$	$\text{DG}^\ddagger$
$\text{NC}(\text{CH}_3)_2\text{C}\cdot$	T1	-21.72	-13.57	21.66	70.67
	T2	-45.90	-35.92	3.87	58.61
	T3	-15.57	-9.88	8.25	64.11
	T4	-15.56	-8.20	11.10	67.72
$\text{CH}_3\cdot$	T1	-86.66	-81.28	2.84	38.77
	T2	-110.84	-103.63	-2.29	35.85
	T3	-80.51	-77.59	1.18	40.41
	T4	-80.49	-75.91	-2.50	38.84
$\text{C}_6\text{H}_5\text{CO}\cdot$	T1	-29.95	-27.20	-2.42	33.96
	T2	-54.13	-49.55	-14.41	33.29
	T3	-23.80	-23.51	-15.02	38.14
	T4	-23.78	-21.83	-16.59	34.55



**Figure S2:** Chemical structures of thiols, formed thiyl radicals from the considered thiols and their radical stabilisation energies (RSE) in kJ/mol.



**Figure S3:** Hydrogen abstraction transition state geometries of NC(CH<sub>3</sub>)<sub>2</sub>C•, CH<sub>3</sub>•, and C<sub>6</sub>H<sub>5</sub>CO• radicals from T1, T2, T3, and T4 thiols.