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A Density Functional Theory Study of Poly (vinyl chloride) (PVC) Free Radical Polymerization

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Summary: Quantum chemistry was applied to the free radical polymerization of Vinyl Chloride with the aim of elucidating the reaction kinetics and especially the formation of structural defects and low molecular weight polymer. The radical reactions were studied using the Density Functional Theory. All calculations were performed with B3LYP functionals and in particular the 6-31G(d,p) basis set was selected to evaluate the exchange and correlation energies. The computational method was first validated by predicting the rate constant of the propagation step and comparing the calculated values to experimental ones. Then intramolecular chain transfer, β-scission and branching reactions were also investigated, due to their direct connection with the production of defects in the growing chains. A comparison of the evaluated kinetic constants of such secondary reactions with other computational evaluations and experimental data was finally made.

Keywords: kinetic; poly (vinyl chloride); polymerization; quantum chemistry; secondary reactions

Introduction

Poly (vinyl chloride) (PVC) is the most world widely produced thermoplastic material, second only to polyolefins as production volume.[1] Whereas the manufacturing of the polymer is a well-known process, during its use PVC can experience conditions that may cause degradation of the material, a process much less studied.[2–3]

In the last two decades investigations on this unpleasant mechanism have shown that the thermal stability of PVC is negatively affected by structural defects in the polymer chains, which act as breaking-labile points during thermal or photo-treatments. One of the foremost irregularities responsible of degradation is the presence of tertiary chlorines, usually located on the roots of branches, which formation is mainly related to the presence of secondary reactions in the polymerization reaction scheme, as well as to the presence of mid-chain radicals.[3,4]

As shown in Figure 1, the formation of branches characterized by the presence of a tertiary chlorine or hydrogen atom on the carbon atom that holds the side-chain, can be ascribed to both intramolecular and intermolecular transfer to polymer reactions, followed by a propagation on a mid-chain radical (MCR). In the first case, a well-defined short chain branch (SCB) is formed. Its length is correlated to the location of the internal radical which propagates, and thus to the secondary reaction that causes the radical shift inside the backbone. On the other hand, the transfer to polymer reaction leads to the formation of a long chain branch (LCB) with indefinite length.

Chain transfer reactions are responsible of the production of mid-chain radicals. These active species, which may be quite stable due to the presence of a tertiary carbon atom bringing the charge, have been recently investigated for various polymerization systems, with the aim of setting their reactivity in comparison to that of secondary

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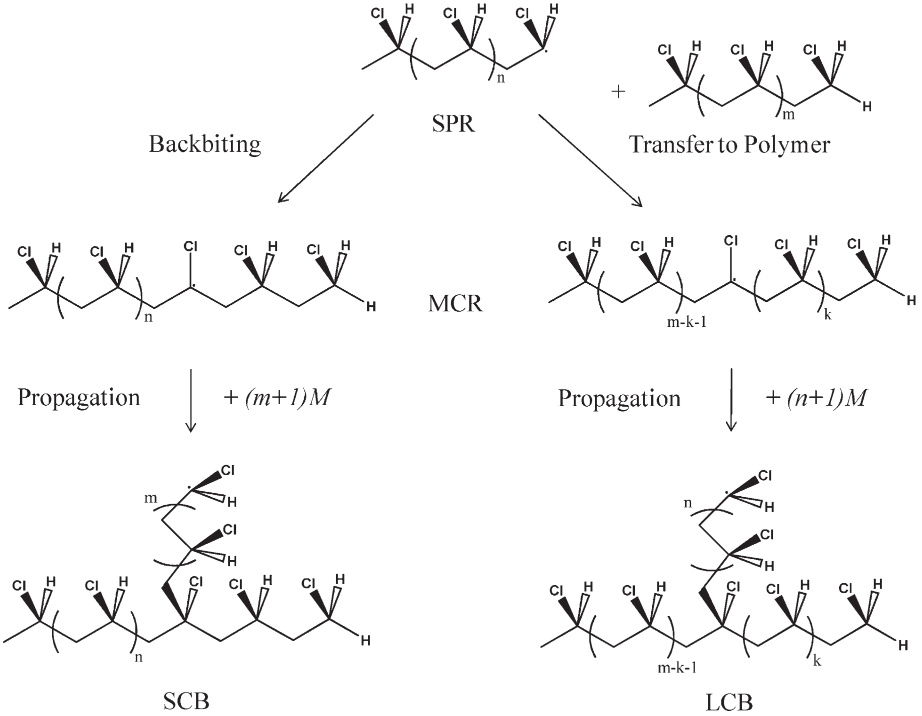

Figure 1.
Production pathways of tertiary chlorines through branching propagation on mid-chain radicals and involved secondary reactions. From a Secondary Propagating Radical (SPR) both intermolecular and intramolecular (in particular the backbiting 1:5) chain transfer reactions originate mid-chain radicals (MCR). Propagation on the internal radical produces Short Chain Branches (SCB) or Long Chain Branches (LCB), depending on the location of the radical charge after the transfer reaction.

radicals.[5] The concentration and reactivity of MCRs can affect the microstructure of the polymer chains as well as produce difficulties in the experimental evaluation of the polymerization kinetics.[6a] Mid-chain radicals are primarily originated by intramolecular transfer reactions, also referred as backbiting, which seems to be the most favorite especially when the internal hydrogen shift reaction is characterized by a transition state that involves a stable six-member ring.[7-8]

An interesting unimolecular reaction involving MCRs is the intramolecular β-scission, which is responsible of molecular weight distribution (MWD) modifications due to the origination of lower molecular weight products, as shown in Figure 2. Recent investigations showed that this secondary reaction requires large activation energy and has an influence on the polymer morphology which is larger at increasing temperature, in particular for oligomer productions or during thermal treatments.[8–10]

The aim of this work is to investigate the secondary reactions in PVC polymerization producing mid-chain radicals and their reactivity by a computational method based on Quantum Chemistry. The attention is focused on those reaction pathways responsible of defect formations, and in particular of tertiary chlorine atoms, as well as on the intramolecular chain scissions that could affect the MWD. In particular, backbiting reactions are investigated to elucidate how MCRs are produced and their propagation reaction is studied to clarify how branches, and thus tertiary chlorines, are originated. Finally, the β-scission reaction is also analyzed to evaluate the contribution of this pathway towards the formation of low

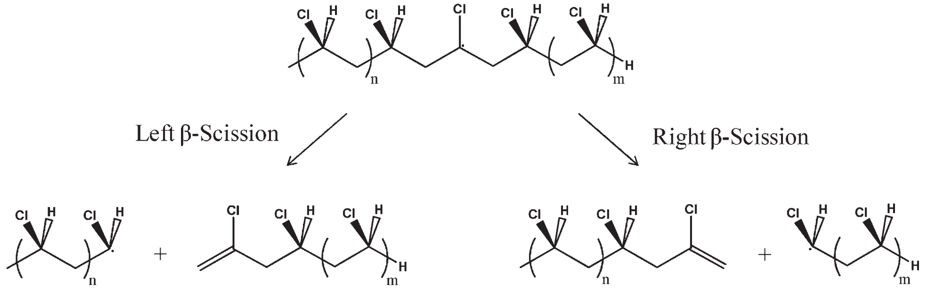

Figure 2.
Left and right β-scission reactions from a mid-chain radical.

molecular weight species All such reactions are very difficult to analyze experimentally, which explain the lack of experimental data still present in the literature for PVC. However improvements have been recently made in the evaluation of the rate coefficients of these secondary reactions for several polymerization systems, and especially for acrylates, due to the applying of pulsed laser polymerization (PLP) technique of analysis.[6]

Computational Details

All the thermodynamic and kinetic parameters have been evaluated through the Density Functional Theory (DFT).[11] DFT is often a cost effective theoretical procedure, widely adopted in a huge number of computational studies involving reactive systems similar to those treated in this study.[8,9] In all DFT calculations the exchange and correlation energies were evaluated with the Becke 3 parameters and the Lee-Yang-Parr functionals (B3LYP).[12,13] Simulations were performed using the all electron 6-31 basis set with added polarization functions (6-31G(d,p)),[12,13] in order to obtain an accurate description of the molecular structure of the investigated compounds (reactants, products and transition states). Activation energies were calculated as the difference between the electronic energy of the transition state and that of the reactant, including zero point energies (ZPE). Enthalpy changes were determined including the thermal correction terms:

$$E_a = (EE + ZPE)_{TST} - \sum_{i=reactants} (EE + ZPE)_i \tag{1}$$

$$\Delta H = \sum_{j=products} (EE + ZPE + TC) - \sum_{i=reactants} (EE + ZPE + TC)_i \tag{2}$$

where *EE* represents the electron energy, *ZPE* is the zero point energy and *TC* the thermal energy correction. The rate constants are expressed through the Arrhenius equation. The evaluation of the frequency factor (A_P) and the activation energy (E_a) has been done through the conventional Transition State Theory (TST) as:

$$k(T) = A_P \cdot T \cdot e^{-Ea/k_b T} = \frac{k_b}{h} \cdot \frac{q_{TS}^{rot} q_{TS}^{vib} q_{TS}^{el}}{\prod\limits_{reactants} q^{rot} q^{vib} q^{el}} \cdot T \cdot e^{-Ea/k_b T} \tag{3}$$

where k_b represents the Boltzmann's constant, h the Plank's constant, T the temperature, q_{TS} the molecular partition function of the transition state (rotational, vibrational and electronic, as specified by the superscript) and E_a the activation energy, calculated as shown in equation (1). The transition state structures were located adopting the synchronous transit guided method and are characterized by a single imaginary vibrational frequency.[14] All quantum chemistry calculations were performed with the Gaussian 03[15] suite of programs and all structures drawn with Molden 4.2.[16]

Results and Discussion

The representative model applied for the simulation of the secondary reactions considers active polymer chains with six monomer units, which is the minimum number of repeating units in order to simulate correctly the effect of chain length and, on the other hand, to minimize the total number of atoms and electrons involved in the calculations.[4,17] The chain model includes vinyl chloride units in syndiotactic configuration, which corresponds to the global energy minimum for PVC.[17] The atom numeration along the backbone, which is used to identify the location of the intramolecular radical carbon atoms, is made considering the first carbon as the one which brings the charge in the corresponding terminal radical. The descriptive model and the atom numeration are shown in Figure 3.

To validate the selected QM-based method, the propagation rate constant of PVC has been calculated with the 6-31G(d,p) basis set and the results are reported in Table 1. The configurations of reactants, products and transition states are shown in Figure 4. A comparison with the experimental data shows a good agreement in terms of activation energy, which was experimentally evaluated as 5.948 kcal · mol^{-1}.[18] However the evaluated kinetic constant is quite larger than the experimental value, which ranges from 1,000 to 12,000 L · mol^{-1} · s^{-1}.[18-19] This mismatch can be due to insufficient accuracy of the selected basis set in the estimation of the pre-exponential factor. With this respect, further investigations with higher level of accuracy are currently in progress.

Table 1.
Calculated values of reaction enthalpy, Arrhenius parameters and rate constant for the propagation reaction in PVC polymerization. Reaction enthalpies and activation energies are reported in kcal · mol^{-1}, A_p in L · mol^{-1} · s^{-1} · K^{-1}, k_p in L · mol^{-1} · s^{-1}. k_p and partition functions are calculated at 330 K.

Reaction	ΔH_R	E_a	$\log_{10}(A_p)$	k_p
$R_1 + M \rightarrow R_2$	−21.637	5.395	6.371	206,534
$R_2 + M \rightarrow R_3$	−21.571	5.649	6.317	123,646
$R_3 + M \rightarrow R_4$	−21.381	5.653	6.416	154,224
$R_4 + M \rightarrow R_5$	−21.424	5.656	6.524	197,127

Backbiting 1:3, 1:5, 1:7 and reverse reactions were examined to investigate the probability to have the shift of the radical charge from the terminal site of an active chain R_n to an intramolecular carbon atom in *j-th* position, thus producing a mid-chain radical $R_{n,j}$. The results in Table 2 show that backbiting 1:5 is the most favored due to the higher stability of the corresponding six-member ring transition state, in agreement with similar investigations previously made for other free radical polymerization systems.[7-9] In particular, this result is remarkably close to the computational evaluation of the backbiting 1:5 reaction rate of a previous work where values of 0.809 s^{-1} for the kinetic constant and 17.39 kcal · mol^{-1} for the activation energy have been reported.[4] Configurations of reactants, products and transition

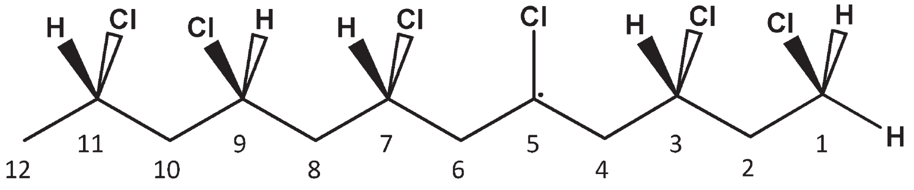

Figure 3.
Descriptive model and backbone atom numeration for the $R_{6,5}$ intramolecular radical chain resulting from backbiting 1:5 reaction.

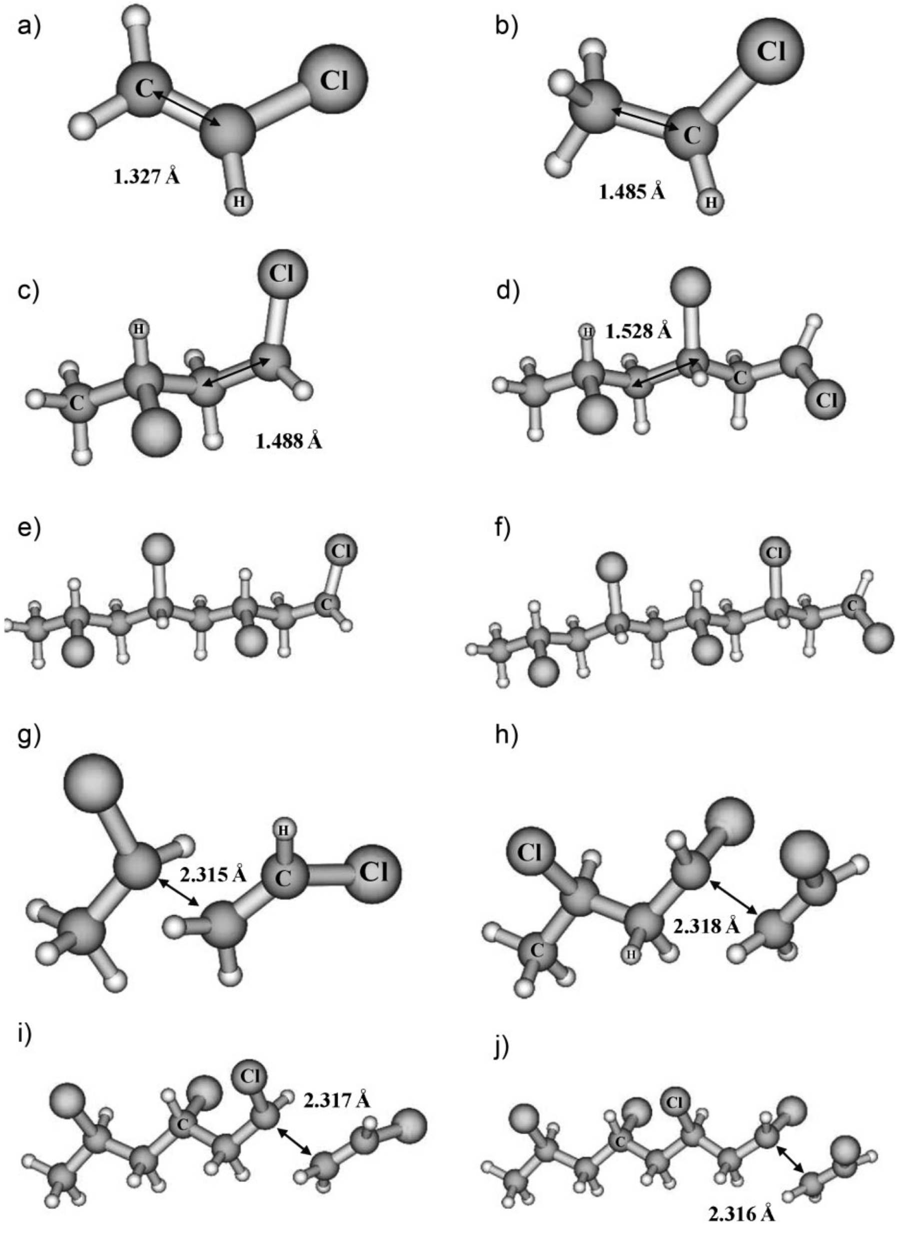

Figure 4.
Optimized configurations of reactants, products and transition states for the PVC propagation steps. a) Vinyl chloride monomer. Terminal active chains: b) R_1, c) R_2, d) R_3, e) R_4, f) R_5. Transition states of propagation reactions on: g) R_1, h) R_2, i) R_3, j) R_4.

states involved in the investigated backbiting reactions are shown in Figure 5.

Scission phenomena may take place from mid-chain radicals, in particular by breaking of one β-bond from the radical carbon. The so called β-scission reactions from the MCRs considered in backbiting investigations have been examined. Both right and left scissions from the radical located on carbon 3, 5 and 7 were simulated,

Table 2.
Calculated values of reaction enthalpy, Arrhenius parameters and rate constant for the backbiting reactions in PVC polymerization. Reaction enthalpies and activation energies are reported in kcal · mol^{-1}, A_{bb} in s^{-1} · K^{-1}, k_{bb} in s^{-1}. k_{bb} and partition functions are calculated at 330 K.

Backbiting	Reaction	ΔH_R	E_a	$\log_{10}(A_{bb})$	k_{bb}
1:3	$R_{6,1} \rightarrow R_{6,3}$	−1.814	38.254	10.257	2.678E-13
3:1	$R_{6,3} \rightarrow R_{6,1}$	1.814	40.156	10.145	1.135E-14
1:5	$R_{6,1} \rightarrow R_{6,5}$	−0.969	17.113	9.128	2.028
5:1	$R_{6,5} \rightarrow R_{6,1}$	0.969	18.196	8.900	0.230
1:7	$R_{6,1} \rightarrow R_{6,7}$	−0.982	24.187	8.471	9.170E-06
7:1	$R_{6,7} \rightarrow R_{6,1}$	0.982	25.281	8.263	1.070E-06

and the computational results in Table 3 show that these secondary pathways have a significant role only at very high temperature, due to their high values of activation energy. These intramolecular terminations originate smaller radical chains which keep alive some propagation capacity but produce dead chains with shorter length. The actual length of these chains is determined by the location of the radical in the MCR

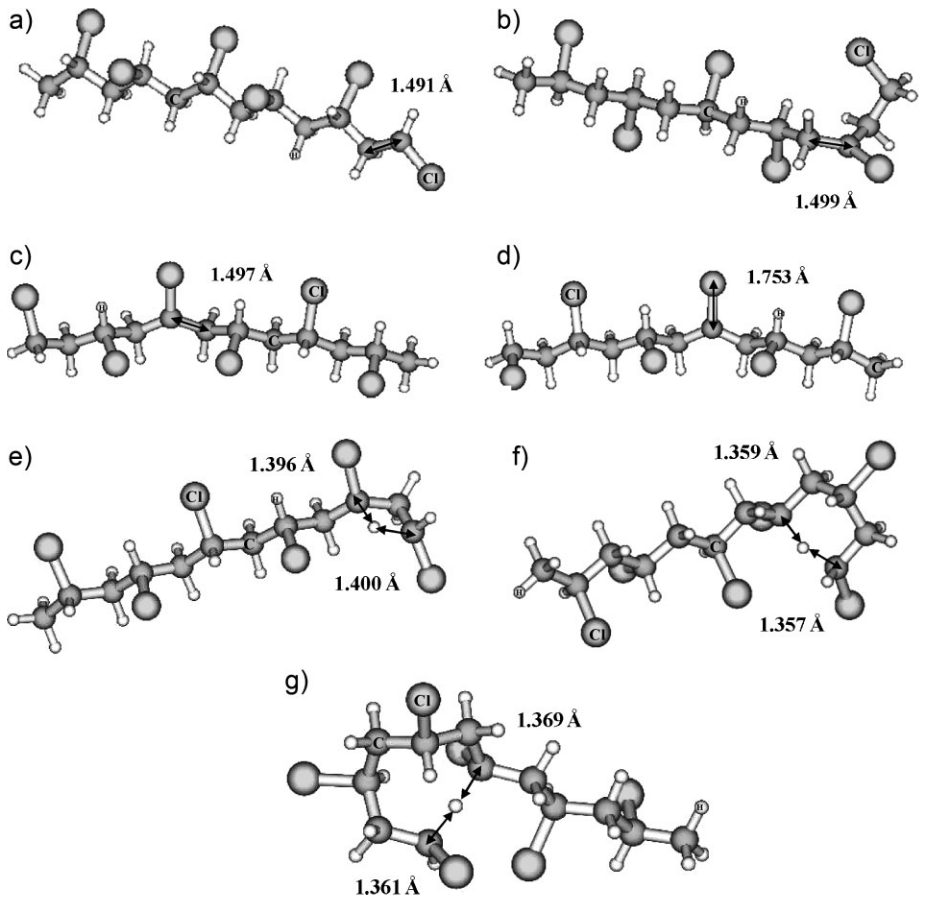

Figure 5.
Optimized configurations of reactants, products and transition states for the backbiting reactions: a) $R_{6,1}$, b) $R_{6,3}$, c) $R_{6,5}$, d) $R_{6,7}$. Transition states of backbiting reactions: e) 1:3, f) 1:5, g) 1:7.

Table 3.
Calculated values of reaction enthalpy, Arrhenius parameters and rate constant for the β-scission reactions in PVC polymerization. Reaction enthalpies and activation energies are reported in kcal · mol^{-1}, $A_{\beta S}$ in s^{-1} · K^{-1}, $k_{\beta S}$ in s^{-1}. $k_{\beta S}$ and partition functions are calculated at 330 K.

β-scission	Reaction	ΔH_R	E_a	$\log_{10}(A_{\beta S})$	$k_{\beta S}$
3-right	$R_{6,3} \rightarrow R_{1^*} + P_{5^*}$	25.959	30.301	10.806	1.767E-07
3-left	$R_{6,3} \rightarrow R_4 + P_2$	20.848	27.204	9.702	1.563E-06
5-right	$R_{6,5} \rightarrow R_{2^*} + P_{4^*}$	20.523	25.460	10.554	1.593E-04
5-left	$R_{6,5} \rightarrow R_3 + P_3$	21.100	24.888	10.241	1.856E-04
7-right	$R_{6,7} \rightarrow R_{3^*} + P_{3^*}$	19.908	24.767	10.266	2.365E-04
7-left	$R_{6,7} \rightarrow R_2 + P_4$	20.045	25.277	10.188	9.070E-05

involved in the β-scission reaction. Configurations of reactants, products and transition states involved in the investigated β-scission reactions are shown in Figure 6.

The propagation reaction of MCR, also referred as branching propagation, is responsible of the formation of branches, which in turn results in labile points prone to degradation on their roots, like tertiary Chlorines. In particular, non-linear, terminal radical chains, $R_n^{b,k}$, with n overall number of vinyl chloride units and a branch of length b and located on the carbon k can be formed by propagation on a MCR. This is a short and well-defined branch in the case of a mid-chain radical resulting from backbiting reaction, and its length and location are once more related to the position of the radical in the MCR. Investigations have been made for the first step of monomer addition on a six-unit active chain with the radical on the fifth carbon atom ($R_{6,5}$), which can be originated by a backbiting 1:5 reaction. Also, the following two steps of monomer addition were studied; therefore, formed non-linear radical chains bring a two-units branch.

The computational results in Table 4 show that the rate constant of the first step of branching propagation (BP1) on MCR is five orders of magnitude smaller than that estimated for terminal radical propagation. However the following propagation step (BP2) is only two orders of magnitude smaller, suggesting that the propagation constant becomes larger the large the distance of the growing radical from the tertiary carbon atom. This assumption seems to be confirmed by the rate constant value estimated for the subsequent propagation step (BP3): this reaction step is fully unaffected by the presence of the branch, thus exhibiting a kinetic constant of the same order of magnitude of the propagation of terminal radicals. Therefore, further propagation steps are most likely taking place at a rate equal to the one of the terminal radicals. Despite the not high accuracy of the chosen basis set in the estimation of the absolute propagation rate constant, there is quite reliability in the evaluated reactivity ratios between terminal radicals and MCRs, as well as in the estimated values of the activation energies. Configurations of reactants, products and transition states involved in the branching propagation reactions are shown in Figure 7.

A disagreement is found comparing the kinetics of the BP1 and BP2 reactions steps with the same reaction rates evaluated by Van Cauter et al., whereas no experimental data can be found regarding this reactions. In particular, in this work the evaluated propagation steps on a MCR are between 2 and 3 orders of magnitude greater than the ones reported in the Van Cauter's work. [4] Should be noticed that in the cited work also the evaluated propagation rate constant on a secondary radical is smaller than the one reported in our results.

Conclusion

The secondary reactions in PVC free radical polymerization have been theoretically investigated by a computational

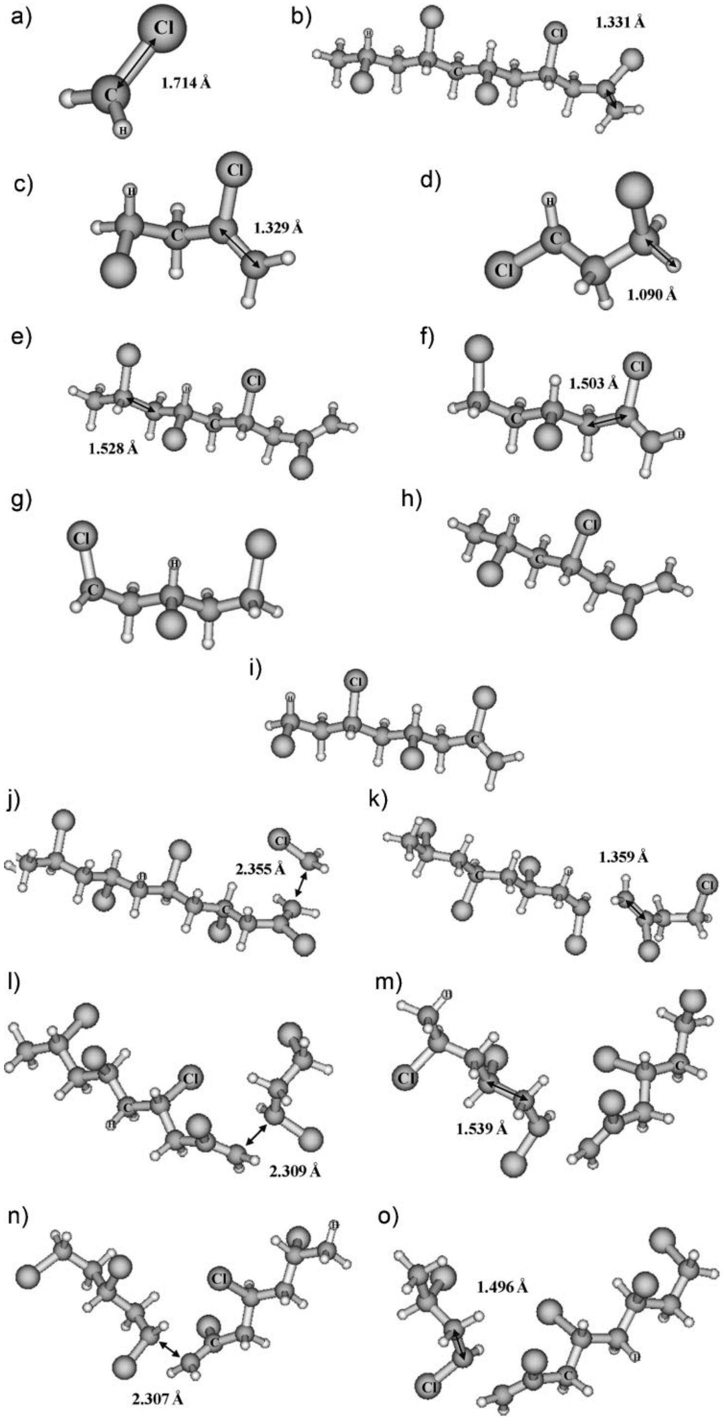

Figure 6.
Optimized configurations of reactants, products and transition states for the β-scission reactions: a) R_{1*}, b) P_{5*}, c) P_2, d) R_{2*}, e) P_{4*}, f) P_3, g) R_{3*}, h) P_{3*}, i) P_4. Transition states of β-scission reactions: j) 3-right, k) 3-left, l) 5-right, m) 5-left, n) 7-right, o) 7-left.

Table 4.

Calculated values of reaction enthalpy, Arrhenius parameters and rate constant for the consecutive propagation reaction steps on mid-chain radicals. Reaction enthalpies and activation energies are reported in kcal · mol^{-1}, A_p in L · mol^{-1} · s^{-1} · K^{-1}, k_p in L · mol^{-1} · s^{-1}. k_p and partition functions are calculated at 330 K.

Propagation	Reaction	ΔH_R	E_a	$\log_{10}(A_p)$	k_p
BP1	$R_{6,5} + M \rightarrow R_7^{2,3}$	−11.330	11.519	5.136	1.052
BP2	$R_7^{2,3} + M \rightarrow R_8^{2,5}$	−17.855	7.243	6.025	5,556
BP3	$R_8^{2,5} + M \rightarrow R_9^{2,7}$	−21.377	5.613	6.851	447,200

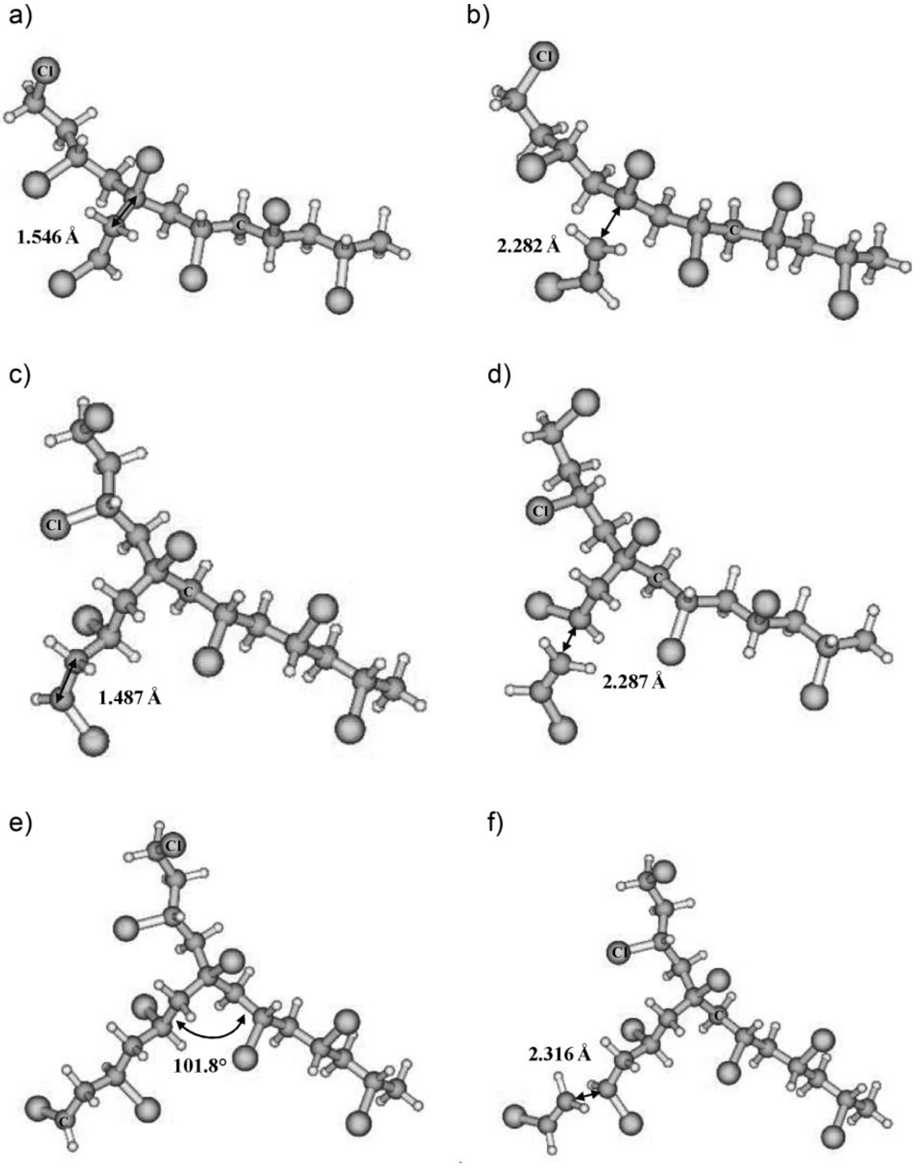

Figure 7.

Optimized configurations of reactants, products and transition states for the propagation reactions of mid-chain radicals. Non-linear terminal active chains: a) $R_7^{2,3}$, c) $R_8^{2,5}$, e) $R_9^{2,7}$. Transition states of branching propagation reactions: b) BP1, d) BP2, f) BP3.

method based on Density Functional Theory. The B3LYP/6-31G(d,p) functional and basis set have been applied. The attention was focused on the reactions forming and then involving mid-chain radicals, because of their impact on defect formation and molecular weight distribution modifications of the final polymer.

The backbiting 1:5 is the most favorite intramolecular transfer reaction responsible of MCRs production. Such radicals are involved in high-energy activated β-scission reactions, which become significant at high temperature. These reactions are also responsible of the production of oligomers. On the other hand, the propagation of MCRs is initially very unfavorable, due to the large stability of the tertiary carbon radical, but further propagation steps exhibit the same value of kinetic constant as the terminal radicals as soon as the radical leaves the branch point, and thus the tertiary chlorine.

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