Theoretical Study of Chain Transfer to Agent Kinetics in Butyl Acrylate Polymerization

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INTRODUCTION

The physical properties of macromolecular compounds are largely determined by the polymer molecular weight and molecular weight distribution (MWD). In a conventional chain-growth polymerization reaction scheme, these features are regulated by the relative extent of propagation and termination events, under the assumption that the active species are characterized by a steady-state behavior. However, a premature termination of the growing chains may occur due to secondary mechanisms, such as chain transfer, which leads to a modification of the expected polymer MWD and average properties.[1]

In free radical polymerization (FRP) the propagation of a radical chain can be arrested by conventional combination and disproportionation termination events, but also the radical can be involved in a chain transfer reaction where a hydrogen atom is abstracted from a monomer, solvent, initiator, or polymer molecule in the system. The result of bimolecular chain transfer reactions is the formation of a dead polymer chain as well as a new radical which is able to initiate a new polymer chain (chain transfer to initiator, to solvent, and to monomer) or capable of further propagation albeit less reactive than secondary radicals (chain transfer to polymer). Radicals of the latter category are produced even after monomolecular hydrogen abstractions (backbiting). In particular, both inter- and intramolecular chain transfer to polymer lead to the formation of less reactive midchain radicals (MCRs).[2] The macroscopic effects of chain transfer reactions on the polymer features are mainly determined by the rates of atom transfer and reinitiation of the newly formed radical. Although chain transfer may occur from any molecule within the polymerization system, a chain transfer agent (CTA) can be intentionally added in order to trace the molecular weight modification back to a specific contribution.[3] As a matter of fact, through a careful choice of CTA and its relative amount, chain transfer reactions can be made the dominant stopping mechanisms of radical chain growth.[4]

In combination with appropriate reaction conditions, CTAs are widely used to control the MWD during FRP and find many applications in emulsion processes for the production of latexes.[5,6] Most of the controlled radical polymerizations occur through a reversible activation−deactivation of growing radicals rather than reversible chain transfer (RAFT); however, CTAs can be also adopted to achieve MWDs characterized by narrow polydispersity as well as to produce block copolymers.[7] Among the most recent applications, CTAs have demonstrated their effectiveness in controlling the polymer chain architecture. Particularly, the formation of branches can be substantially reduced with the addition of a sufficient amount of CTA.[8−10] Lastly, for polymerization systems in which cross-link reactions are favorable, as in the case of acrylate systems, CTAs are useful in controlling the formation of gel polymers.[5,11−13]

Given the importance of CTAs in a wide range of polymerization processes, the understanding of chemical structure becomes valuable information which is required to assess their reactivity. The most important classes of CTAs are halocarbons and mercaptans, whose weak S−H bonds[14] and the highly reactive thiyl radicals[15] render them almost ideal CTAs. The presence of a weak S−H or C−Hal bond (with Hal = Cl, Br, or I) promotes the chain transfer of the hydrogen or halogen atom to a growing radical chain.

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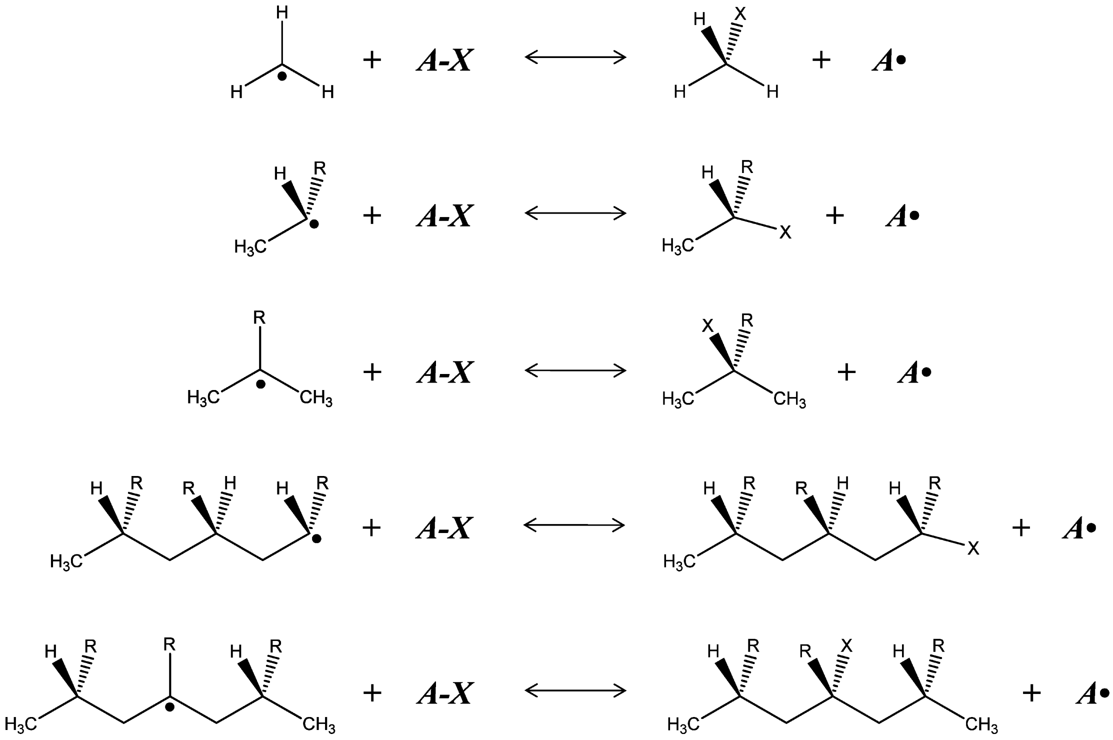

Figure 1. Reaction schemes of the chain transfer to agent steps investigated: (top to bottom) radical transfer from a methyl radical, a BA monomeric chain-end radical, a BA monomeric MCR, a BA trimer chain-end radical, and a BA trimer MCR. In the formulas, R is a $COOC_4H_9$ group, and A−X is the CTA, where X is H, Cl, or Br as long as A stands for EtS, CCl_3, or CBr_3, respectively.

The reactivity of the most common CTAs can be compared on the basis of the relative strength of their labile bonds. Many experimental and theoretical studies on the hydrogen or halogen atom transfer reaction have been conducted in order to evaluate the relationship between polarity and reactivity.[16−18] Whereas the effect of the CTA on chain transfer kinetics can be deduced a priori, it is much more complicated to predict the influence of the propagating radical nature. In this sense, both the identity of the monomer species, which compose the growing chain, as well as the radical chain length contribute to the reaction kinetics along with the selected CTA and nature of the radical carbon.[19]

Recent studies have shown that MCRs can undergo most of the reactions that are usually only associated with chain-end radicals, therefore it is expected that MCRs are also involved in the chain transfer to agent mechanisms.[20−24] It is not easy to determine the reaction kinetics of secondary mechanisms which involve MCRs especially when the aim of the investigation is to evaluate rate coefficients for individual specific reactions. Therefore, due to the complexity of the reaction network, most of the rate parameters can be estimated through data fitting.

A detailed evaluation of the reaction kinetics over a wide range of chain transfer events can be more easily achieved through computational methods in which individual reaction steps can be investigated by focusing on active reaction sites. In particular, the application of quantum chemistry methods based on density functional theory (DFT) to the investigation of polymer reaction kinetics has been extensively used in recent decades.[25−28] This theoretical approach has been applied to estimate kinetic parameters of several reaction classes,[29−33] more recently with a close focus on chain transfer kinetics.[34−37] In this work, a computational investigation of CTA reactivity has been performed with a focus on the reactions of ethanethiol (EtSH), tetrachloromethane (CCl_4), and tetrabromomethane (CBr_4) transfer agents with radical chains of poly butyl acrylate (PBA). In this way, the reactivity of most common CTAs toward a relevant acrylate polymer is studied in order to provide a comprehensive overview of chain transfer to agent kinetics which involves both chain-end and midchain radicals. In such manner, it has been investigated whether the patching effect, that defines the ability of CTAs to prevent the propagation from MCRs, is relevant to the mechanism of chain transfer to agent reactions.

■ COMPUTATIONAL DETAILS

DFT has been adopted in this work to evaluate thermodynamic and kinetic parameters of the investigated reactions.[38] Computational quantum chemistry applying different methodologies can help to improve the understanding of FRP.[39] Various computational approaches have been used, with the aim of testing the performances of methods and basis sets in the description of CTA reactivity. Beside the conventional B3LYP functional,[40,41] which has been primarily applied to perform geometry optimizations, frequency calculations, estimation of pre-exponential factors, and detection of transition state structures,[27,30,31,42−46] the hybrid meta DFT method MPWB1K[47] has been selected to perform single point calculations in order to evaluate the electronic and the zero-point energies. The 6-31G and 6-311G basis sets have been adopted, with the addition of polarization functions, in the way that is discussed hereafter.[48,49] Moreover, the CBS-QB3 approach has been selected in order to perform high-level energy estimations.[50] Rate coefficients have been calculated through the conventional transition state theory (TST), which

Table 1. Summary of Quantum Tunneling Factors, Reaction Enthalpies, Activation Energies, Pre-exponential Factors, and Rate Coefficients Calculated at 323 K for Chain Transfer between EtSH and Methyl Radical Using Different Computational Methods

method	Q_{tun}	ΔH [kJ mol^{-1}]	E_a [kJ mol^{-1}]	A [L mol^{-1} s^{-1}]	k [L mol^{-1} s^{-1}]
experimental data[54]			9.7	2.51×10^8	6.70×10^6
B3LYP/6-31G(d,p)	1.11	−92.2	5.2	2.50×10^8	3.98×10^7
MPWB1K/6-31G(d,p)	1.12	−92.2	11.1	2.50×10^8	4.58×10^6
MPWB1K/6-311G(d,p)	1.12	−85.2	15.1	2.50×10^8	1.02×10^6
CBS-QB3	1.12	−76.0	13.2	2.50×10^8	2.02×10^6

implies the calculation of the reaction rate constant through the Arrhenius formula defined in eq 1:

$$k(T) = Ae^{(-E_a/k_bT)} = \frac{k_bT}{h}\frac{Q_{trans}^{TS}Q_{rot}^{TS}Q_{vib}^{TS}Q_{el}^{TS}}{\prod_i^{N_r} Q_{trans}^{i}Q_{rot}^{i}Q_{vib}^{i}Q_{el}^{i}}Q_{tun}e^{(-E_a/k_bT)} \quad (1)$$

where k_b and h are the Boltzmann and Planck constants, respectively, T is the temperature, N_r is the number of reactants, and E_a is the activation energy of the process, calculated as the difference between the electronic energy of the transition state and that of the reactants including zero-point energy. The translational, rotational, vibrational, and electronic partition functions of the transition state and of the *i*th reactant are identified respectively with the superscripts TS and *i*. The quantum tunneling effect has been considered for chain transfer reactions involving EtSH, while the tunneling factors (Q_{tun}) have been estimated on the basis of the Eckart model.[51,52] All quantum chemistry calculations have been performed with the Gaussian 09 suite of programs.[53]

RESULTS AND DISCUSSION

Atom chain transfer reactions of the selected CTAs toward various radical molecules have been investigated. A preliminary study has been carried out for a methyl radical. The purpose was to test the ability of different computational methods to accurately predict rate coefficients for relatively simple systems, and to compare the computational results to experimental values in order to select the best method. Next, the focus of the study was directed toward the reactivity of a butyl acrylate (BA) monomeric radical where a first distinction between the reactivity of chain-end and midchain radicals was made. However, the FRP system under consideration was still rather approximate, and therefore the modeling of chain transfer reactions was improved by the extension of the studied BA monomeric radicals to trimer radicals of both types. In this way, a more realistic description of the reaction kinetics within the feasibility limits of the quantum chemistry approach has been achieved. An overview of the investigated reactions is provided in Figure 1.

During the first stage of the present study, radical transfer from a methyl radical to EtSH, CCl_4, and CBr_4 agents have been studied using various quantum chemistry methods. As discussed above, this was an attempt to check which methods adequately predict the behavior of the different CTAs, particularly the halogenated ones. The results for kinetic parameters and rate coefficient estimation along with experimental values[54−56] are reported in Tables 1−3.

Transition state configurations corresponding to the investigated reactions are shown in Figure 2.

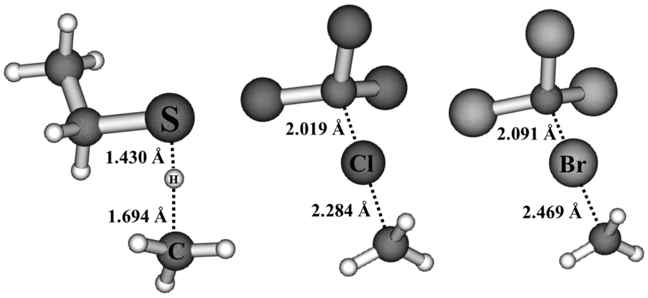

Figure 2. Transition state geometries optimized at the B3LYP level of theory for chain transfer from methyl radical to ethanethiol, tetrachloromethane, and tetrabromomethane presented from left to right.

Data in Table 1 indicate that, when compared to experimental values, the MPWB1K/6-31G(d,p) level of theory provides the most accurate parameter estimations for mercaptan chain transfer to methyl radical, in agreement with our previous works where this approach has been adopted extensively.[35,36] The B3LYP method does not provide adequate estimations for activation energies, even if for the investigated reactions it is able to predict pre-exponential factors very well. Despite the pre-exponential factor's temperature dependence, the computational estimate is within 10% of the experimental data over the studied temperature range. As far as it concerns the calculations using other methods an overestimation of the activation energy by 4−5 kJ mol^{-1} has been observed, which is within the commonly accepted range of uncertainty assumed for quantum chemistry calculations.

In regard to halocarbons, the results for CCl_4 reported in Table 2 lead to discussions which are similar to those concerning EtSH. In Table 2, the simulations underestimate the experimental values for the pre-exponential factor by a factor of 2, although the estimated parameter is fitted on a wide range of temperatures (i.e., up to 523 K, temperature at which the predicted value of the pre-exponential factor is again within 10% of the experimental data). On the other hand, the activation energy calculated at the MPWB1K/6-31G(d,p) level

Table 2. Summary of Reaction Enthalpies, Activation Energies, Pre-exponential Factors, and Rate Coefficients Calculated at 323 K for Chain Transfer between CCl_4 and Methyl Radical Using Different Computational Methods

method	ΔH [kJ mol^{-1}]	E_a [kJ mol^{-1}]	A [L mol^{-1} s^{-1}]	k [L mol^{-1} s^{-1}]
Experimental data[55]		41.4	1.26×10^9	2.53×10^2
B3LYP/6-31G(d,p)	−89.8	25.6	5.61×10^8	4.00×10^4
MPWB1K/6-31G(d,p)	−93.7	41.5	5.61×10^8	1.09×10^2
MPWB1K/6-311G(d,p)	−86.6	45.6	5.61×10^8	2.33×10^1
CBS-QB3	−56.6	37.0	5.61×10^8	5.75×10^2

is in a very good agreement with the experimental value, while the estimates with the other methods are again within the 4 kJ mol^{-1} range of uncertainty.

The last CTA that has been examined is CBr_4 whose results are reported in Table 3. Focusing on the activation energy is clear that is not only the B3LYP that fails to predict this parameter, but even the other approaches are not enough accurate. In all cases the activation energy parameter for the chain transfer to CBr_4 is underestimated by a factor of 2, even in the best case. However, a careful analysis shows that the pre-exponential factor is also underestimated by 2 orders of magnitude; therefore, the corresponding rate coefficient is in a fair agreement with the experimental data when the MPWB1K/6-311G(d,p) and CBS-QB3 methods are employed. Even when CBS-QB3 level is used, the predicted rate coefficient for the CBr_4 chain transfer reaction is still different by a factor of 6 from the experimental data, which is indeed an appreciable difference over the studied temperature. Although the reduced complexity of the system was expected to improve the accuracy of parameter calculation, the observed inaccuracies can be attributed to the high level of detail required to describe the large and greatly polarizable Bromine atoms. In this work, the choice of the most appropriate quantum chemistry method is dictated by the need to maintain a reasonable computational feasibility adequate for polymer systems. In this context, the CBS-QB3 approach provides very accurate energy calculations, but its computational demand is not acceptable when dealing with macromolecular species. Therefore, the results at the CBS-QB3 level of theory are considered as benchmark data for assessing the feasibility of the other DFT approaches. The parameter estimates in Table 3 show that the performance of MPWB1K/6-311G(d,p) is similar to that of the CBS-QB3 method, and therefore, the MPWB1K/6-311G(d,p) approach has been chosen to describe CBr_4 reactivity. Contrarily, the MPWB1K/6-31G(d,p) approach is sufficient to adequately investigate the CCl_4 and EtSH chain transfer reactions. In accordance with these remarks, the selected computational methods have been applied to further study the chain transfer reactions with larger radicals. More specifically, reactions of radical transfer from BA monomeric radicals to the selected CTAs have been investigated, taking into account the reactivity of secondary and tertiary carbon radicals. The aim was to highlight the difference in reactivity for methyl, BA monomeric, and BA trimer radicals as well as the difference in reactivity of both midchain and chain-end BA radicals toward chain transfer agents. The results are reported in Table 4, while the corresponding transition state configurations are shown in Figure 3.

Table 3. Summary of Reaction Enthalpies, Activation Energies, Pre-exponential Factors, and Rate Coefficients Calculated at 323 K for Chain Transfer between CBr_4 and Methyl Radical Using Different Computational Methods

method	ΔH [kJ mol^{-1}]	E_a [kJ mol^{-1}]	A [L mol^{-1} s^{-1}]	k [L mol^{-1} s^{-1}]
Experimental data[56]	-	33.1	1.58×10^{11}	7.02×10^{5}
B3LYP/6-31G(d,p)	−73.9	−2.5	1.54×10^{9}	3.83×10^{9}
MPWB1K/6-31G(d,p)	−75.8	7.1	1.54×10^{9}	1.08×10^{8}
MPWB1K/6-311G(d,p)	−97.7	16.3	1.54×10^{9}	3.57×10^{6}
CBS-QB3	−61.5	15.5	1.54×10^{9}	4.73×10^{6}

The extension of the computational study from the less stable methyl radical to BA monomeric radicals reduces the probability of chain transfer due to the combined increase of activation energy (11−22 kJ mol^{-1}) and decrease of pre-exponential factor (about 2 orders of magnitude). The observed changes in the kinetic parameters reflect the BA monomeric radical reduced susceptibility to chain transfer attributed to its less accessible radical configuration. Moreover, the relative reactivities of the CTAs are consistent with the trend observed for chain transfer reactions from a methyl radical.

The results in Table 4 corresponding to the chain transfer reactions from tertiary radicals show that the addition of a methyl group to BA monomeric radical is not enough to adequately mimic the behavior of a MCR. During a chain transfer to agent from an MCR both the activation energy and pre-exponential factor are expected to be different than those estimated for chain-end radicals, but as seen in Table 4, this is not the case. The pre-exponential factor is reduced by roughly one order of magnitude, in accordance with the previous comment on radical accessibility, while the changes in activation energy are negligible. Therefore, the rate coefficients estimated for MCRs are smaller than those estimated for chain-end radical transfer reactions by a difference that ranges from a factor of 5 to almost 2 orders of magnitude, where the greatest gap is calculated for the reaction with EtSH. Furthermore it is interesting to note that the simple radical molecule used for the study of the MCR of BA in Figure 3 is identical to the butyl methacrylate (BMA) monomeric radical. In fact with the adopted model the chain transfer to agent reaction from the monomeric MCR of BA is equivalent to chain transfer reaction form the monomeric BMA radical. All of the above lead to the conclusion that longer polymer chain simulations are required for a better description and the more realistic investigation of MCR behavior.

The kinetic study of chain transfer reactions involving monomeric radicals has been extended to the reactivity of trimer PBA chains to facilitate a more realistic investigation of

Table 4. Summary of Quantum Tunneling Factors, Reaction Enthalpies, Activation Energies, Pre-exponential Factors, and Rate Coefficients Calculated at 323 K for Chain Transfer from Monomeric BA Radicals to EtSH, CCl_4, and CBr_4

CTA	radical	Q_{tun}	ΔH [kJ mol^{-1}]	E_a [kJ mol^{-1}]	A [L mol^{-1} s^{-1}]	k [L mol^{-1} s^{-1}]
EtSH	chain-end	2.71	−33.4	22.3	3.78×10^{6}	2.53×10^{3}
	midchain	3.62	−12.7	28.0	7.37×10^{5}	7.96×10^{1}
CCl_4	chain-end		−38.3	63.9	1.08×10^{7}	5.08×10^{-4}
	midchain		−30.5	64.6	2.64×10^{6}	9.49×10^{-5}
CBr_4	chain-end		−45.2	35.4	1.61×10^{7}	3.03×10^{1}
	midchain		−35.3	36.1	3.92×10^{6}	5.71×10^{0}

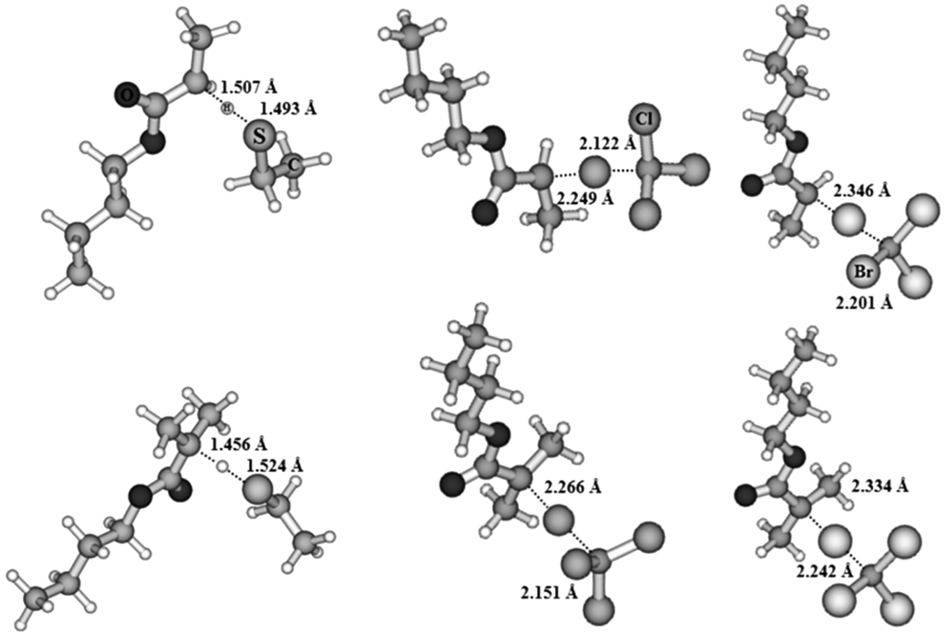

Figure 3. Transition state geometries corresponding to the chain transfer reactions investigated in Table 3: (left to right) chain transfer from monomeric BA chain-end radical (top) and monomeric BA midchain radical (bottom) to EtSH, CCl_4, and CBr_4.

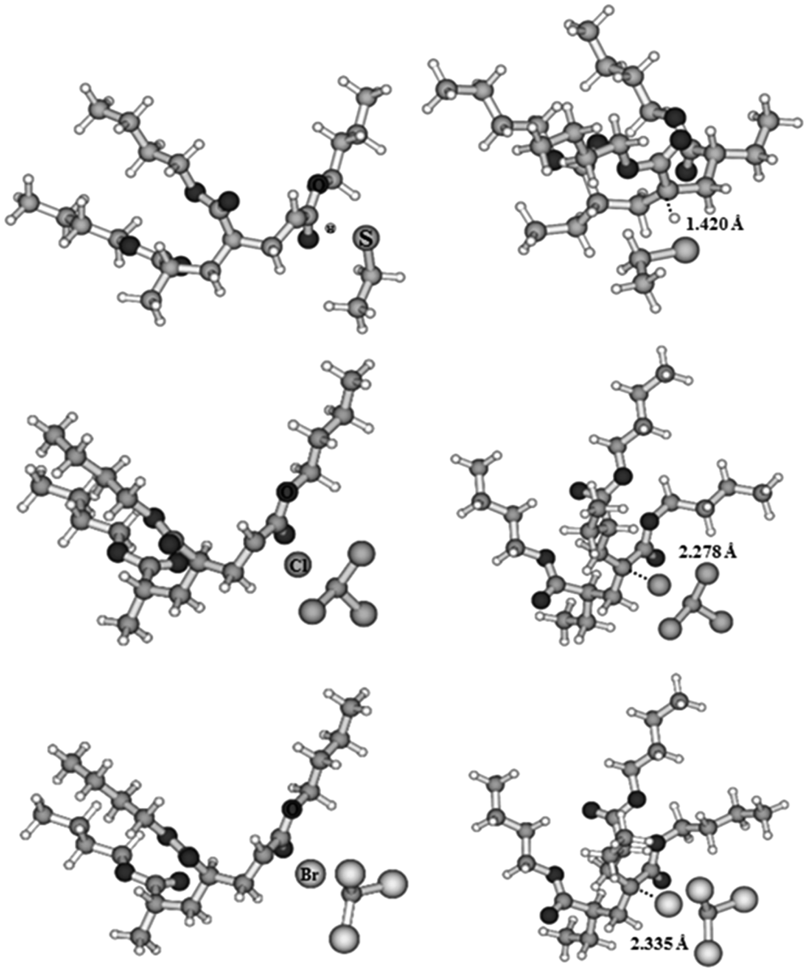

Figure 4. Transition state geometries corresponding to the reactions investigated in Table 5: (top to bottom) chain transfer to EtSH, CCl_4, and CBr_4 from a BA trimer chain-end radical (left) and a BA midchain radical (right).

the polymer systems. Furthermore, the reactivities of both chain-end and midchain radicals have been studied in order to better characterize the two different radical types where the corresponding transition state configurations are shown in Figure 4.

The results reported in Table 5 show that trimer radicals are sufficient to model the difference in reactivity between BA chain-end and BA midchain radicals. As expected, for all systems the calculated activation energies are higher for midchain radicals than for chain-end radicals with differences of 9−23 kJ mol $^{-1}$. On the other hand, the pre-exponential factors estimated using trimer radicals (for details please refer to Supporting Information Table S1) are similar to those reported in Table 4 with the same observed difference of 1 order of magnitude for the pre-exponential factors of chain-end and midchain radicals.

Table 5. Summary of Quantum Tunneling Factors, Activation Energies, and Ratio of Rate Coefficients for Midchain and Endchain Radical Reactivities of BA Trimer Towards Chain Transfer Agent Calculated at 323 K for Chain Transfer from Trimer BA Radicals to EtSH, CCl_4, and CBr_4

CTA	radical	Q_{tun}	E_a [kJ mol^{-1}]	$k_{midchain}/k_{chain\text{-}end}$
EtSH	chain-end	2.76	19.0	4.16×10^{-4}
	midchain	5.15	42.0	
CCl_4	chain-end		63.9	6.54×10^{-3}
	midchain		73.3	
CBr_4	chain-end		34.0	6.62×10^{-5}
	midchain		51.5	

The rate coefficient ratios in Table 5 clearly show that chain-end radicals are more reactive toward the chain transfer agent than midchain radicals. The same behavior was observed for all of the agents studied, where the biggest difference in rate coefficient ratio is for the CBr_4 system. The computational results in Table 5 are in agreement with recent published values for the hydrogen abstraction reactions from both tertiary and secondary carbon on poly methyl acrylate backbone. In particular according to the authors the hydrogen abstraction from a tertiary carbon is characterized by higher energy barrier while the rate constant is 3 orders of magnitude lower than those for the hydrogen abstraction from a secondary carbon.[57] The predicted rate coefficients along with additional information about the rate of chain transfer to agent from different radical configurations can be used to improve polymerization models and provide estimates for unknown kinetic parameters. Moreover, an improved knowledge of side-reaction FRP kinetics facilitated by quantum chemistry can be helpful in understanding the mechanisms that cannot be individually measured experimentally. In this regard, the importance of chain transfer to agent to the kinetics of acrylate polymerization is well-known, but the details of the mechanism which describe the influence of the CTAs and polymerization conditions on the degree of branching are still unclear.

Recent studies on BA polymerization have shown that if a relatively large amount of CTA is added (i.e., up to 0.4 mol L^{-1} in a bulk system), the degree of branching of the final polymer can be considerably reduced. In particular, a mechanism has been proposed for MCR patching where an atom from the CTA is transferred to the MCR to mitigate further propagation. This phenomenon is in agreement with the experimental results obtained for BA polymerization in the presence of 1-octanethiol which leads to a decrease in both the measured degree of branching at various temperatures and the amount of β-scission products.[8]

Experimental investigations of the same polymerization system using CBr_4 as CTA have determined a reduced level of branching similar to the result obtained in the study with 1-octanethiol.[8] However, no tertiary C−Br carbon structures (i.e., the result of chain transfer to agent from MCRs) were detected, in disagreement with the proposed mechanism of radical patching as the main contributor to the reduction in branching level.[10] This conclusion is supported by the results shown in Table 5 which clearly show that the chain transfer to agent is more easily accomplished for a chain-end radical than a midchain radical. Although the population of MCRs under certain specific conditions (e.g., very low monomer concentration in reaction mixture during semibatch processes) may be up to four times the amount of chain-end radicals, the reactivity of the former toward chain transfer agent CBr_4 is substantially smaller than that of the chain-end radicals (5 orders of magnitude in terms of reaction rate coefficients). Therefore, it is likely that the majority of the CBr_4 interactions are with terminal radicals, not MCRs. Moreover, according to the estimated chain transfer rate coefficients the competition between MCR patching by bromine atoms and MCR propagation is strongly in favor of the latter mechanism.[58]

The kinetics of chain transfer to EtSH, which are globally estimated to be faster than for other CTAs, are in agreement with the previous results. In particular, the radical patching by hydrogen atoms is kinetically less favored than MCR propagation by 2 orders of magnitude and the reactivity difference between chain-end and midchain radicals is 4 orders of magnitude in terms of reaction rate coefficients. Despite the uncertainty in the estimation of absolute rate coefficients by quantum chemistry, the obtained results suggest that for both EtSH and CBr_4 an additional mechanism needs to be considered in order to elucidate the correlation between branching and the presence of a CTA. The reactivity of MCRs with CTAs has been proven to be of little relevance to this regard.

The instantaneous degree of branching ($DB_{\%}{}^{inst}$) has been defined for a simplified FRP system, as shown by eq 2, by inserting the investigated chain transfer to agent kinetics on chain-end and midchain radicals, on the basis of the evaluated rate coefficients for the reactions between BA trimer radicals and both CBr_4 and EtSH. The number of branches per monomer unit is defined as the ratio between the rate of branching formation (i.e., given primarily by number of MCR propagation events) and the total rate of radical addition to monomer.

$$DB_{\%}^{inst} = \frac{k_{bb}}{k_p M + k_{fC} C} \frac{k_p^{MCR} M}{k_p^{MCR} M + k_{fC}^{MCR} C} \tag{2}$$

Under the assumption of a dynamic equilibrium between the radical species, eq 2 describes the $DB_{\%}^{inst}$ value in terms of rate coefficients for backbiting (k_{bb}), propagation of chain-end and midchain radicals (k_p and k_p^{MCR}), and chain transfer to agent from chain-end and midchain radicals (k_{fC} and k_{fC}^{MCR}) as well as the concentrations of monomer (M) and CTA (C). However, the estimated $DB_{\%}^{inst}$ value in presence of CTA, obtained using k_{bb} (390 s^{-1}),[58] k_p (28000 L mol^{-1} s^{-1}),[8] and k_p^{MCR} (25 L mol^{-1} s^{-1})[58] values reported in the literature, does not change significantly from the value obtained without considering chain transfer to agent kinetics (i.e., the calculated parameter is reduced by less than 1% at 60 °C when both CBr_4 and EtSH are employed as CTAs, while according to the experimental data for CBr_4 under the same conditions, it is expected to decrease by 60−80%).[10] In conclusion, the effect of CTA on the degree of branching by means of a redistribution of the radical species does not manifest in the instantaneous properties.

■ CONCLUSION

Reaction kinetics of chain transfer to agent from BA radicals has been investigated using quantum chemistry by employing EtSH, CCl_4, and CBr_4 as representative industrial CTAs. The first part of the study was dedicated to the selection of the most appropriate method to estimate the kinetics of chain transfer reaction to each of the studied CTAs. For this purpose, simple reactions of chain transfer from a methyl radical have been modeled, while experimental data were used to validate the computational approach. A good agreement was obtained when the consolidated B3LYP/6-31G(d,p)//MPWB1K/6-31G(d,p) method was applied to EtSH and CCl_4 systems, while the MPWB1K/6-311G(d,p) method was required to perform sufficiently accurate single point calculations for CBr_4. Next, chain transfer reactions were simulated to investigate the distinction between midchain and chain-end radicals as well as the polymer chain length (monomeric versus trimer radicals) for PBA radicals. The results show that a difference in reactivity between the two types of PBA radicals is small for monomeric radicals, but becomes significant when trimer chains are used because they can better mimic the behavior of both the studied chain-end and midchain radicals. These differences in behavior are consistent among all of the investigated CTAs, and reveal that the MCR patching is less prominent than anticipated. The estimated chain transfer kinetics from BA radicals to the CTAs examined are comparable in terms of ratios of rate constants albeit quite different in terms of absolute chain transfer rate coefficients.

The estimated kinetics of chain transfer to agent reactions have been used to shed light on the mechanism that controls the decrease of branching when a CTA is added to a bulk acrylate polymerization systems. The computational results support experimental evidence which indicates that MCR patching is not relevant to the mechanism which governs the observed reduction in branching level upon introduction of a large amount of CTA to the system. The attention must be focused on the effect that the addition of CTAs has on the reactions that lead to the formation of MCR since a potential competition between CTA reactions and reactions such as backbiting and chain transfer to polymer may lead to a lower concentration of MCRs in the reactive system and thus to a lower value for the degree of branching.

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Notes

The authors declare no competing financial interest.

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