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A Missing Reaction Step in Dithiobenzoate-Mediated RAFT Polymerization

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Summary: The debate on the mechanism of dithiobenzoate-mediated RAFT polymerization may be overcome by taking the so-called "missing step" reaction between a highly reactive propagating radical and the three-arm star-shaped product of the combination reaction of an intermediate RAFT radical and a propagating radical into account. The "missing step" reaction transforms a propagating radical and a not overly stable three-arm star species into a resonance-stabilized RAFT intermediate radical and a stable polymer molecule. The enormous driving force behind the "missing step" reaction is estimated via DFT calculations of reaction enthalpies and reaction free enthalpies.

Keywords: kinetics (polym.); living polymerization; quantum chemistry; reaction mechanism; reversible addition fragmentation chain transfer (RAFT)

Introduction

Despite the enormous success of RAFT polymerization[1] for producing polymer of controlled architecture and well-defined molecular weight, the RAFT mechanism is not yet fully understood, which is particularly true for reactions with dithiobenzoates, $C_6H_5{-}C({=}S)S{-}R$, being the RAFT agent.[2] With these systems extended induction periods with virtually no polymerization are observed as well as significant rate retardations in comparison to conventional free-radical polymerizations (without RAFT agent) under otherwise identical conditions. Two divergent mechanisms have been proposed for interpreting rate retardation: (*i*) The intermediate RAFT radical produced by fast addition of a propagating radical to the RAFT species undergoes *irreversible termination* with an other radical species (cross-termination) or with itself (self-termination), which processes are associated with radical loss and thus result in rate retardation.[3–5] (*ii*) The second mechanism assigns rate retardation to *slow fragmentation* of the intermediate RAFT radical, but neglects participation of intermediate RAFT radicals in irreversible termination reactions.[6–8] Monomer conversion-vs.-time curves which have been measured for a range of dithiobenzoate-mediated RAFT polymerizations are not capable of distinguishing between these two limiting mechanisms, as the experimental data may be fitted equally well by the *irreversible termination* and the *slow fragmentation* models, although with the fragmentation rate coefficients for the intermediate RAFT radical differing by orders of magnitude.[5,7] Electron-spin-resonance (ESR) experiments on dithiobenzoate-mediated polymerizations are in conflict with the *slow fragmentation* model because the measured concentration of intermediate RAFT radicals is far below the one predicted by this model.[4,9,10] The *irreversible termination* model, on the other hand, can account for such low concentrations of intermediate RAFT radicals, but the three-arm star products of irreversible termination,[11] are not found in the product mixture of dithiobenzoate-mediated acrylate RAFT polymerizations, although

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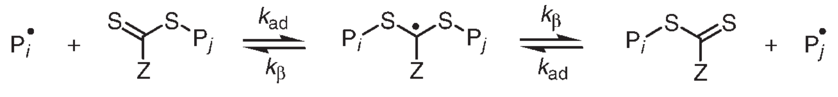
these reactions exhibit significant rate retardation.[12,13] For styrenic systems such three-arm star species were demonstrated to be stable at typical polymerization temperatures.[14]

Even more complex models, which include reversible termination into the slow fragmentation scheme,[15,16] or consider both irreversible termination and slow fragmentation of RAFT intermediate radicals,[17] or assume different kinetics under RAFT pre-equilibrium and main-equilibrium conditions,[10,17] provide no satisfactory mechanistic description of dithiobenzoate-mediated RAFT polymerization. Within a recent paper from our group,[18] arguments have been put forward for an important kinetic step having not yet been included into the RAFT schemes discussed so far. This so-called "missing step" occurs between a highly reactive propagating radical and the star-shaped product from irreversible (or reversible) termination of a propagating radical and an intermediate RAFT radical. This step definitely needs to be considered in RAFT polymerizations of acrylate monomers. In the present contribution, the arguments for the relevance of this "missing step" are briefly summarized and the driving force behind this reaction is estimated via DFT calculations of reaction enthalpies and reaction free enthalpies.

Results and Discussion

The subsequent discussion will focus on RAFT polymerizations under main-equilibrium conditions. The kinetic scheme is presented in Eq. (1), where **1** refers to the propagating radical, **2** to the polymeric dithiobenzoate, and **3** to the intermediate RAFT radical. Because of their close similarity, the macroradicals $P_i^\bullet$ and $P_j^\bullet$ are both indicated by **1** and the two polyRAFT agents in Eq. (1) by **2**. Also represented by identical notations are the two addition and the two fragmentation rate coefficients, k_{ad} and k_β, respectively.

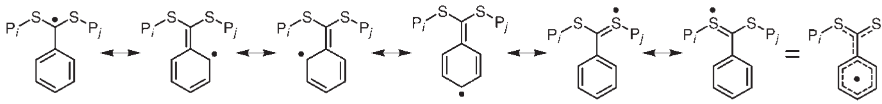


(1)

1 **2** **3** **2** **1**

RAFT polymerizations mediated by dithiobenzoates experience significant rate retardation due to resonance stabilization of **3**. Delocalization of the radical functionality, as is illustrated in Scheme 1, affords resonance structures with significantly reduced steric hindrance for radical-radical combination (or disproportionation) reactions.[16]

The consequences of resonance stabilization of **3** may be summarized: (*i*) the reaction of **1** + **2** to **3**, in which a resonance-stabilized radical **3** is produced from a reactive radical **1**, should be very fast which is indeed reported;[19] (*ii*) the resonance stabilization of **3** disfavors fragmentation; (*iii*) delocalization of the radical functionality, e.g., into the para position, reduces problems for radical reactions of **3** due to steric hindrance, which may be severe in the case that the radical functionality is localized exclusively at the carbon atom between the sulfur atoms; (*iv*) radical reactions of **3** are favored, as the resonance-stabilized species **3** occurs in significantly larger concentrations than, e.g., in situations where the

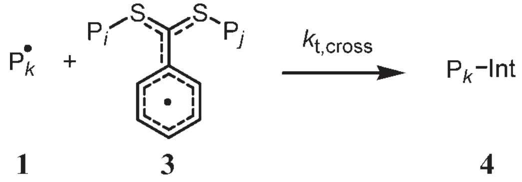


3

Scheme 1.
Resonance structures of the intermediate radical occurring in dithiobenzoate-mediated RAFT polymerizations.

Z-group of the RAFT agent is benzyl rather than phenyl; (*v*) even at significant concentrations of **3**, propagation reactions starting from this intermediate RAFT radical are unlikely because of the resonance stabilization of **3**.

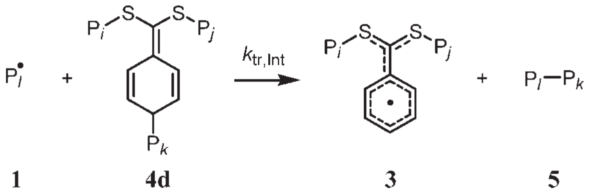
By combination of the radicals **1** and **3**, the cross-combination product **4**, P_k–Int, is formed:



(2)

As is illustrated in Scheme 2, **4** will actually be a mixture of several regioisomers. The relative amounts to which isomers such as **4a** to **4f** are produced from **1** and **3** may be rather different.

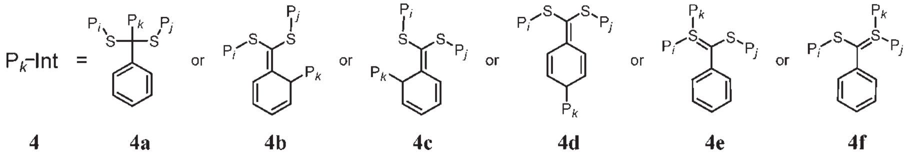
Implementing the individual steps presented in Eqs. (1) and (2) into the kinetic treatment is not sufficient for adequately describing all essential features of dithiobenzoate-mediated RAFT polymerization of acrylates. Even including reversibility of the combination step in Eq. (2) or taking both irreversible termination of **1** and **3** and slow fragmentation of **3** into account, does not provide a fully consistent kinetic description. As has been pointed out in our previous paper,[18] the puzzling kinetic behavior of finding neither significant concentrations of three-arm star components **4** nor of intermediate radicals **3** in dithiobenzoate-mediated acrylate polymerizations may be explained by including, as an additional step, the reaction between **4** and a highly reactive acrylate propagating radical **1**. An example of this so-called "missing step" reaction of **1** + **4d** to yield, **3** + dead polymer **5** is illustrated in Eq. (3):



(3)

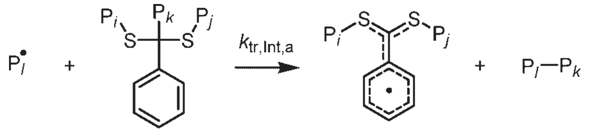
It needs to be noted that the reaction depicted in Eq. (3) is just one example out of several processes, which the different regioisomers of **4** may undergo. The reactions of **1** + **4a**, of **1** + **4b**, and of **1** + **4e** are illustrated in Eqs. (4) to (6), respectively.

The variety of **1** + **4** reactions may be even larger, as for a given regioisomer **4** radical attack of **1** may occur in different ways. As has been noted in Ref.[18], the driving force of the **1** + **4** reaction should be sufficiently high to also give rise to



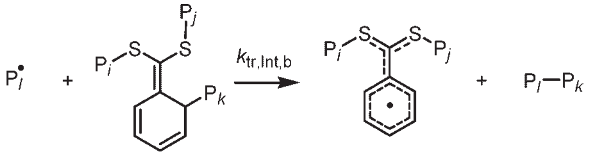
Scheme 2.

Structures of regioisomers **4** produced by combination of a propagating radical **1** with the intermediate RAFT radical **3**.



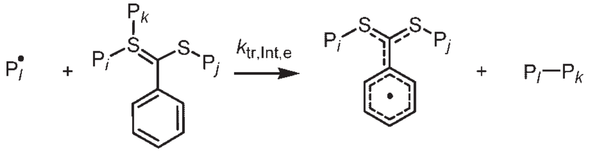
1 **4a** **3** **5**

(4)



1 **4b** **3** **5**

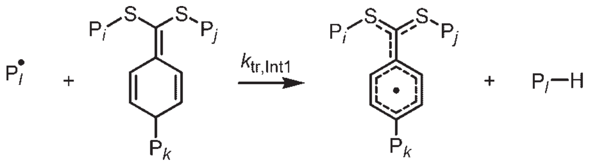
(5)



1 **4e** **3** **5**

(6)

hydrogen abstraction from **4**. As an example, hydrogen abstraction is illustrated for the **1** + **4d** reaction in Eq. (7):



1 **4d** **6** **7**

(7)

Irrespective of the particular regioisomer that undergoes the **1** + **4** reaction and of the reaction pathway, which may either proceed via radical abstraction according to Eqs. (3) to (6) or via hydrogen abstraction according to Eq. (7), all **1** + **4** "missing step" reactions have an important feature in common: A reactive propagating radical **1** and a weakly bound star-shaped molecule **4** are transformed into a resonance-stabilized radical, such as **3** or **6**, and a very stable polymeric (or oligomeric) molecule, such as **5** or **7**. Each of these reactions is associated with a strong driving force and is thus expected to be very fast.

The value of the rate coefficient of the "missing step" reaction in Eq. (3), $k_{\mathrm{tr,Int}}$, may come close to or even exceed that of k_{ad}, which is the **1** + **2** addition rate coefficient (see Eq. (1)), because within both reactions, at least in the case of acrylate polymerizations, a highly reactive propagating radical is transformed into a resonance-stabilized one. PREDICI simulations including the reactions presented in Eqs. (2) and (3) have been carried out for dithiobenzoate-mediated methyl acrylate polymerizations under main-equilibrium conditions assuming $k_{\mathrm{tr,Int}}$ and k_{ad} to be of identical size.[18] The concentration-vs.-time correlations for both the acrylate monomer and the intermediate radical **3** turned out to be almost insensitive toward the "missing step" reaction, whereas the concentration of the three-arm star combination product **4** becomes negligibly small when the **1** + **4** reaction is included. This result is in full agreement with the experimental finding that noticeable amounts of **4** may not be detected in the product mixture from dithiobenzoate-mediated acrylate polymerizations.[12,13]

The essence of the RAFT mechanism with the "missing step" being included is visualized in Figure 1. Starting from the intermediate RAFT radical **3**, two successive irreversible reactions occur. The first one, with rate coefficient $k_{\mathrm{t,cross}}$, yields the combination product **4**, and the subsequent one, with rate coefficient $k_{\mathrm{tr,Int}}$, yields **3** back again. In both steps, a propagating radical is involved. In the second step, the radical $P_l^\bullet$ picks up the P_k species from **4** to yield **5**, which component is identical to the combination product of two propagating radicals. The reaction sequence resembles a catalytic cycle in which two propagation radicals, $P_l^\bullet$ and $P_k^\bullet$, via the dithiobenzoate components **3** and **4**, are transformed into a polymer molecule P_l–P_k. It should be stressed that the concentration of **3** remains unchanged, which may explain the excellent control of dithiobenzoate-mediated RAFT polymerizations even under conditions of irreversible termination. Figure 1 does not apply to situations where the reaction presented in Eq. (7) plays a major role, although even in this case retardation due to irreversible radical termination does occur.

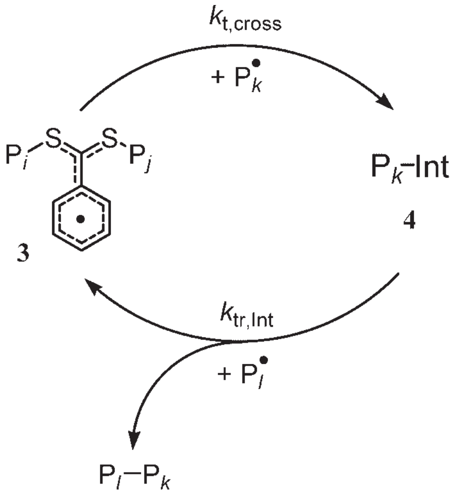


Figure 1.
The lower part of the figure illustrates the "missing step" reaction according to Eq. (3) for dithiobenzoate-mediated polymerizations. This reaction needs to be considered in RAFT polymerizations with highly reactive propagating radicals. The dithiobenzoate compounds **3** and **4** assist the termination of the two radicals, $P_l^\bullet$ and $P_k^\bullet$.

The mechanism of the "missing step" reaction has not yet been investigated in any detail. Because of the multitude of regioisomers **4**, a considerable number of **1** + **4** transition state structures needs to be analyzed. Moreover, several reaction channels may be relevant for a given regioisomer, as is illustrated for the **1** + **4d** reaction in Figure 2. According to the upper reaction pathway in Figure 2, the propagating radical, ($P_l^\bullet = \mathbf{1}$) picks up the P_k moiety from the six-membered ring. The second pathway, which is illustrated in the lower part of Figure 2, suggests that $P_l^\bullet$ first adds to one of the double bonds of the six-membered ring and the polymer molecule P_l–P_k is released after bond rearrangement.

According to the high reactivity of the "missing step" reaction, the kinetics of the **1** + **4** step is not easily accessed by experimental methods. The star-shaped component **4** needs to be prepared by a non-radical route, that is, without highly reactive radicals **1** being present. For styrenic species, a model experiment for producing **4** has been designed and successfully carried out by the Fukuda group.[11] Several three-arm star products **4** were obtained by reacting polystyrene-dithiobenzoate and polystyrene bromide (with well defined, very similar lengths of the polystyryl moieties) in solution of *tert*-butyl benzene and in the presence of a CuBr/

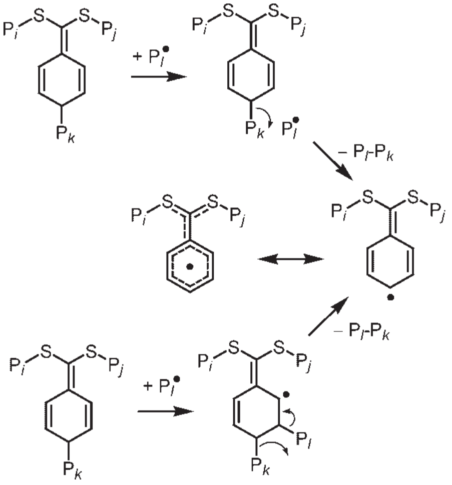


Figure 2.
Two suggestions for mechanisms of the **1** + **4d** → **3** + **5** "missing step" reaction.

Me_6TREN complex. Applying a corresponding strategy toward an acrylate system did not yield convincing evidence for the production of three-arm star cross-combination product **4**.[20] The results of the latter experiments may even be interpreted in such a way that a significant amount of **5**, the radical–radical combination product P_l–P_k, is formed. Adopting this interpretation would provide another experimental indication of the "missing step" reaction being relevant for acrylate systems. The capability of adequately representing the experimental observations made for dithiobenzoate-mediated acrylate polymerizations, however, constitutes the most striking evidence for the validity of the extended RAFT kinetic scheme that includes "missing step" reactions, such as the ones shown in Eqs.(3) to (7).

To deduce further information on the "missing step" reaction, density functional theory (DFT) calculations have been applied toward estimating reaction enthalpies, ΔH_R, and reaction free enthalpies, ΔG_R, at 298.15K for several of the **1** + **4** processes. The ΔG_R value provides a measure of the driving force behind the individual reaction channels. Although such calculations for small molecules are closer to conditions as are met in the pre-equilibrium period of RAFT polymerizations, it appears rewarding to use this quantum-chemical tool for some general analysis of the "missing step" reaction. The program package Gaussian03[21] was used for the quantum-chemical calculations. The structures of all species involved were fully optimized employing the DFT variant UB3LYP in conjunction with the 6-31G(d,p) basis set (333 contracted Gaussian-type orbitals for the **1** + **4** reactions). The B3LYP hybrid method[22] combines the Becke three-parameter exchange functional[23] with the Lee, Yang and Parr[24] correlation functional. The full conformational space of the system was scanned to find the lowest energy conformation of each species. To establish the existence of true minima on the potential energy surface, the Hessian matrices at the stationary points were determined. The calculated harmonic vibrational frequencies and equilibrium rotational constants were used to estimate the thermal contribution to thermodynamic quantities within the harmonic-oscillator-rigid-rotor model.

DFT estimates of ΔH_R and of ΔG_R have been made for the two reaction steps of the cyclic pathway, **1** + **3** → **4** and **1** + **4** → **3** + **5** (Figure 1). The P moieties in the compounds **3**, **4**, and **5** have been chosen to be ethyl and **1** is an ethyl radical. The calculations have been performed for reactions via the four characteristic types of the 3-arm star combination products: **4a**, **4b**, **4d**, and **4e** (see Scheme 2). The so-obtained reaction enthalpies and reaction free enthalpies for 298.15K are summarized in rows [3] to [6] of Table 1 with $\Delta H_{R,C}$ and $\Delta G_{R,C}$ referring to the **1** + **3** → **4** combination reactions and $\Delta H_{R,MS}$ and $\Delta G_{R,MS}$ referring to the **1** + **4** → **3** + **5** missing step reactions. Presented in row [7] is the reaction enthalpy for the "missing step" reaction of **4d** proceeding via hydrogen-abstraction, i.e., the reaction shown in Eq. (7). Listed in the first row of Table 1 are the DFT-estimated enthalpies for the **1** + **2** → **3** addition reaction. Given in row [2] are the enthalpies for the **1** + **1** → *n*-butane combination reaction.

Table 1.

Reaction enthalpies, ΔH_R, and reaction free enthalpies, ΔG_R, at 298.15 K estimated via DFT calculations (UB3LYP, 6-31G(d,p)) for the addition of an ethyl radical to ethyl dithiobenzoate, for several radical-radical combination reactions, and for the "missing step" reactions of the four cross-combination products (**4a**, **4b**, **4d**, and **4e**) with an ethyl radical **1**. The reaction enthalpy and reaction free enthalpy values are given in units of $kJ \cdot mol^{-1}$.

Reaction	$\Delta H_{R,ad}$	$\Delta G_{R,ad}$		
[1] $\mathbf{1}+\mathbf{2}\rightarrow\mathbf{3}$	−80.4	−33.5		
Reaction	$\Delta H_{R,C}$	$\Delta G_{R,C}$	$\Delta H_{R,MS}$	$\Delta G_{R,MS}$
[2] $\mathbf{1}+\mathbf{1}\rightarrow$ *n*-butane	−344.4	−282.9		
[3] $\mathbf{1}+\mathbf{3}\rightarrow\mathbf{4a}$;	−237.1	−170.5		
$\mathbf{1}+\mathbf{4a}\rightarrow\mathbf{3}+\mathbf{5}$			−107.3	−112.4
[4] $\mathbf{1}+\mathbf{3}\rightarrow\mathbf{4b}$;	−134.4	−73.1		
$\mathbf{1}+\mathbf{4b}\rightarrow\mathbf{3}+\mathbf{5}$			−210.0	−209.8
[5] $\mathbf{1}+\mathbf{3}\rightarrow\mathbf{4d}$;	−152.2	−90.4		
$\mathbf{1}+\mathbf{4d}\rightarrow\mathbf{3}+\mathbf{5}$			−192.2	−192.5
[6] $\mathbf{1}+\mathbf{3}\rightarrow\mathbf{4e}$;	−47.3	17.6		
$\mathbf{1}+\mathbf{4e}\rightarrow\mathbf{3}+\mathbf{5}$			−297.1	−300.3
[7] $\mathbf{1}+\mathbf{4d}\rightarrow\mathbf{6}+\mathbf{7}$			−203.7	−200.3

The data in rows [1] and [2] essentially serve the purpose of validating the DFT procedure. The enthalpy for the ethyl + ethyl dithiobenzoate reaction given in row [1], $\Delta H_{R,ad} = -80.4\ kJ \cdot mol^{-1}$, is close to the value from quantum-chemical calculations reported by Coote and Radom[25] for the related addition of a methyl radical to methyl dithiobenzoate: $\Delta H_{R,ad} = -95.2\ kJ \cdot mol^{-1}$. The slightly larger exothermicity for the methyl system results from the higher reactivity of the methyl radical as compared to the ethyl radical. The comparison of the two numbers indicates that the DFT-derived enthalpy for the $\mathbf{1}+\mathbf{2}\rightarrow\mathbf{3}$ reaction is of reasonable size, which suggests that the DFT procedure used within the present study should be capable of providing reliable ΔH_R values. The entry in row [2] of Table 1 supports this conclusion, as the absolute value of the combination enthalpy of two ethyl radicals **1**, $\Delta H_{R,C} = -344.4\ kJ \cdot mol^{-1}$, is relatively close to the reported value for the dissociation enthalpy of *n*-butane into two ethyl radicals, $\Delta H_{R,diss} = 367.7\ kJ \cdot mol^{-1}$.[26] On the basis of the satisfying match with literature data of our DFT-derived ΔH_R values (entries [1] and [2]) it is assumed that the other reaction enthalpies (and the reaction free-enthalpies) in Table 1, for which no reference data is available, are also reliable.

The sum of the reaction enthalpies of associated $\mathbf{1}+\mathbf{3}\rightarrow\mathbf{4}$ and $\mathbf{1}+\mathbf{4}\rightarrow\mathbf{3}+\mathbf{5}$ reactions (entries [3] to [6] in Table 1) adds up to $-344.4\ kJ \cdot mol^{-1}$, as the net reaction of each of the cyclic processes, via **4a**, **4b**, **4d**, or **4e**, is the combination of two ethyl radicals to produce *n*-butane. Thus, in cases where the first step is poorly exothermic, such as with the cross-combination of $\mathbf{1}+\mathbf{3}\rightarrow\mathbf{4e}$, where the ethyl radical adds to one of the sulfur atoms, the second step, $\mathbf{1}+\mathbf{4}\rightarrow\mathbf{3}+\mathbf{5}$, is highly exothermic. A different type of behavior is seen with the **4a** regioisomer, where the first step is highly exothermic, as a carbon-carbon bond is formed without any accompanying reduction of aromatic delocalization of the phenyl moiety. The associated missing step reaction, $\mathbf{1}+\mathbf{4a}\rightarrow\mathbf{3}+\mathbf{5}$, has a significantly lower reaction enthalpy than, e.g., the $\mathbf{1}+\mathbf{4e}$ reaction, but even this lower value exceeds the enthalpy of the $\mathbf{1}+\mathbf{2}\rightarrow\mathbf{3}$ reaction. With the two other regioisomers, **4b** and **4d**, the (negative) reaction enthalpies of the "combination step" and the "missing step" are both well above the enthalpy of the $\mathbf{1}+\mathbf{2}\rightarrow\mathbf{3}$ reaction. In both cases the "missing step" has a higher exothermicity than the associated combination step. For the **4d** regioisomer entry [7] in Table 1 allows for a comparison of the reaction enthalpies for hydrogen abstraction and ethyl abstraction reactions, i.e., for the $\mathbf{1}+\mathbf{4d}\rightarrow\mathbf{6}+\mathbf{7}$ vs. the $\mathbf{1}+\mathbf{4d}\rightarrow\mathbf{3}+\mathbf{5}$ steps. The two reaction enthalpies differ by no more than about 5%.

Rough information about the driving force of the "missing step" reaction may be deduced from an inspection of the reaction free enthalpies, $\Delta G_{R,MS}$. As with the reaction enthalpies, the sum of the reaction free enthalpies of associated $\mathbf{1}+\mathbf{3}\rightarrow\mathbf{4}$ and $\mathbf{1}+\mathbf{4}\rightarrow\mathbf{3}+\mathbf{5}$ reactions (see rows [3] to [6] in Table 1) adds up to the same value: $\Delta G_{R,C}+\Delta G_{R,MS}=-282.9\ \mathrm{kJ\cdot mol^{-1}}$, which is the reaction free enthalpy for the net reaction of each of the cyclic processes, via **4a**, **4b**, **4d**, or **4e**, that is the combination of two ethyl radicals to produce *n*-butane. The $\Delta G_{R,MS}$ values are rather close to the associated $\Delta H_{R,MS}$ values. Thus the arguments put forward for $\Delta H_{R,MS}$ also apply to $\Delta G_{R,MS}$. The highest driving force is expected for the "missing step" reaction of $\mathbf{4e}+\mathbf{1}$. This reaction may however not take place to a significant extent, as the $\Delta G_{R,MS}$ value for the $\mathbf{1}+\mathbf{3}\rightarrow\mathbf{4e}$ reaction indicates that the production of **4e** is not favored. The reaction of $\mathbf{4a}+\mathbf{1}$ should exhibit the lowest driving force among the "missing step" processes. Even this slower reaction, however, has a larger negative $\Delta G_{R,MS}$ than the $\mathbf{1}+\mathbf{2}\rightarrow\mathbf{3}$ reaction, which is generally considered to be a fast process in well controlled RAFT polymerizations. The $\Delta G_{R,MS}$ data in Table 1 thus suggests that the missing step reactions according to the entries in rows [3] to [7] are relatively fast reactions in the case of **1** being a reactive radical, such as ethyl. The difference in the $\Delta G_{R,MS}$ values for the "missing step" channels according to rows [5] and [7] is too small as to allow for deducing any firm conclusions about the relative weight of these two reaction channels.

For obtaining such detailed information, high-level quantum-chemical calculations of activation energies and pre-exponential factors are required, which are not easily obtained for large species, such as **2**, **3**, **4**, and **6**. Thus further reactions in conjunction with detailed product analyses, as in ref.[20], need to be carried out in order to identify the contribution of "missing step" reactions occurring via hydrogen abstraction. If cross combination of $\mathbf{1}+\mathbf{3}$ yields **4a** and **4e**, hydrogen abstraction is not expected to play a significant role.

Although the arguments on the "missing step" reaction have essentially been made on the basis of reaction free enthalpies rather than on reaction barriers or activation energies, the results strongly indicate that the missing step should be a very fast in the case of reactive propagating radicals, as in acrylate polymerization. It is highly recommendable, if not mandatory, to consider this step in the kinetic modeling of dithiobenzoate-mediated acrylate polymerizations. Including the "missing step" into the kinetic scheme allows for the first time to consistently represent the entire body of experimental observations made under main-equilibrium conditions during dithiobenzoate-mediated acrylate polymerizations.

It goes without saying that further reaction steps may be added to the overall kinetic scheme. A star-star coupling reaction of $\mathbf{3}+\mathbf{3}$ and follow-up processes of products from this reaction may be included, as should be chain-length and conversion dependent rate coefficients for the diffusion-controlled processes. Such modifications are useful for fine-tuning of dithiobenzoate-mediated RAFT kinetics.

Analysis of RAFT polymerizations via the kinetic scheme that contains the "missing step" reaction is not restricted to dithiobenzoate-mediated polymerizations, but should be generally used with RAFT-mediated polymerizations, even in situations where **3** is high in energy and the fragmentation rate is very fast. Under such conditions, the reactions presented in Eq. (2) and, in particular, the one in Eq. (3) will however be of minor importance.

It appears to be a matter of priority to carry out DFT estimates for reactions in which the ethyl radical and ethyl moieties are replaced by styryl or by acrylate-type units. The results of such DFT calculations should indicate to which extent the "missing step" reaction contributes to dithiobenzoate-mediated polymerizations of different types of monomers under main-equilibrium conditions. The existence of three-arm star cross-combination products in styrenic systems suggests that the ''missing step'' is less important in case of lower-energy propagating radicals. An obvious reason for such different behavior is seen in lower reaction free enthalpies. As the free enthalpy of combination of two styryl radicals, which is identical to the sum of the free enthalpies for the $\mathbf{1}+\mathbf{3}\rightarrow\mathbf{4}$ and $\mathbf{1}+\mathbf{4}\rightarrow\mathbf{3}+\mathbf{5}$ reaction steps, is significantly lower than the one of combination of two ethyl radicals, also the individual free enthalpies, including $\Delta G_{\mathrm{R,MS}}$, should be much smaller in styrenic systems. Moreover, the activation barriers may be higher for these systems. The quantitative analysis of the ''missing step'' kinetics for a range of monomers will largely benefit from DFT estimates of transition-state structures. Such calculations are currently underway in our laboratory.

Conclusions

Introducing the reaction of propagating radicals, **1**, with the cross-combination product from irreversible termination, **4**, resolves the major problem encountered in kinetic analyses of dithiobenzoate-mediated acrylate polymerizations via the *irreversible termination* model. The reaction of $\mathbf{1}+\mathbf{4}$ to yield $\mathbf{3}+\mathbf{5}$ or $\mathbf{6}+\mathbf{7}$ which has been overlooked so far, can fully account for the loss of the three-arm star product **4**. Without introducing any new species, the extended kinetic scheme adequately represents all essential observations made for the main-equilibrium period of dithiobenzoate-mediated RAFT polymerizations. The novel reaction is expected to be very fast, due to the enormous driving force associated with transforming a highly reactive propagating radical **1** and a loosely bound star-shaped molecule **4** into a resonance-stabilized radical **3** and a very stable dead polymer molecule **5**. The ''missing step'' reaction applies irrespective of cross-termination being reversible or irreversible. It seems advisable to generally use the extended kinetic scheme for analysis of reactivity and selectivity in RAFT polymerizations, although reaction $\mathbf{1}+\mathbf{4}\rightarrow\mathbf{3}+\mathbf{5}$ is less important in the case that the intermediate RAFT radical **3** is not significantly stabilized or the propagating radical is of lower reactivity.

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