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Addition-Fragmentation Kinetics of Fluorodithioformates (F-RAFT) in Styrene, Vinyl Acetate, and Ethylene Polymerization: An Ab Initio Investigation

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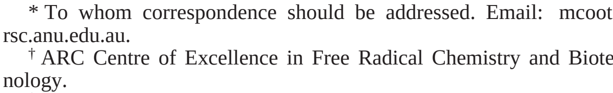
ABSTRACT: The kinetics and thermodynamics of the addition-fragmentation equilibrium in fluorodithioformate ($S{=}C(F)SR$; F-RAFT) mediated polymerization of styrene and vinyl acetate were investigated via high-level ab initio molecular orbital calculations. The fragmentation efficiencies of a wide range of leaving groups (R = $C(CH_3)_2CN$, CH_2CN, $C(CH_3)_2Ph$, $CH(Ph)CH_3$, CH_2Ph, $CH(COOCH_3)CH_3$, CH_2COOCH_3, $CH(OCOCH_3)$, CH_2OCOCH_3, $C(CH_3)_3$, CH_2CH_3, CH_3) were also investigated. The calculations confirm earlier predictions, on the basis of thermodynamic considerations alone, that these agents are likely to function as genuine multipurpose RAFT agents. Thus, stable propagating radicals (as in styrene polymerization) are capable of adding to the RAFT agent with high rate coefficients (1.8×10^6 L mol^{-1} s^{-1} at 333.15 K), comparable to those observed with normal dithioesters such as $S{=}C(CH_3)SR$ (3.8×10^6 L mol^{-1} s^{-1}). Concurrently, unstable propagating radicals (as in vinyl acetate polymerization) are capable of undergoing fragmentation with significantly higher rate coefficients (1.7×10^4 s^{-1}) than that for $S{=}C(CH_3)SR$ (8.4 s^{-1}) and are not expected to be rate retarded. On the basis of an examination of leaving group abilities and known reinitiation rate coefficients, the agents $S{=}C(F)SC(CH_3)_2CN$ or $S{=}C(F)SC(CH_3)_2Ph$ are identified as optimal F-RAFT agents for styrene polymerization, while $S{=}C(F)SCH_2CN$ or $S{=}C(F)SC(CH_3)_3$ are identified as optimal F-RAFT agents for vinyl acetate and ethylene polymerization. The potential suitability of employing F-RAFT to invoke living free radical polymerization of ethylene has been tested by a general kinetic screening exercise as well as specific simulations that employ quantum chemically predicted F-RAFT rate coefficients. These results indicate that F-RAFT is expected to control ethylene free radical polymerization.

Introduction

The reversible addition-fragmentation transfer (RAFT) process is an important new method for controlling the molecular weight and architecture in free radical polymerization.[1] The process can be used to generate complex macromolecular architectures such as comb, star, and block copolymers for use in bioengineering and nanotechnology applications.[2] Control is achieved by protecting the majority of the propagating species from bimolecular termination through their reversible trapping into a dormant thiocarbonyl compound as (1). A delicate balance of the rates of these various reactions is required so as to ensure that the dormant species is orders of magnitude greater in concentration than the active species, and the exchange between the two forms is rapid. Although the RAFT process has been successfully applied to a wide range of olefinic monomers,[2] the choice of RAFT agent substituents (i.e., R and Z) that strike this optimal balance is sometimes problematic. By providing detailed information on the mechanism, kinetics, and thermodynamics of these individual steps, computational quantum chemistry can greatly assist in the design of optimal RAFT agents.



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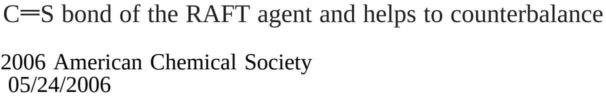
Recently, we utilized computational quantum chemistry to design a new class of RAFT agent, the fluorodithioformates ($S{=}C(F)SR$, or "F-RAFT").[3] These were designed as multipurpose RAFT agents, capable of controlling monomers with stable propagating radicals and also those with unstable propagating radicals. Other current RAFT agents for unstable monomers promote fragmentation of unstable propagating radicals by stabilizing the thiocarbonyl product of fragmentation (i.e., the RAFT agent itself) via resonance (2). As a result, they are not sufficiently reactive for controlling monomers with stable propagating radicals. In contrast, F-RAFT promotes fragmentation by destabilizing the RAFT-adduct radical without deactivating the C=S bond of the RAFT agent. The fluorine Z group achieves this through its strong σ-withdrawing capacity, which contributes a destabilizing influence to both the radical and the C=S bond of the RAFT agent and helps to counterbalance the



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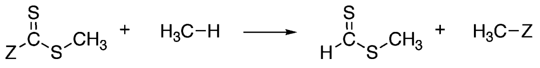
stabilizing influence of its lone pair donor capacity. This not only allows the RAFT agent to remain sufficiently reactive for the control of stable monomers, but their increased reactivity should also help to improve the control of unstable monomers such as vinyl acetate and ethylene.

Although the performance of F-RAFT agents for unstable monomers is yet to be tested experimentally, a recent study has indicated that the F-RAFT agent benzyl fluorodithioformate is capable of controlling the polymerization of styrene, a prototypical stable monomer.[4] In this work, although living characteristics were clearly evident, an initial rapid increase in the molecular weight of the polymer was also observed. This behavior, termed "hybrid behavior", is usually indicative of slow transfer of the initial RAFT agent and can result from preferential fragmentation of the polymeric radical (rather than the R group) in the preequilibrium and/or slow addition of the propagating radical to the RAFT agent.[5] In the former case, the hybrid behavior arises merely from a poor choice of R group and can be addressed in a relatively straightforward manner. In the latter case, the hybrid behavior would be of much greater concern, as it would imply that the fluorine Z group has deactivated the C═S double bond, and thus all F-RAFT agents would be affected. Although, in a previous work[4] we used ab initio calculations to show that the chosen R group (benzyl) was not optimal for controlling styrene and was a likely cause of the hybrid behavior, the possibility that slow addition of the propagating radical is a contributing factor cannot as yet be ruled out.

Our original computational predictions were based on simple thermodynamic considerations. In particular, we measured the "reactivity" of the RAFT agents on the basis of the simple isodesmic reaction (3). We have previously[6] shown that unreactive RAFT agents (i.e., suitable only for controlling reactive propagating radicals) such as xanthates and dithiocarbamates have large positive stabilities (>80 kJ mol^{-1}), while "normal" dithioesters (such as those with alkyl or aryl Z groups that are capable of controlling stable monomers) have significantly lower stabilities (ca. 30−40 kJ mol^{-1}). Because the calculated stability of the fluorine-substituted agent is 43.5 kJ mol^{-1}, it was concluded that its reactivity was similar to that of a normal dithioester.[3] Although these simple thermodynamic considerations usually provide a reasonable qualitative guide to the kinetic behavior of RAFT agents, subtle stereoelectronic effects (such as homoanomeric effects and H-bonding interactions) can sometimes dramatically affect the results.[6−8] It is thus important to investigate the addition-fragmentation kinetics more directly to establish whether F-RAFT agents are indeed sufficiently active for the control of stable monomers.



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To this end, in the present work, we present high-level ab initio calculations of the rate and equilibrium constants for F-RAFT-mediated polymerization of styrene and vinyl acetate and compare these with prototypical dithioesters and xanthates. In this way, we hope to establish whether slow addition is likely to be a concern in styrene polymerization and whether slow fragmentation is likely to be a concern in vinyl acetate polymerization. We also calculate the equilibrium constants for a wide range of R groups so as to allow for the selection of optimal F-RAFT agents for a range of monomers. Finally, we combine quantum chemical calculations with PREDICI simulations to show that F-RAFT offers improved prospects for the control of ethylene polymerization.

Computational Procedures

Standard ab initio molecular orbital theory and density functional theory calculations were carried out by using GAUSSIAN 03[9] and MOLPRO 2000.6.[10] All DFT calculations on radicals were performed with an unrestricted wave function, while all ab initio calculations on radicals were performed with restricted open-shell wave functions.

Calculations were performed at a high level of theory, chosen on the basis of previous assessment studies[11−13] for radical addition to C═S double bonds. The geometries of the reactants and products were optimized at the B3-LYP/6-31G(d)[14] level of theory, and frequencies were also calculated at this level and scaled by the appropriate scale factors.[15] Care was taken to ensure that each optimized structure was the global (rather than merely local) minimum energy structure via extensive conformational searching, and the nature of all stationary points was confirmed via frequency calculations. Because DFT methods such as B3-LYP significantly overestimate the length of the forming bond in the transition state for these types of reaction,[11,12] all transition structures were further optimized using an IRCmax[16] version of variational transition state theory (VTST) as follows. The minimum energy path (MEP) of the reaction was first calculated at the B3-LYP/6-31G(d) level of theory as a relaxed scan along the forming C···S bond length. We have previously shown that this provides a good approximation to a full IRC calculation for this type of reaction.[12] At several points along the MEP, improved energies were then obtained at the RMP2/6-311+G(3df,2p) level of theory, and partition functions were calculated by using scaled B3-LYP/6-31G(d) frequencies under the harmonic oscillator approximation. These were then used to calculate the Gibb's free energy (G), and the VTST transition structure was identified as the species corresponding to the maximum Gibbs free energy (G) of the reaction.

By using the B3-LYP/6-31G(d) optimized structures for the reactants and products and the VTST-corrected transition structures, improved energies were obtained at the G3(MP2)-RAD level of theory[17] and then corrected to the W1 level of theory[12] by using a two-layer ONIOM-based approach as follows. For each reaction (R$^•$ + S═C(Z)SR′), the barrier or enthalpy at the W1 level of theory for the general reaction is approximated as the sum of the corresponding value for the "inner core" ($^•$CH$_3$ + S═CH$_2$) reaction and the substituent effect of the full system, as calculated using G3(MP2)-RAD.[17]

Having obtained the geometries, frequencies, and energies of all species, the rate $k(T)$ and equilibrium $K(T)$ constants of the addition and fragmentation reactions were calculated using the standard textbook formulas (4) and (5), respectively.[18,19]

$$k(T) = \kappa(T)\frac{k_{\mathrm{B}}T}{h}(c^\circ)^{1-m}\, e^{(-\Delta G^\ddagger/RT)} = \kappa(T)\frac{k_{\mathrm{B}}T}{h}(c^\circ)^{1-m}\frac{Q_\ddagger}{\prod\limits_{\text{reactants}} Q_i}\, e^{(-\Delta E^\ddagger/RT)} \quad (4)$$

$$K(T) = (c^\circ)^{\Delta n}\, e^{(-\Delta G/RT)} = (c^\circ)^{\Delta n}\left(\frac{\prod\limits_{\text{products}} Q_j}{\prod\limits_{\text{reactants}} Q_i}\right) e^{(-\Delta E/RT)} \quad (5)$$

In these formulas, $\kappa(T)$ is the tunneling correction factor, T is

Table 1. Calculated Rate Coefficients and Equilibrium Constants (333.15 K) for $R^{\bullet} + S{=}C(Z)SCH_3 \rightarrow RSC^{\bullet}(Z)SCH_3$ for Prototypical Xanthates, Fluorodithioformates, and Standard Dithioesters in Styrene and Vinyl Acetate Polymerization[a]

$R^{\bullet}$	$S{=}C(Z)SCH_3$	k_{add} L mol^{-1} s^{-1}	k_{frag} s^{-1}	K_{eq} L mol^{-1}
styrene: $^{\bullet}CH(Ph)CH_3$	$S{=}C(CH_3)SCH_3$	3.8×10^6	7.5×10^4	5.1×10^0
	$S{=}C(F)SCH_3$	1.8×10^6	2.1×10^8	8.8×10^{-3}
	$S{=}C(OCH_3)SCH_3$	4.4×10^4	2.5×10^8	1.8×10^{-4}
vinyl acetate: $^{\bullet}CH(OCOCH_3)CH_3$	$S{=}C(CH_3)SCH_3$	4.2×10^8	8.4×10^0	5.0×10^7
	$S{=}C(F)SCH_3$	5.6×10^8	1.7×10^4	3.4×10^4
	$S{=}C(OCH_3)SCH_3$	5.0×10^7	3.5×10^6	5.1×10^1

[a] Rate coefficients and equilibrium constants (333.15K) were calculated at the W1−ONIOM level of theory in conjunction with the hindered rotor model. In calculating the rate coefficients, variational (rather than standard) transition state theory was used (see text).

Table 2. Equilibrium Constants (K, 333.15 K) and Associated Thermodynamic Parameters (ΔH, ΔS, and ΔG) for $R^{\bullet} + S{=}C(F)SCH_3$ and Experimental Rate Coefficients for Reinitiation (k_{reint} 298.15 K) by $R^{\bullet}$ for Various Monomers[a]

R	$-\Delta H_{333}$ kJ mol^{-1}	$-\Delta S_{333}$ J mol^{-1} K^{-1}	ΔG_{333} kJ mol^{-1}	K_{333} L mol^{-1}	k_{reint} (STY) L mol^{-1} s^{-1}	k_{reint} (VA) L mol^{-1} s^{-1}	k_{reint} (Et) L mol^{-1} s^{-1}
$C(CH_3)_2CN$	30.8	178.5	28.5	9.4×10^{-4}	2410	41	
$C(CH_3)_2Ph$	27.4	167.9	28.5	9.2×10^{-4}	1200[b]		
$CH(CH_3)Ph$	24.8	156.8	28.2	1.0×10^{-3}	1100	15	
CH_2Ph	25.4	148.4	25.3	2.9×10^{-3}			
$CH(Ph)CH_2C(CH_3)_2CN$	29.2	161.6	24.6	3.7×10^{-3}			
CH_2CN	30.8	143.8	17.1	5.7×10^{-2}	3.8×10^5	1.3×10^4	3300
$CH(CH_3)COOCH_3$	42.7	165.0	12.3	3.2×10^{-1}			
CH_2COOCH_3	51.4	156.5	0.8	2.1×10^1			
$CH(CH_3)OCOCH_3$	69.4	173.6	−11.8	2.0×10^3			
CH_2OCOCH_3	62.7	152.4	−12.2	2.3×10^3			
$C(CH_3)_3$	72.4	175.7	−13.9	4.1×10^3	1.3×10^5	4200	1250
CH_2CH_3	70.2	158.7	−17.4	1.5×10^4			
CH_3	50.2	126.5	−23.1	1.2×10^5	2.6×10^5	1.4×10^4	3500

[a] Equilibrium constants (333.15 K) and associated thermodynamic parameters (enthalpy H, entropy S, and Gibbs free energy G) calculated at the W1-ONIOM//B3-LYP/6-31G(d) level of theory in conjunction with the harmonic oscillator approximation. Experimental data (298 K) for reinitiation of styrene (STY), vinyl acetate (VA), and ethylene (Et) by $R^{\bullet}$ are taken from ref 26 unless noted otherwise. [b] From ref 27.

the temperature (K), k_B is Boltzmann's constant (1.380658×10^{-23} J·mol c^{-1}·K^{-1}), h is Planck's constant ($6.6260755 \times 10^{-34}$ J·s), $c°$ is the standard unit of concentration (mol·L^{-1}), R is the universal gas constant (8.3142 J·mol^{-1}·K^{-1}), m is the molecularity of the reaction, and Δn the change in moles upon reaction, $Q_{\ddagger}$, Q_i, and Q_j are the molecular partition functions of the transition structure, reactant i and product j, respectively, $\Delta G^{\ddagger}$ is the Gibbs free energy of activation, ΔG is the Gibbs free energy of reaction, $\Delta E^{\ddagger}$ the 0 K, zero-point energy corrected energy barrier for the reaction, and ΔE is the 0 K, zero-point energy corrected energy change for the reaction. Tunneling can be assumed to be negligible (i.e., $\kappa \approx 1$) for the addition of carbon-centered radicals to thiocarbonyl compounds at typical polymerization temperatures (such as 333.15 K) because the masses of the rearranging atoms are large and the barriers for the reactions are relatively broad.[11] The molecular partition functions and their associated thermodynamic functions (i.e., enthalpy, H, and entropy, S) were calculated by using the standard textbook formulas,[18,19] based on the statistical thermodynamics of an ideal gas under the harmonic oscillator/rigid rotor approximation.

It is known that the harmonic oscillator approximation can lead to the underestimation of the equilibrium constants by approximately 1−2 orders of magnitude,[20] and cause smaller but nonetheless significant errors in the rate coefficients for these systems.[11] Because, for the rate and equilibrium constants in Table 1, it was necessary to obtain accurate absolute values, all low-frequency torsional modes (<300 cm^{-1}) were treated as hindered internal rotations, using the standard procedure described elsewhere.[11] However, in the case of the equilibrium constants in Table 2, it was necessary only to obtain accurate relative values. Because the main source of error in the harmonic oscillator approximation arises in the treatment of the C−S single-bond rotations, which are common to all of the reactions considered, we do not expect the harmonic oscillator approximation to affect the relative trends in the data. For this reason, the significantly less computationally intensive harmonic oscillator approximation was adopted for the data in Table 2.

Although direct comparison with experimental data for addition-fragmentation reactions is problematic, studies of related systems indicate that the computational approach is capable of achieving chemical accuracy. For example, Scaiano and Ingold have reported an experimental equilibrium constant (based on laser flash photolysis studies) of 1.2×10^6 L mol^{-1} for the addition of *tert*-butyl radicals to di-*tert*-butyl thioketone at 25 °C. The theoretical equilibrium constant of 7.9×10^5 L mol^{-1}, obtained by using the theoretical procedure outlined above, is in good agreement with experiment,[21] the theoretical number being slightly lower due to the neglect of solvent effects. Likewise, the calculated propagation rate coefficients for the free-radical polymerization of vinyl chloride and acrylonitrile are within a factor of 2 of the experimental data.[22]

PREDICI Simulations. All simulations were carried out using the program package PREDICI, version 5.36.5, on a Pentium III 800EB, or Athlon XP 2500+ IBM-compatible computer. The basic implementation of the RAFT process into the PREDICI program package has been described in detail before and will thus not be reiterated here.[23] The ethylene model detailed by Busch[24] was employed in parallel, with the RAFT implementation superimposed on the basis ethylene model. The RAFT model assumes identical addition and fragmentation rate coefficients for the pre- and main equilibrium. The rate coefficients for the reaction conditions of 150 °C and 2500 bar were also taken from ref 24. All simulations were carried out to 40% ethylene conversion by using *tert*-butylperpivalte (TBPP) as the thermally decaying initiator.

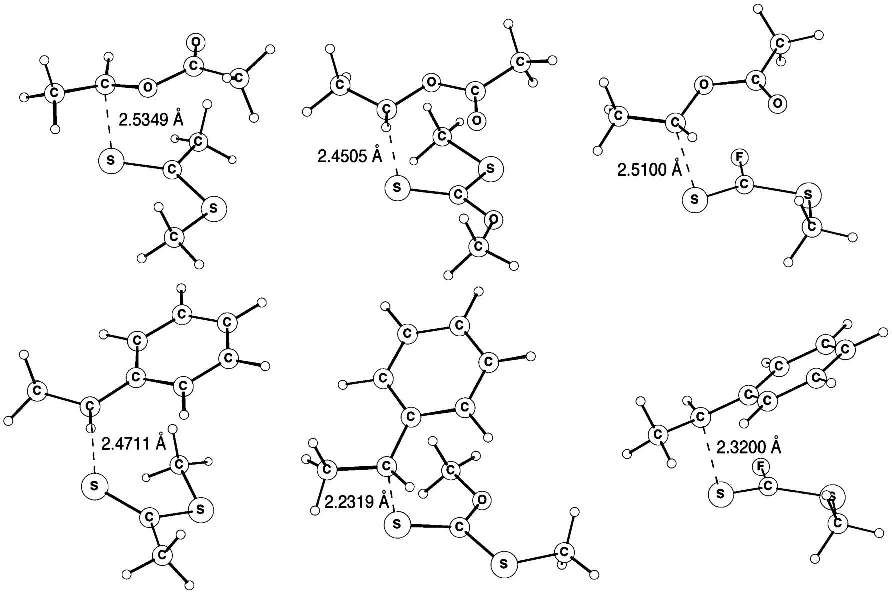

Figure 1. B3-LYP/6-31G(d) optimized geometries of the VTST transition structures in styrene and vinyl acetate polymerization.

Results and Discussion

Rate coefficients and equilibrium constants for addition of model styryl ($^{\bullet}CH(Ph)CH_3$) and vinyl acetate ($^{\bullet}CH(OCOCH_3)CH_3$) radicals to $S{=}C(F)SCH_3$ are shown in Table 1. Corresponding rate and equilibrium constants for their addition to a prototypical dithioester ($S{=}C(CH_3)SCH_3$) and a prototypical xanthate ($S{=}C(OCH_3)SCH_3$) are also included for purposes of comparison. Table 2 shows the equilibrium constants for addition of a wide range of radicals to $S{=}C(F)SCH_3$. The geometries of the transition structures are displayed in Figure 1, and complete geometries for all species are provided in the Supporting Information. In what follows, we first examine the kinetic performance of F-RAFT agents in styrene and vinyl acetate polymerization, and we then conclude with an examination of the prospects for using F-RAFT to control ethylene.

Styrene Polymerization. Considering first the case of styrene polymerization, we recall that the propagating radical is relatively stable and that slow addition to the RAFT agent can be thus a problem if the RAFT agent is not sufficiently activated. It is for this reason that the xanthates and dithiocarbamates normally used to control monomers with unstable propagating radicals do not offer adequate control over less active monomers such as styrene.[25] By examining Table 1, however, we find that this is not the case for fluorodithioformates; addition of a model styryl propagating radical to the agent is fast (1.8×10^6 L mol^{-1} s^{-1} at 333 K). This is not only comparable to addition rate coefficients for standard dithioesters at the same temperature, such as $S{=}C(CH_3)SCH_3$ (3.8×10^6 L mol^{-1} s^{-1}), but significantly faster than addition to standard xanthates (4.4×10^4 L mol^{-1} s^{-1}). It is clear that the fluorine Z group does not deactivate the C═S double bond of the RAFT agent, and this is in accord with earlier predictions based on simple thermodynamic considerations.

The rate coefficients in Table 1, therefore, indicate that the hybrid behavior reported previously for styrene polymerization in the presence of benzyl fluorodithioformate is not likely to result from slow addition to the RAFT agent but rather from an inappropriate choice of leaving group (i.e., R in $S{=}C(F)SR$). The question thus arises, what leaving groups are appropriate for controlling styrene? To function as a suitable leaving group, the $R^{\bullet}$ must fragment preferentially from the RAFT adduct in the early stages of the polymerization process and be concurrently capable of reinitiating polymerization. From Table 2, it is seen that the addition of the benzyl radical to F-RAFT occurs with a higher equilibrium constant ($2.9 \cdot 10^{-3}$ L mol^{-1}) than the addition of the unimeric styryl radical, $CH_3CH(Ph)^{\bullet}$ ($1.0 \cdot 10^{-3}$ L mol^{-1}). Thus, on a thermodynamic basis at least, benzyl is expected to be a less effective leaving group than the styryl radical, consistent with the experimentally observed hybrid behavior. Of the R-groups listed in Table 2, those with lower equilibrium constants than the unimeric styryl radical include $^{\bullet}C(CH_3)_2CN$ and $^{\bullet}C(CH_3)_2Ph$. However, because all of these *K* values fall into a narrow range (differing by a factor of 3 at most), it is important to consider the influence of the penultimate unit in the propagating styryl radical. The equilibrium constant for a true unimeric styryl radical (using the common initiator 2,2′-azobis(isobutyronitrile)), $^{\bullet}CH(Ph)CH_2C(CH_3)_2CN$, was therefore calculated. The value obtained ($3.7 \cdot 10^{-3}$ L mol^{-1}) is slightly higher than that for $CH_3CH(Ph)^{\bullet}$ ($1.0 \cdot 10^{-3}$ L mol^{-1}), and this reinforces the conclusion that $^{\bullet}C(CH_3)_2CN$ and $^{\bullet}C(CH_3)_2Ph$ would fragment favorably during the early stages of the polymerization. Because both of these leaving radicals are also known to reinitiate polymerization of styrene with a sufficiently high rate coefficient,[26,27] they are therefore predicted to be suitable for controlling styrene.

Vinyl Acetate. The propagating radical in vinyl acetate polymerization, being relatively unstable, is normally expected to undergo fast addition to the RAFT agent, but unless special precautions are taken, its polymerization can be adversely affected by slow fragmentation. This is evident in Table 1, where it is seen that the calculated rate coefficient for addition to an ordinary dithioester is extremely fast ($4.2 \cdot 10^8$ L mol^{-1} s^{-1}) and, although slower, even addition to xanthates occurs with a reasonable rate coefficient ($5.0 \cdot 10^7$ L mol^{-1} s^{-1}). However, the fragmentation rate coefficient for the dithioester (8.4 s^{-1}) is very slow and the equilibrium constant is very large ($5.0 \cdot 10^7$ L mol^{-1}), within the limits ($K \geq 10^6$ L mol^{-1})[28] where slow fragmentation would be predicted to cause rate retardation. In contrast, the xanthate, being designed to promote fragmentation of unstable radicals through the stabilization of its thiocarbonyl bond, shows much higher fragmentation rate coefficients (3.5·

10^6 s^{-1}) and an equilibrium constant ($5.1 \cdot 10^1$ L mol^{-1}) well below the limit for which rate retardation would be expected. From Table 1, it is seen that the fluorinated RAFT agent also promotes fragmentation of the vinyl acetate radical. Although the equilibrium constant is intermediate to those of the xanthate and dithioester, it is well below the limit at which fragmentation would be expected and, more importantly, the fragmentation rate coefficient is very high ($1.7 \cdot 10^4$ s^{-1}). This high fragmentation rate coefficient reflects the destabilization of the RAFT adduct radical by the fluorine substituent and confirms our earlier predictions, on the basis of thermodynamic considerations alone, that fluorinated RAFT agents have the potential to effect nonretarded controlled polymerization of unstable monomers such as vinyl acetate.

From Table 2, it is clear that a wide range of leaving groups are expected to fragment preferentially over the unimer vinyl acetate propagating radical, $CH_3CH(OCOCH_3)^{\bullet}$, including: $C(CH_3)_2CN$, $C(CH_3)_2Ph$, $CH(CH_3)Ph$, CH_2Ph, CH_2CN, $CH(CH_3)COOCH_3$, and CH_2COOCH_3. However, few of these radicals are likely to be capable of affording fast reinitiation. For example, on the basis of experimental studies, the rate of addition of the benzyl radical to vinyl acetate at room temperature is only 15 L mol^{-1} s^{-1}, while that for $C(CH_3)_2CN$ is only 41 L mol^{-1} s^{-1}.[26] However, CH_2CN has a reinitiation rate coefficient ($1.3 \cdot 10^4$ L mol^{-1} s^{-1})[26] more comparable to the propagation rate coefficient of vinyl acetate, and because it also is expected to fragment preferentially, it is suggested as a promising leaving group for this system. The *tert*-butyl leaving group, which also has a fast initiation rate (4200 L mol^{-1} s^{-1})[26] and has a similar K value to that of the vinyl acetate unimer, would also be worthy of investigation.

The slow reinitiation of vinyl acetate by the benzyl radical suggests a more general problem with one of the proposed applications of F-RAFT agents. In designing a multipurpose RAFT agent, capable of controlling monomers with disparate reactivities, one of the intentions was to facilitate the formation of block copolymers of such monomers. However, in the specific case of styrene−vinyl actetate, the formation of block copolymers may be limited by a more fundamental problem, that of persuading significant concentrations of the polystyryl propagating radical to reinitiate vinyl acetate polymerization. Nonetheless, there are many other pairs of stable and unstable monomers (such as methyl acrylate−vinyl acetate) for which the reinitiation by the propagating radical of the more stable monomer is promoted on polar grounds. For these systems, the availability of a multipurpose RAFT agent would be helpful for block copolymer synthesis. More importantly, fluorinated RAFT agents, due to their higher inherent reactivity, are likely to afford improved control of unstable monomers compared with that offered by their xanthate or dithiocarbamate counterparts. This increased reactivity is clearly evident in Table 1, where it is seen that the rate of addition by the vinyl acetate propagating radical to F-RAFT is approximately an order of magnitude faster than that for the corresponding xanthate. This higher addition rate would be expected to lead to a faster exchange rate and narrow molecular weight distributions, particularly for higher-molecular-weight polymers.

Ethylene. The increased reactivity of fluorodithioformates would be expected to be especially valuable for the control of other unstable monomers, such as ethylene, for which the satisfactory control has yet to be achieved by using the xanthates and dithiocarbamates. Although in thermodynamic terms, the propagating radical in ethylene polymerization is even less stable than the vinyl acetate propagating radical, its addition rate coefficient to xanthates is much lower. For example, even by using the highly reactive methyl radical as a model for propagating species, the rate of radical addition to the xanthate $S{=}C(OCH_3)SCH_3$ (1.4×10^5 L mol^{-1} s^{-1}) is approximately 2 orders of magnitude slower than that of the vinyl acetate propagating radical to the same substrate, the latter being facilitated by favorable hydrogen-bonding interactions in the transition structure.[7] Using the same radical model, addition to the fluorodithioformates is substantially faster (9.3×10^6 L mol^{-1} s^{-1}) due to the increased activation of the C═S double bond. At a more practical polymerization temperature for this monomer, 150 °C, the corresponding addition and fragmentation rate coefficients would be 3.8×10^7 L mol^{-1} s^{-1} and 3.9×10^4 s^{-1}, respectively.

To assess the general feasibility of the RAFT polymerization of ethylene, a model scenario was tested based on the following assumption that the RAFT agent has a fast addition and fast fragmentation rate coefficient. For this purpose, the reference 60 °C rate coefficient values for a system known to work effectively (under an ideal RAFT scenario) in the polymerization of more conventional monomers such as methyl acrylate were employed (i.e., $k_{add} = 10^6$ L mol^{-1} s^{-1} and $k_{frag} = 10^5$ L mol^{-1} s^{-1}).[29] These were subsequently scaled with temperature under the assumption of an activation energy of 5 kJ mol^{-1} for the addition reaction and 100 kJ mol^{-1} activation energy for the fragmentation reaction (see for example ref 11), resulting in the corrected (for 150 °C) rate coefficients of $k_{add}{=}1.7 \cdot 10^6$ L mol^{-1} s^{-1} and $k_{frag}{=}1.1 \cdot 10^8$ L mol^{-1} s^{-1}, respectively. Both rate coefficients were assumed to be identical for the pre- and main equilibrium for this initial study. The ratio of wt % RAFT agent and wt % initiator were then incrementally varied, and the resulting polydispersities were plotted for both the dead polymeric species and the macroRAFT agent. The outcome of such a procedure is depicted in Figure 2.

Inspection of Figure 2 demonstrates that there is a specific region where a minimum polydispersity for the macroRAFT agent and the dead polymeric species are observed. Not surprisingly, the minimum polydispersity is achieved for both the dead polymer and the macroRAFT agent at reaction mixture compositions having a small ratio of TBPP to RAFT agent (for the dead polymer species at TBPP:RAFT = 0.2 and for the macroRAFT agent at 0.035). Such an observation is completely congruent with observations made for more conventional RAFT systems, where the lowest polydispersities are obtained at small initiator to RAFT ratios.[28] The predicted polydispersities for the entire concentration regime depicted in Figure 2 are well below those typically expected for polyethylene prepared via conventional radical polymerization. It goes without saying that the given ratio of initiator to RAFT agent (i.e., the individual weight fractions) can be multiplied by variable (but identical) factors to access different molecular weight regimes while maintaining optimum polymerization control. Further, it should be noted that, at these low initiator to RAFT ratios, the overwhelming proportion of chains are capped with a macroRAFT end group and are thus living. Further, a series of alternative rate coefficients was employed to test the feasibility of RAFT under typical ethylene reaction conditions via the assumption of different activation energies for the addition (0−10 kJ mol^{-1}) and fragmentation reaction (80−100 kJ mol^{-1}), resulting in a span for k_{add} from roughly $6 \cdot 10^6$ to $5 \cdot 10^5$ L mol^{-1} s^{-1} and for k_{frag} from $2 \cdot 10^{10}$ to $1 \cdot 10^8$ L mol^{-1} s^{-1}. The respective variation in these rate coefficients only marginally affects the polydispersities of the terminated and living species (ranging from 1.33 to 1.46 for the macroRAFT agent and 2.1 to 2.3 for

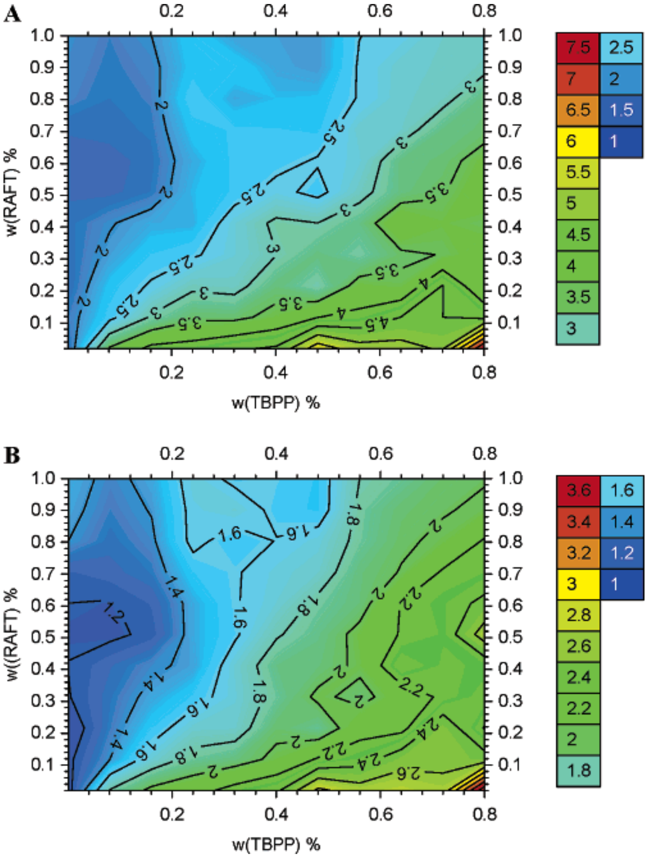

Figure 2. Contour diagrams mapping the polydispersity, PDI, of the generated dead (i.e., terminated) polymer species (A) and the macroRAFT agent (B) (i.e., living polymer) as a function of the reaction mixture composition (initial RAFT agent concentration vs TBPP (initiator concentration) in an ethylene polymerization at 150 °C. Depicted is the case where the addition rate coefficient is close to $6 \cdot 10^6$ L mol^{-1} s^{-1} and the fragmentation rate coefficient close to $1.1 \cdot 10^8$ L mol^{-1} s^{-1}. Both rate coefficients were assumed identical for the pre- and main equilibrium.

the terminated polymer). It can thus be concluded that rate coefficients within this range should be suitable to effect living free radical polymerization of ethylene.

In a further step, to determine whether the quantum chemically determined rate coefficients (see above, $k_{\mathrm{add}}=3.8 \times 10^7$ L mol^{-1} s^{-1} and $k_{\mathrm{frag}}=3.9 \times 10^4$ s^{-1}) are equally capable of giving rise to living behavior in the ethylene system, kinetic simulations identical to those performed above were carried out with PREDICI, using the reaction mixture composition yielding minimum polydispersities for the macroRAFT agent (see Figure 2, mixture composition (in wt %: ethylene 0.99793, TBPP $7 \cdot 10^{-5}$, RAFT $2 \cdot 10^{-3}$). It is gratifying to note that the quantum chemically determined rate coefficients yield a polydispersity of 1.03 for the macroRAFT agent at 15% conversion and 1.61 for the terminated polymer, with a significant excess of living over terminated chains (24:1). It is not entirely surprising that the rate coefficients suggested from the quantum chemical results yield improved polydispersities: (i) The addition rate coefficient is somewhat larger, thus allowing for a more efficient establishment of the RAFT equilibrium, which in turn leads to lower polydispersities at lower conversions.[28] Further, (ii) it has been shown that a lower fragmentation rate coefficient does not adversely affect the polymerization control; on the contrary, large equilibrium constants can decrease the resulting polydispersities by invoking an additional quasipersistent radical effect (resulting from an elevated equilibrium constant),[28] however, at the potential expense of a reduced rate of polymerization at earlier reaction times.[30]

On the basis of the above simulations, we predict that F-RAFT should offer improved prospects for control of ethylene polymerization. On the basis of the leaving group abilities given in Table 2, together with experimental reinitiation data,[26] the agent $\mathrm{S{=}C(F)SCH_2CN}$ or $\mathrm{S{=}C(F)SC(CH_3)_3}$ is predicted to offer control of this monomer. It must be noted that ethylene polymerizations are not as facile to carry out as polymerizations of more conventional monomers such as styrene and methyl methacrylate, as they require higher temperatures and the application of elevated pressures. Thus, establishing the thermal stability of the suggested RAFT agents at ethylene reaction conditions is mandatory. Although the above modeling procedures have fully taken into account reactions such as transfer to polymer as well as short- and long-chain branching (which are prominent in ethylene polymerization), it remains to be established how the presence of a RAFT agent (RAFT end group) affects these processes. However, it does appear that the development of F-RAFT agents foreshadows a potential pathway to controlling ethylene free radical polymerization by reversible addition fragmentation chain transfer chemistry. Experimental work is currently underway in our laboratories to evaluate F-RAFT agents for ethylene systems.

Conclusions

The kinetics and thermodynamics of addition-fragmentation equilibria in polymerizations mediated by fluorodithioformates (F-RAFT) have been studied via high-level ab initio molecular orbital calculations. The calculations confirm earlier predictions, on the basis of thermodynamic considerations alone, that these agents should function as genuine multipurpose RAFT agents. Thus, stable propagating radicals (as in styrene polymerization) are capable of adding to the RAFT agent with high rate coefficients, comparable to those observed with normal dithioesters. Concurrently, unstable propagating radicals (as in vinyl acetate polymerization) are capable of undergoing fragmentation with high rate coefficients, comparable to those in xanthate-mediated polymerizations. On the basis of an examination of leaving group abilities and known reinitiation rates, the agents $\mathrm{S{=}C(F)SC(CH_3)_2CN}$, or $\mathrm{S{=}C(F)SC(CH_3)_2Ph}$ are identified as optimal F-RAFT agents for styrene polymerization, while $\mathrm{S{=}C(F)SCH_2CN}$ and $\mathrm{S{=}C(F)SC(CH_3)_3}$ are identified as optimal F-RAFT agents for vinyl acetate and ethylene.

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Supporting Information Available: B3-LYP/6-31G(d) geometries in the form of GAUSSIAN archive entries, scans of ΔH, ΔS, and ΔG along the minimum energy paths for the reactions (as used in identifying the variational transition structures), and full rotational potentials (as used in calculating the hindered rotor partition functions). This material is available free of charge via the Internet at http://pubs.acs.org.

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