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A Synthetic Approach to a Novel Class of Fluorine-Bearing Reversible Addition–Fragmentation Chain Transfer (RAFT) Agents: F-RAFT

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A synthetic route is described to a novel class of reversible addition–fragmentation chain transfer (RAFT) agents bearing a fluorine Z-group. Such F-RAFT agents are theoretically predicted to allow living free radical polymerization of various monomers without affecting the rate of polymerization, and should also facilitate the construction of block copolymers from monomers with disparate reactivity. The class of F-RAFT agents is exemplified by the example of benzyl fluoro dithioformate (BFDF) in styrene free-radical polymerizations and the process is shown to induce living polymerization.

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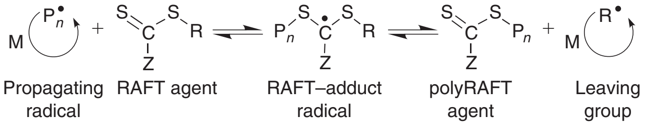
Introduction

Reversible addition–fragmentation chain transfer (RAFT) polymerization[1–3] has—along with other equally important living free radical techniques[4,5]—revolutionized free-radical polymerization as it allows for the generation of complex macromolecular architectures such as comb, star, and block copolymers with narrow polydispersities. RAFT polymerization is increasingly finding applications for generating novel structures and materials in bioengineering and nanotechnology applications. Lowe et al. used copolymers made by RAFT to stabilize transition metal nanoparticles[6] and materials based on nano- and micro-porous polymers have also been reported.[7,8] Other applications include the manufacture of biocompatible nanocontainers for drug delivery applications.[9]

The RAFT approach was developed by the CSIRO group,[1] by combining their earlier work on addition–fragmentation reactions of macromonomers[10] with the radical chemistry of small organic molecules of Zard and coworkers.[11] In a typical RAFT process, thiocarbonylthio compounds (known as RAFT agents, see Scheme 1) reversibly react with the growing polymeric radical via the chain transfer reaction depicted in Scheme 1. This reversible addition–fragmentation equilibrium is superimposed on a conventional free-radical polymerization process. Ideally, the chain-transfer process should be fast and the intermediate RAFT–adduct radical should be short lived. Because of the rapid transfer of the growing polymeric radicals between their free and dormant forms, living characteristics (i.e., a linear increase of molecular weight with monomer-to-polymer conversion) are imparted on the polymerizing system.



Scheme 1. Degenerative chain transfer—basis of the RAFT processes.

One of the outstanding challenges is the design of RAFT agents capable of controlling monomers with disparate reactivities. Currently, the RAFT agents used for controlling monomers with unstable propagating radicals (such as vinyl acetate) are not suitable for controlling monomers with stable propagating radicals (such as styrene), and vice versa. The problem arises because unstable propagating radicals (as in vinyl acetate polymerization) are poor radical leaving groups from the RAFT–adduct radical. As a result, the RAFT agents used to control the more stable systems (such as styrene) retard or inhibit its polymerization. Current RAFT agents for vinyl acetate address this problem through the use of lone-pair donor alkoxy or amino Z-groups. These promote fragmentation by stabilizing the other fragmentation product, the RAFT agent itself, by resonance (Scheme 2).

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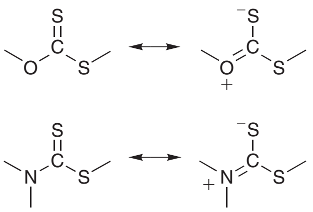
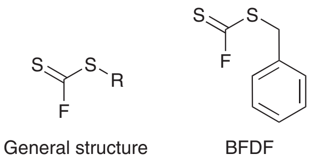


Scheme 2. Resonance stabilization in xanthates and dithiocarbamates.



Scheme 3. Novel class of F-RAFT agents: General structure and structural image of BFDF.

Unfortunately, by stabilizing the S=C bond, its reactivity towards radical addition is reduced, and the agents are not sufficiently reactive for controlling monomers with relatively stable propagating radicals. As a result, existing RAFT agents are not suitable for the production of well-defined styrene–vinyl acetate block copolymers.*

In order to be capable of controlling monomers with disparate reactivities, it is necessary to find RAFT agent substituents that promote fragmentation of unstable propagating radicals by destabilizing the RAFT–adduct radical rather than stabilizing the RAFT agent. Recently, high-level ab initio molecular orbital calculations were used to address this problem.[13] It was demonstrated that a fluorine Z-substituent significantly destabilizes the RAFT–adduct radical, relative to those derived from all known RAFT agents.[14] It was further shown that this destabilization should be sufficient to promote non-retarded fragmentation of the RAFT–adduct radical without stabilizing the RAFT agent. It was proposed that, provided appropriate R-groups were chosen, RAFT agents with a fluorine Z-group (denoted as 'F-RAFT' agents) should be capable of controlling monomers with disparate reactivities.

Although F-RAFT agents appear promising, they have been entirely designed by computational studies and it is of course necessary to demonstrate that: (*a*) they can be synthesized; and (*b*) they can control polymerization. A feasible approach to the synthesis of fluoro dithioformates starting from the corresponding chloro dithioformates has been previously reported by Sturm and Gattow.[15] However, based on the calculations for $S{=}C(F)SCH_3$,[13] the reported $S{=}C(F)SC_2H_5$ and $S{=}C(F)S(n\text{-}C_3H_7)$ agents are unlikely to be successful in a polymerization context. It is thus necessary to prepare novel F-RAFT agents (Scheme 3) S=C(F)SR with appropriate leaving groups, and examine their polymerization behaviour. The aim of the present work is thus to demonstrate a viable synthetic route to F-RAFT agents, and to examine their ability to control styrene polymerization.

Experimental

Benzyl Chloro Dithioformate (BCDF)

Thiophosgene (15.00 g, 130 mmol, Aldrich, 97%) and benzyl mercaptan (16.20 g, 130 mmol, Lancaster, 99%) were dissolved in 30 mL of carbon disulfide (Ajax Unilab). The solution was stirred in a flask with a gas outlet for 48 h at room temperature. The HCl gas produced was passed through a bubble counter and subsequently neutralized in alkaline potassium permanganate solution. After the reaction had finished, the solvent was evaporated and the product was distilled under vacuum to yield 13.31 g (50%) of benzyl chloro dithioformate (BCDF; yellow liquid), bp 104°C/0.4 mbar. δ_H (300 MHz, $CDCl_3$) 4.44 (2H, s, CH_2), 7.25–7.40 (5H, m, C_6H_5). δ_C (75 MHz, $CDCl_3$) 45.45 (1C, CH_2), 128.15 (1C, *para* C_6H_5), 128.82/129.20 (4C, *ortho*/*meta* C_6H_5), 133.08 (1C, $-C_6H_5$), 196.35 (1C, C=S). ν_{max} (ATR)/cm^{-1} 3085vw (CH valence), 3061w (CH valence), 3028m (CH valence), 2914vw (CH_2 valence), 1600vw (ar CH valence), 1494m (CH rocking), 1452m (CH rocking), 1399vw(br) (CH_2 bending), 1236w(br) (CH_2 wagging), 1195w (CH bending), 1095vs (C=S valence), 1070m (ar, def), 1028w (ar, def), 915vw (CH twist), 853vw (CH_2 rocking), 824w (ar, def), 770vs (as, Cl–C–S valence), 693s (CH wagging). λ_{max}/nm (CH_2Cl_2) 307 (log ε 4.13).

Benzyl Fluoro Dithioformate (BFDF)

A mixture of 5.81 g (100 mmol) of potassium fluoride (Ajax Unilab, >97%, dried under vacuum before use), 0.26 g (10 mmol) of 18-crown-6 (Aldrich, 99%), and 30 mL of anhydrous acetonitrile (Ajax Univar, >99.5%) was stirred under nitrogen with the exclusion of light for 1 h. Subsequently, 9.31 g (46 mmol) of BCDF was added within 10 min. After the solution was stirred at 40°C for 6 h, the solid content was filtered off, and the solvent was evaporated under vacuum. The crude product was distilled at 0.4 mbar and purified by chromatography over silica gel with toluene to yield 4.3 g (50%) of the pure BFDF (pale yellow liquid). δ_H (300 MHz, $CDCl_3$) 4.41 (2H, d, $^4J_{HF}$ 1.1, CH_2), 7.30–7.45 (5H, m, C_6H_5). δ_C (75 MHz, $CDCl_3$) 43.14 (1C, d, $^3J_{CF}$ 5.1, CH_2), 128.26 (1C, *para* C_6H_5), 128.85/129.12 (4C, *ortho*/*meta* C_6H_5), 133.32 (1C, – C_6H_5), 205.75 (1C, d, $^1J_{CF}$ 361.9, C=S). δ_F (282 MHz, $CDCl_3$) 71.56 (s). ν_{max} (ATR)/cm^{-1} 3087vw (CH valence), 3063w (CH valence), 3030m (CH valence), 2921vw (CH_2 valence), 1602vw (ar, C–C valence), 1495m (CH rocking), 1453m (CH rocking), 1419vw(br) (CH_2 bending), 1249w (br) (CH_2 wagging), 1202s (CH bending), 1160vs (C=S valence), 1070m (ar, def), 1013m (ar, def), 994vs (as, F–C–S valence), 916vw (CH twist), 857vw (CH_2 rocking), 814vw (ar, def.), 764m (CH wagging), 693s (CH wagging). λ_{max}/nm (CH_2Cl_2) 288 (log ε 4.12).

Polymerizations

Styrene (Aldrich, 99%) was purified by drying for one day over molecular sieves (4 Å) and subsequent distillation under vacuum. The thermally decaying initiator 2,2′-azoisobutyronitrile (AIBN, Aldrich, 99%) was purified twice by crystallization from ethanol. A solution of 10.00 g of styrene, 57.5 mg of BFDF, and 12.4 mg of AIBN was prepared and mixed thoroughly. The solution was subsequently subjected to four freeze–pump–thaw cycles to remove any residual oxygen. A small amount of solution was then transferred under nitrogen atmosphere into a 2-mm optical path length Infrasil cell (Starna Optical) which was subsequently sealed with a rubber septum. Monomer conversions were determined using on-line Fourier-transform near infrared (FT-NIR) spectroscopy by following the decrease of the intensity of the first vinylic stretching overtone of the monomer [ν_{max} (styrene)/cm^{-1} 6134]. The FT-NIR measurements were performed using a Bruker IFS66\S Fourier-transform spectrometer equipped with a tungsten halogen lamp, a CaF_2 beam splitter, and a liquid nitrogen-cooled InSb detector. Each spectrum in

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*It should be noted that xanthates and dithiocarbamates can be used to control monomers such as styrene, provided the alkoxy or amino Z-group is designed so as to minimize the resonance stabilization of the C=S bond. For example, xanthates in which the alkoxy group is substituted with strong electron withdrawing groups that reduce the lone pair donating ability of the oxygen (for example, see ref. [12*a*]) or dithiocarbamates in which the lone pair of the nitrogen in the dithiocarbamates is included as part of an aromatic system (for example, see ref. [12*b*]), can control styrene. However, when modified in this way, such agents do appear to be suitable for controlling vinyl acetate.

the spectroscopic region of 8000–4000 cm^{-1} was calculated from the co-added interferograms of 50 scans with a resolution of 2 cm^{-1}. For conversion determination, a linear baseline was selected between 6200 and 6100 cm^{-1}. The integrated absorbance between these two points was subsequently used to calculate the monomer-to-polymer conversion by Beer–Lambert's law. In regular intervals, a small sample was withdrawn from the reaction mixture with an airtight syringe that had been flushed three times with nitrogen gas. The sample was transferred into a flask containing tetrahydrofuran (THF) with hydroquinone as inhibitor and immediately subjected to size-exclusion chromatography (SEC) analysis.

Molecular Weight Analysis

Molecular weight distributions were measured by size-exclusion chromatography (SEC) on a Shimadzu modular system comprised of an auto injector, a Polymer Laboratories (PL) 5.0 μm bead-size guard column ($50 \times 7.5\ \mathrm{mm}^2$), followed by three PL columns (10^5, 10^4, and 10^3 Å) and a differential refractive index detector. The eluent was THF at 40°C with a flow rate of 1 $\mathrm{mL\ min}^{-1}$. The system was initially calibrated using narrow polystyrene standards ranging from 540 to $2 \times 10^6\ \mathrm{g\ mol}^{-1}$.

Results and Discussion

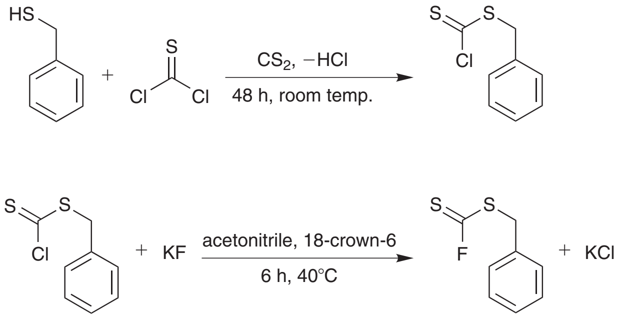
In contrast to the known dithioester or xanthate RAFT reagents, which are usually prepared by a nucleophilic attack of carbon disulfide by organometallic compounds or alcoholates, the synthetic approach to halogen bearing RAFT reagents requires a completely different strategy. Since recently published results suggest that (because of a homo-anomeric effect) a benzyl R-group would be a good leaving group for styrene polymerization,[14] we prepared BFDF in an analogous reaction to that described elsewhere,[15] using the commercially available benzyl mercaptan. In a first step, benzyl chloro dithioformate was prepared by treating thiophosgene with equivalent amounts of benzyl mercaptan. Subsequently, the remaining chlorine atom was replaced by fluorine in a Finkelstein analogous reaction. The reaction sequence is depicted in Scheme 4.

The overall yield of both synthetic steps is 25%. According to the ^{1}H NMR data, the BFDF is free of any residual BCDF and the purity is higher than 95%. The assignment of the IR absorption bands was done by means of density functional theory calculated vibrations at the B3-LYP 6-31G(d) level of theory.

To test the ability of the novel RAFT agent to induce living free radical polymerization, we polymerized styrene using $2.81 \times 10^{-2}\ \mathrm{mol\ L}^{-1}$ BFDF with AIBN ($[\mathrm{AIBN}]_0$ $6.86 \times 10^{-3}\ \mathrm{mol\ L}^{-1}$) as initiator. At 5, 10, 20, 30, and 40% conversion, samples were taken and the molecular weight distribution was determined.

Fig. 1 depicts the evolution of the full molecular weight distributions with monomer-to-polymer conversion in a BFDF-mediated RAFT polymerization of styrene at 80°C. The distributions are mono-modal and shift to higher molecular weights with increasing conversion. For a more detailed analysis, a molecular weight versus conversion plot is given in Fig. 2, with the corresponding $\overline{M}_\mathrm{n}$ values being collated in Table 1 alongside the associated polydispersities (*PDI*s).

Inspection of Figs 1 and 2 clearly demonstrates that the novel class of RAFT agent induces living/controlled behaviour. However, inspection of Fig. 2 also shows that an initial increase to high molecular weight material occurs. Such behaviour has been observed also with other RAFT agents and has been termed hybrid behaviour.[16] Hybrid behaviour is frequently observed when the addition rate



Scheme 4. Synthetic route to BFDF.

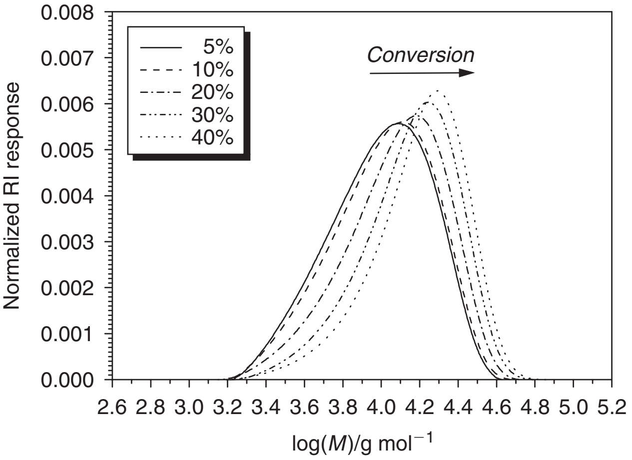


Fig. 1. Evolution of the full molecular weight distributions in BFDF-mediated styrene free-radical polymerizations at 80°C. The initial BFDF concentration was $2.81 \times 10^{-2}\ \mathrm{mol\ L}^{-1}$, with an AIBN concentration of $6.86 \times 10^{-3}\ \mathrm{mol\ L}^{-1}$.

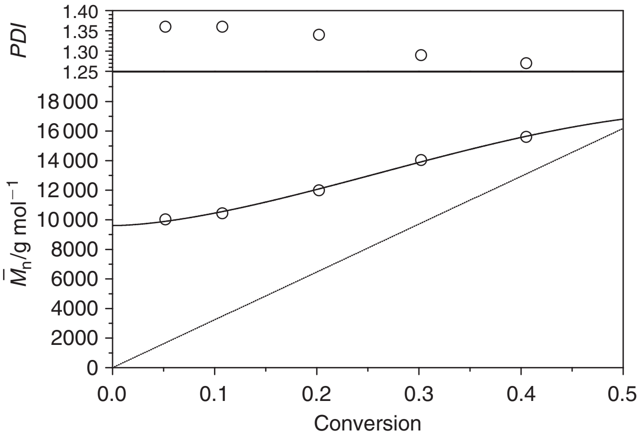


Fig. 2. Number-average molecular weight, $\overline{M}_\mathrm{n}$, versus monomer-to-polymer conversion in BFDF-mediated styrene free radical polymerizations at 80°C. The initial BFDF concentration was $2.81 \times 10^{-2}\ \mathrm{mol\ L}^{-1}$, with an AIBN concentration of $6.86 \times 10^{-3}\ \mathrm{mol\ L}^{-1}$. The full line represents the best fit for the molecular weight versus time evolution, the dotted line depicts the theoretically expected values. The upper part of the figure gives the corresponding polydispersity indices, *PDI*s.

coefficient to the initial RAFT agent is too low in comparison with the propagation rate coefficient or the propagating radical, polystyrene, leaves the adduct radical in preference to the R-group, i.e., Bz. Assuming that the rate of the reverse reaction between the leaving group $R^\bullet$ and the polymeric RAFT agent is negligible, the chain transfer constant, $C_{tr} = k_{tr}/k_p$, can be estimated by the degree of polymerization of the polymer formed instantaneously, DP_n^{inst}, using Eqn 1.

$$C_{tr} = \frac{[M_0]}{(DP_n^{inst} - 1) \cdot [RAFT_0]} \qquad (1)$$

Extrapolation of the determined molecular weights to zero conversion yields a DP_n^{inst} value of 92. Hence, via Eqn 1, a value of 3.4 for C_{tr} is returned, indicating a relatively slow transfer.

To determine whether the slow transfer is caused by a slow monomer addition or a poor leaving group, further molecular orbital studies have been undertaken. The equilibrium constant at 80°C was calculated for the model addition–fragmentation reaction (2), for R = 1-PhEt and R = Bz.[†]

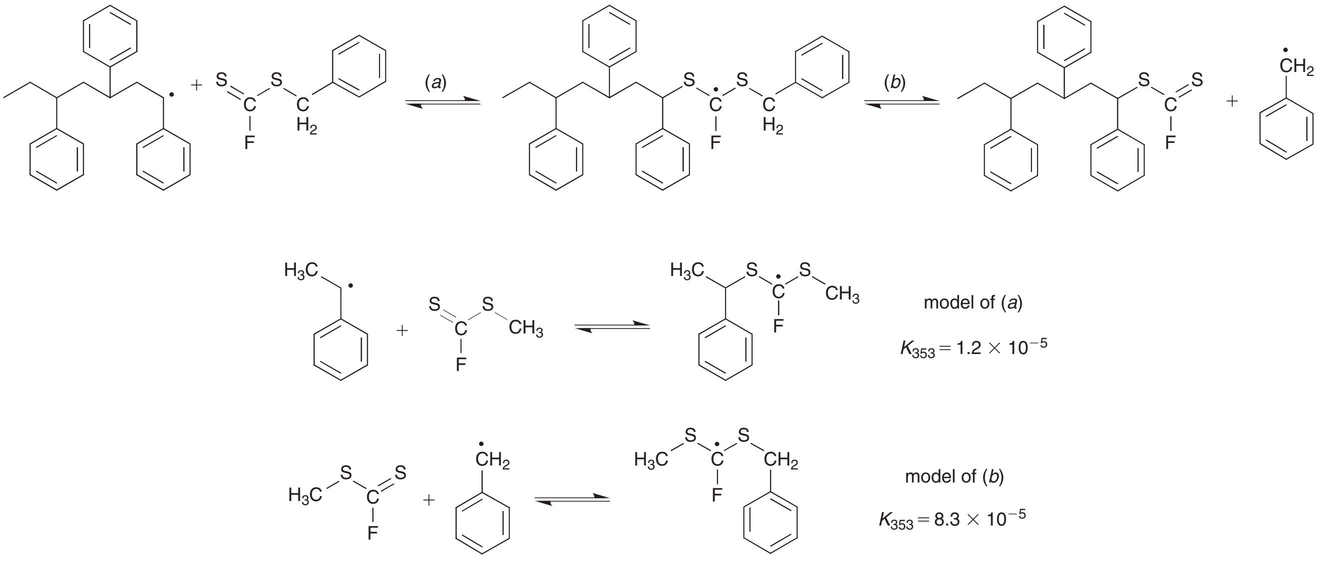
$$^\bullet R + S{=}C(F)SCH_3 \rightarrow R{-}SC^\bullet(F)S{-}CH_3 \qquad (2)$$

Table 1. Monomer-to-polymer conversions, number-average molecular weight, $\overline{M}_n$, and polydispersity, *PDI*, in BFDF-mediated styrene free-radical polymerization at various polymerization times

The initial BFDF concentration was 2.81×10^{-2} mol L^{-1}, with the AIBN concentration being 6.86×10^{-3} mol L^{-1}

Time [min]	Conversion [%]	$\overline{M}_n$ [g mol^{-1}]	$\overline{M}_n^{theo}$ [g mol^{-1}]	*PDI*
24	5.17	10 000	1673	1.36
50	10.75	10 400	3478	1.36
107	20.21	12 000	6539	1.34
195	30.22	14 000	9778	1.29
362	40.51	15 600	13 108	1.27

These two systems were selected to model the two steps, (*a*) and (*b*), of the chain-transfer reaction that occurs during the initial equilibration period in the RAFT process (see Scheme 5). Although only the thermodynamics have been considered in the present case, it has been shown elsewhere that these radical additions to C=S bonds are virtually barrierless, and the trends in the kinetics follow those in the thermodynamics.[17] The calculated equilibrium constants (L mol^{-1}) for each of the reactions are displayed in Scheme 5, from which it is seen that, on a thermodynamic basis, the 1-PhEt group has a sevenfold preference for fragmentation over the Bz group, consistent with the observed hybrid behaviour. This trend differs from that reported recently[14] for the R = Bz and 1-PhEt substituents in $CH_3SC^\bullet(CH_3)SR$ and $CH_3SC^\bullet(Ph)SR$ RAFT–adduct radicals. In this previous work it was shown that the Bz R-group is a better leaving group than 1-PhEt, despite the latter radical being both more bulky and more stable. This counter-intuitive trend in the $CH_3SC^\bullet(CH_3)SR$ and $CH_3SC^\bullet(Ph)SR$ radicals was previously attributed to an interesting homo-anomeric effect; the current results suggest that the fluorine Z-group is sufficient to diminish the effect and thereby reverse the order of leaving group ability. This ability to enhance or diminish the homo-anomeric effect, and hence manipulate the leaving group ability without changing the R-group itself, may prove useful in other RAFT-agent design problems, such as reversing the block order in block copolymers. Of course, whether this will work in practice will depend on whether the original



Scheme 5. Model addition–fragmentation reactions (for details see text).

[†] Equilibrium constants (353 K, L mol^{-1}) were calculated at the G3(MP2)-RAD//B3-LYP/6-31G(d) level of theory using the standard textbook formulae, based on the statistical thermodynamics of an ideal gas under the rigid-rotor/harmonic oscillator approximation. Full details of the calculations, together with complete geometries in the form of GAUSSIAN archive entries, are provided in the Accessory Material.

block order was strongly influenced by the homo-anomeric effect (as in the ordering of 2-cyanopropyl compared with cumyl). This would not be expected to be the case when the radical stabilities are very dissimilar (as in styrene–vinyl acetate block copolymers). However, there may be some applications where this manipulation of the homo-anomeric effect may be exploited; further investigations of this possibility are now underway.

Recently, we have shown how hybrid behaviour can indeed be used (in cases where the initial RAFT agent R-group is identical in electronic structure to the propagating radical) to estimate the magnitude of the addition rate coefficient.[18] It would be thus instructive to synthesize an F-RAFT agent with a 1-PhEt R-group, which is analogous to a propagating polymer chain with chain length one, and exploit the presence and, if applicable, the magnitude of the hybrid behaviour under this condition.

We further compared the leaving group ability of several R-groups with that of the 1-PhEt group. Based on these calculations we found that a better R-group for this system would be 2-cyanopropyl, since the equilibrium constant of reaction (1) at 80°C ($8.4 \times 10^{-6}\,\mathrm{L\,mol^{-1}}$) is lower than those for Bz and even 1-PhEt. This group is also known to be a good re-initiator in styrene polymerization, and it could be predicted that the F-RAFT agent $S{=}C(F)SC(CH_3)_2CN$ would induce less or even no hybrid behaviour in styrene polymerizations. Synthetic procedures towards a range of R-groups are currently being developed in our laboratories.

Conclusions

In the present work we present a viable synthetic pathway to a new class of RAFT agent, F-RAFT agents, and exemplify it in the case of benzyl fluoro dithioformate (BFDF). F-RAFT agents had previously been theoretically predicted to be suitable for the control of monomers with disparate reactivities; which could in turn provide a means of preparing block copolymers from such monomers. In the present work, we demonstrate that such agents are capable of controlling stable monomers, such as styrene. Experiments to test its behaviour in the polymerization of vinyl acetate and further optimize the R-group are currently underway in our laboratories.

Accessory Materials

Full details of the calculations, together with complete geometries in the form of *GAUSSIAN* archive entries, are available from the author or, until June 2010, the *Australian Journal of Chemistry*.

Acknowledgments

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