An ESR Approach to the Estimation of the Rate Constants of the Addition and Fragmentation Processes Involved in the RAFT Polymerization of Styrene

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Dedicated to the memory of Emeritus Professor Dr. *Hanns Fischer*

The reversible-addition-fragmentation chain transfer (RAFT) controlled radical polymerization of such vinylic monomers as styrene (=ethenylbenzene) has gained increasing popularity in current years. While there is a general agreement on the mechanism of RAFT polymerization, there is an ongoing debate about the values of the rate constants of its key steps, *i.e.*, the addition of the propagating radicals to the mediator and the fragmentation of the resulting spin adducts. By carrying out an ESR spectroscopic investigation of the AIBN-initiated polymerization of styrene (AIBN = 2,2′-azobis[2-methylpropanenitrile]), mediated by benzyl (diethoxyphosphoryl)dithioformate (**5**) as RAFT agent, we were able to detect and characterize four different radical species involved in the process. By reproducing their concentration–time profiles through a kinetic model, the addition and fragmentation rate constants at 90° of the propagating radicals to and from the mediator were estimated to be *ca.* 10^7 $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ and *ca.* 10^3 s^{-1}, respectively. The validity of the kinetic model was supported by hybrid meta DFT calculations with the BB1K functional that predicted addition- and fragmentation-rate-constant values in good agreement with those estimated from the ESR experiments.

Introduction. – The industrial relevance of radical polymerizations resides in the large number of available monomers capable of undergoing chain reactions, and in the possibility of carrying them out under relatively mild conditions, either in solution or in the bulk phase. In addition, radical mechanisms are well understood and extension of the concepts to new monomers is generally straightforward. On the other hand, due to the impossibility to control chain transfer and termination, classical radical processes cannot normally be applied when well defined polymers are desired. To overcome this impasse, several techniques have been devised to control radical polymerizations, all of which are aimed at keeping the radical concentration as low as possible at any time to disfavor wild termination processes. Among these, the RAFT (reversible-addition-

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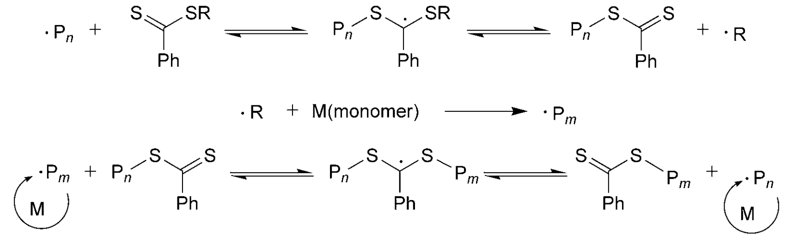
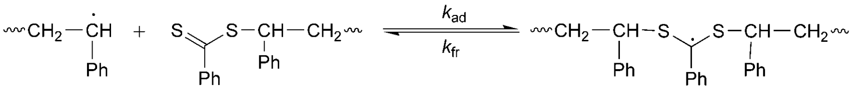
fragmentation chain transfer) method has rapidly attracted the attention of many a research group [1–12], and is likely to become the technique of choice for the production of well-defined custom-tailored polymers. According to the RAFT methodology, a normal radical polymerization is carried out in the presence of an additive that, as outlined in *Scheme 1*, acts as an efficient reversible-addition-fragmentation chain-transfer agent (CTA). CTAs are typically dithioesters ZC(S)SR, where R must be a good radical leaving group, which as an expelled radical $R^\bullet$ should be effective in re-initiating polymerization, and Z should be a group exerting a stabilizing action on an adjacent radical center. Cumyl and '2-cyanoprop-2-yl' dithiobenzoates (=1-methyl-1-phenylethyl and 1-cyano-1-methylethyl benzenecarbodithioates) do fulfil these conditions and are widely used as CTAs.

Scheme 1. *Simplified Mechanism of a Dithiobenzoate-Mediated RAFT Polymerization.* ${}^\bullet P_n$ and ${}^\bullet P_m$ are propagating radicals of different length, M is the monomer, PhC(S)SR is the initial CTA, while PhC(S)SP$_n$ and PhC(S)SP$_m$ are macro-CTAs.



In a few cases, ESR spectroscopy has been used to detect and characterize the radical species involved in the polymerization processes. Thus, a spectrum attributed to the intermediate radical **1** (see *Scheme 2*) was observed during the polymerization of styrene (=ethenylbenzene) in the presence of cumyl dithiobenzoate, *Cu*SC(S)Ph [3][11], polystyryl dithiobenzoate, *St*SC(S)Ph [9], or benzyl dithiobenzoate, *Bn*SC(S)Ph [13][4]).

Scheme 2. *Key Step of the RAFT Polymerization of Styrene Controlled by a Dithiobenzoate*



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The rate constants for the addition of the propagating radicals (k_{ad}) to the CTA and the macro-CTAs and for the fragmentation of the resulting spin adducts (k_{fr}) are critical for an efficient control of the polymerization, and it has been stated [1][2] that they should be fast relative to the rate of propagation. Attempts have also been made to gain kinetic information from ESR experiments by monitoring the time evolution of

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[4]) In the following, *Cu* indicates a cumyl (=1-methyl-1-phenylethyl) radical, *Bn* a benzyl radical, *Pr* a 1-cyano-1-methylethyl (='2-cyanoprop-2-yl') radical, and *St* a polystyryl radical of whatever length.

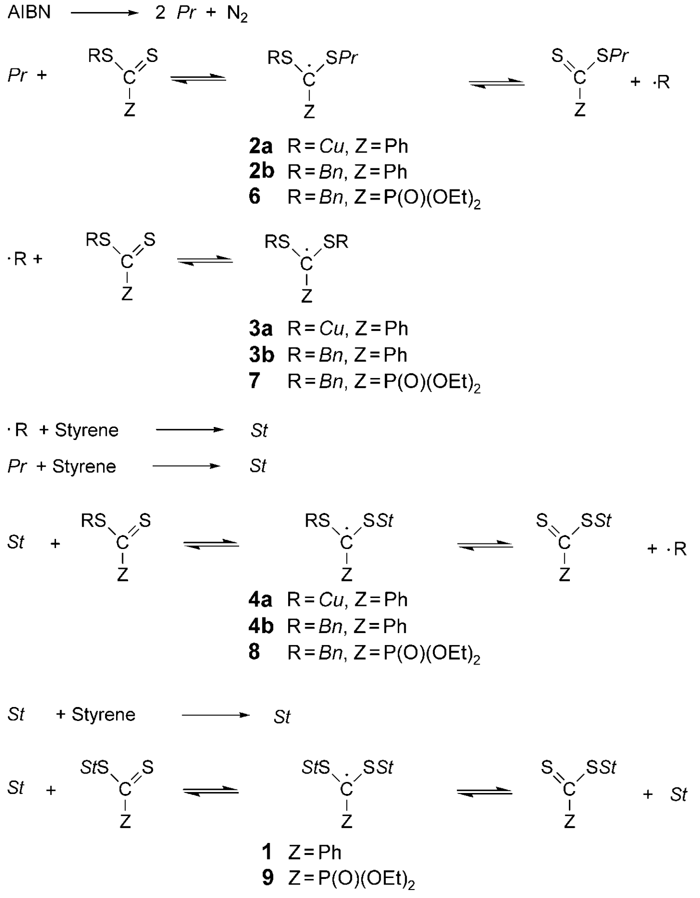
the radical concentration *via* double integration of the signal [9][11]; in this way, the rate of addition of the growing styryl radical *St* to the dithiobenzoate C=S bond to give **1** has been estimated as $k_{ad} \approx 4 \cdot 10^6$ $\text{M}^{-1}\text{s}^{-1}$ and that of fragmentation of the S–*St* bond in **1** as $k_{fr} \approx 7 \cdot 10^4$ s^{-1} at 60° [9]. Similar k_{fr} values, *i.e.*, $k_{fr} = 10^4 - 10^5$ s^{-1}, have been reported for the system styrene/*Cu*SC(S)Ph [14][15]. However, conflicting data have also been published, and there is an ongoing debate about these rate-constant values. Actually, while the somewhat smaller value for the addition rate constant of *St* ($k_{ad} = 5.6 \cdot 10^5$ $\text{M}^{-1}\text{s}^{-1}$) reported earlier [8] may reflect the use of a different RAFT agent (cumyl phenyldithioacetate, *Cu*SC(S)CH_2Ph), it is hard to explain the large discrepancy concerning the fragmentation rate constants, values as low as $k_{fr} \approx 10^{-2}$ s^{-1} having been reported for the systems styrene/*Cu*SC(S)CH_2Ph [8] and styrene/*Cu*SC(S)Ph [16]. Slow fragmentation rates have also been predicted in *ab initio* computational studies [10][17].

Returning to the use of ESR spectroscopy in investigating RAFT polymerization, a major problem is that the actual process (see *Scheme 3*) is rather more complex than as represented in *Scheme 1* (AIBN = 2,2′-azobis[2-methylpropanenitrile]). Besides, the most popular RAFT agents are *tert*-alkyl dithiobenzoates, and *tert*-alkyl groups do not normally affect the ESR spectral pattern. Actually, in the typical case of the styrene/*Cu*SC(S)Ph/AIBN system, radicals **2a**, **3a**, and **4a** must be present along with species **1**, with concentrations that vary as the polymerization proceeds.

Radicals **2a** and **3a** are bis(*tert*-alkylthio)-substituted benzyl radicals, and their ESR spectral pattern will only reflect the coupling of the unpaired electron with the H-atoms of the aromatic ring bound to the radical C-atom. Although **4a** and **1** also are disubstituted benzyl radicals, they should exhibit an additional *d* or *t* splitting due to the coupling of the unpaired electron with one or two styryl H–C(γ) atoms, respectively. Because these splittings are too small to be resolved, radicals **1**, **2a**, **3a**, and **4a** will exhibit nearly identical ESR spectra that, overlapping each other, may falsely appear as if due to a single species. As a result, the double integration of the observed signal will represent the '*overall*' radical concentration with no possibility of partitioning the value among the different species concurring to its formation. Replacing the *tert*-alkyl dithiobenzoate with benzyl dithiobenzoate *Bn*SC(S)Ph would not be any better because, although the number of the methylene H-atoms as well as their couplings would differ in radicals **2b**, **3b**, and **4b**, the overlapping of the different signals would nonetheless result in spectra impossible to deconvolute into their individual components. Again, double integration will provide the '*overall*' radical concentration.

The situation may be drastically different if RAFT agents other than dithiobenzoates are used. In previous studies [7][12], we have shown that benzyl (diethoxyphosphoryl)dithioformate (= phenylmethyl diethoxyphosphinecarbodithioate 1-oxide; **5**; *Bn*SC(S)P(O)$(OEt)_2$) is a CTA especially suitable for ESR investigations that can control the polymerization of styrene leading to a polymer with an acceptable polydispersity index *PDI*. Indeed, the system styrene/**5**/AIBN in the molar ratio 50 : 1 : 0.5 afforded, after 20 h at 90°, a polymer with M_n 6200 and a *PDI* = 1.40 with a conversion of *ca.* 20%. We also found that the ESR-spectral pattern of the system changed drastically during the first hour, and the reproduction of the spectra at different times by assuming the simultaneous presence of variable amounts of the four radicals **6**–**9**

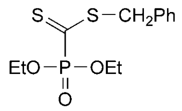
Scheme 3. *Detailed Outline of the Mechanism of the AIBN-Initiated Radical Polymerization of Styrene Controlled by a Dithioester* (termination reactions are not included)[4])



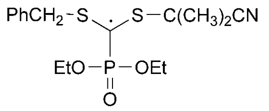
Cu$=Me_2C(Ph)$, *Pr*$=Me_2C(CN)$, *Bn*$=PhCH_2$, *St*=polystyryl

(see *Scheme 3*) allowed the determination of the time profiles of their concentration [12].

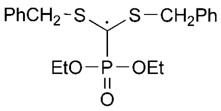
We report here on an estimation of the rate constants of the addition and fragmentation reactions involved in the RAFT polymerization of styrene controlled by benzyl (diethoxyphosphoryl)dithioformate (**5**) obtained by modelling the concentration–time profiles of radicals **6**–**9**, and on DFT calculations of the rate constants for the addition of styryl radicals to styryl (diethoxyphosphoryl)dithioformate (*St*$SC(S)P(O)(OEt)_2$) and to styryl dithiobenzoate (*St*SC(S)Ph) and for the fragmentation of the resulting spin adducts.



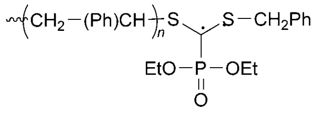
5 (*Bn*SC(S)P(O)(OEt)$_2$)



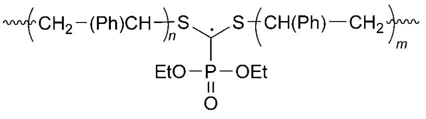
6 (*Bn*S$\dot{\mathrm{C}}$(S*Pr*)P(O)(OEt)$_2$)



7 (*Bn*S$\dot{\mathrm{C}}$(S*Bn*)P(O)(OEt)$_2$)



8 (*St*S$\dot{\mathrm{C}}$(S*Bn*)P(O)(OEt)$_2$)



9 (*St*S$\dot{\mathrm{C}}$(S*St*)P(O)(OEt)$_2$)

Results and Discussion. – *Fig. 1* shows the spectra observed when the AIBN-initiated polymerization of styrene controlled by the RAFT agent **5** (molar ratio styrene/**5**/AIBN 50 : 1 : 0.5)5)) was carried out at 90° inside the cavity of an ESR spectrometer.

The spectral parameters of the species contributing to the ESR signals had previously been determined [12] by generating the authentic radicals in benzene solution under steady-state conditions, *i.e.*, **6** (*Pr*S$\dot{\mathrm{C}}$(S*Bn*)P(O)(OEt)$_2$; $a_P = 2.226$ mT, $a_{2H} = 0.250$ mT, $g = 2.0057_1$) was obtained by photolyzing **5** and AIBN, **7** (*Bn*S$\dot{\mathrm{C}}$(S*Bn*)P(O)(OEt)$_2$; $a_P = 2.235$ mT, $a_{4H} = 0.168$ mT, $g = 2.0057_3$) by heating **5** in the presence of dibenzylmercury, **8** (*St*S$\dot{\mathrm{C}}$(S*Bn*)P(O)(OEt)$_2$; $a_P = 2.197$ mT, $a_{2H} = 0.229$ mT, $g = 2.0057_4$) by photolysis of **5** in the presence of polystyryl bromide ($PhCH_2St_{11}Br$, *PDI* = 1.096) and hexabutyldistannane, while **9** (*St*S$\dot{\mathrm{C}}$(S*St*)P(O)(OEt)$_2$; $a_P = 2.172$ mT, $g = 2.0058_5$) was obtained in a similar fashion by replacing **5** with a polystyryl (diethoxyphosphoryl)dithioformate ($(EtO)_2(O)PC(S)SSt_{40}C(Me)_2CN$, *PDI* = 1.09). Double integration of the ESR spectra yielded the overall radical concentration after comparison with a standard solution of DPPH and correction for the spectrometer sensitivity in the two cases, whereas the variation in time of the concentration of **6**–**9** was derived from simulation of the spectra (see *Fig. 2,a*) (DPPH = '2,2-di(4-*tert*-octylphenyl)-1-picrylhydrazyl' = 2,2-bis[4-(1,1,3,3-tetramethylbutyl)phenyl]-1-(2,4,6-trinitrophenyl)hydrazyl). In a parallel experiment carried out inside the probe of an NMR spectrometer at 90°, the time profile of the concentration of *Bn*SC(S)P(O)(OEt)$_2$ (**5**) could be determined by monitoring the intensity of the signal from the methylene H-atoms of the benzyl group (see *Fig. 2,b*).

The AIBN-initiated polymerization of styrene controlled by **5** as outlined in *Scheme 3* can be schematized by the set of reactions shown in *Scheme 4*4)), where *M* stands for a styrene monomer. The scheme includes all possible addition and fragmentation pathways although, as usual [9], the hypothetical termination reactions involving the coupling of two *X*S$\dot{\mathrm{C}}$(S*Y*)P(O)(OEt)$_2$ (*X*, *Y* = *Pr*, *Bn*, *St*) radicals are not considered.

The rate constants for some of these reactions are available in the literature. In particular $k_1/\mathrm{s}^{-1} = 1.6 \cdot 10^{15} \cdot \mathrm{e}(-128900/RT)$ [18], $k_2/\mathrm{M}^{-2}\mathrm{s}^{-1} = 2.19 \cdot 10^5 \cdot \mathrm{e}(-114830/RT)$ [19], $k_3/\mathrm{M}^{-1}\mathrm{s}^{-1} = 3.2 \cdot 10^7 \cdot \mathrm{e}(-24300/RT)$ [20], $k_4/\mathrm{M}^{-1}\mathrm{s}^{-1} = 3.2 \cdot 10^8 \cdot \mathrm{e}(-30800/RT)$ [20],

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5) In normal styrene RAFT polymerizations, a ratio styrene/CTA/AIBN of *ca.* 900 : 1 : 0.5 is used. A smaller styrene/**5** ratio was used here to obtain stronger ESR signals.

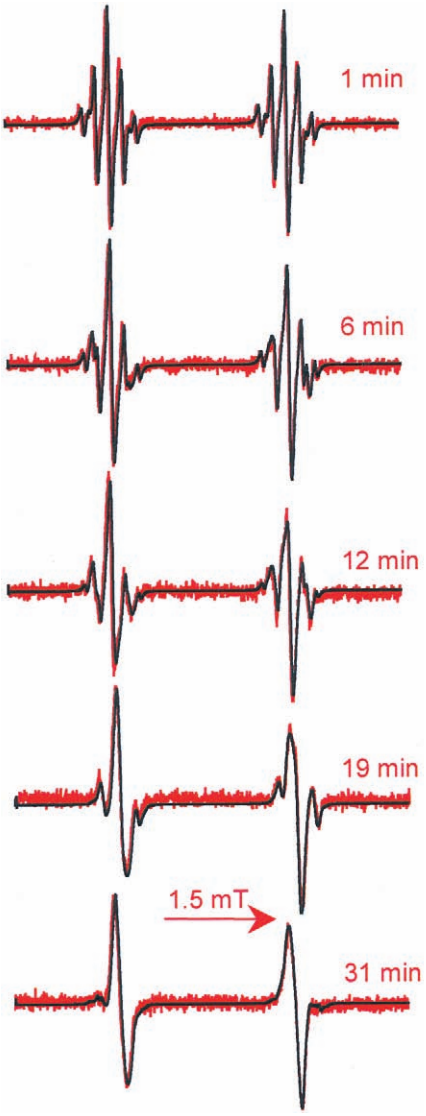


Fig. 1. *Experimental* (red traces) *ESR spectra observed at different times during the AIBN-initiated polymerization of styrene in the presence of* **5** (styrene/**5**/AIBN 50 : 1 : 0.5) at 90°. Computer simulations obtained by assuming the simultaneous presence of radicals **6**–**9** in different proportions are also shown (black traces).

$k_5/\mathrm{M}^{-1}\,\mathrm{s}^{-1} = 4.7 \cdot 10^7 \cdot \mathrm{e}(-32500/RT)$ [21], the last value being assumed to be independent of the polystyryl chain length. The termination rate constants k_{24}, k_{25}, and k_{26} should be diffusion-controlled at $T > 20°$ with values of 10^9 to $10^{10}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$, k_{29} should be smaller than k_{24-26} (and depend on the chain length), whereas k_{27} and k_{28} are normally well approximated by $\sqrt{(k_{24-26} \cdot k_{29})}$. As for the values of k_{30-41}, they should be similar to or slightly smaller than k_{24-26} [9][21], while k_{42-47} should be probably similar to or slightly smaller than k_{29}.

To try and reproduce the concentration–time profiles derived from the ESR measurements, the kinetic equations derived from *Scheme 4* were numerically integrated by

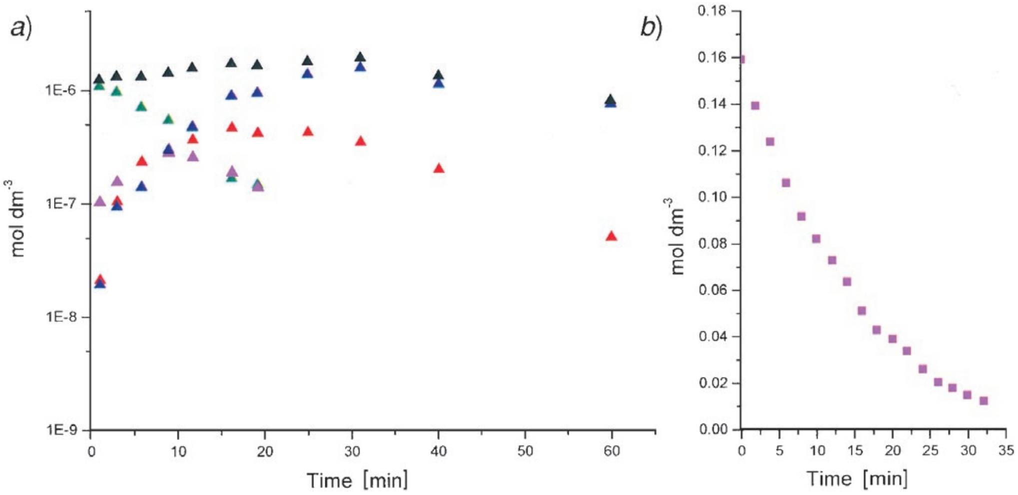


Fig. 2. *Concentration–time profiles of some of the species involved in the AIBN-initiated polymerization of styrene controlled by* **5** *at 90°.* a) *Pr*S$\dot{C}$(S*Bn*)P(O)(OEt)$_2$ (**6**; ▲), *Bn*S$\dot{C}$(S*Bn*)P(O)(OEt)$_2$ (**7**; ▲), *St*S$\dot{C}$(S*Bn*)P(O)(OEt)$_2$ (**8**; ▲), *St*S$\dot{C}$(S*St*)P(O)(OEt)$_2$ (**9**; ▲), and total radical concentration (▲); b) *Bn*SC(S)P(O)(OEt)$_2$ (**5**; ■).

using Mathlab 6.1 (*The Math Works Inc.*). The start parameters were $f=1$, $k_{24–26}=k_{30–41}=5\cdot10^9$ M^{-1}s^{-1}, $k_{29}=k_{42–47}=1\cdot10^9$ M^{-1}s^{-1}, $k_{6–14}=1\cdot10^7$ M^{-1}s^{-1}, and $k_{15–23}=5\cdot10^4$ s^{-1}. While the values of $k_{1–5}$ were kept constant as given above, the other initial values were varied by repetitive trial and error until a reasonable agreement between the calculated and experimental time profiles was obtained. The relevance of the resulting parameters was thereafter tested by additional variations and judged from the resulting deviations. The results are shown in *Fig. 3*, where both the experimental and calculated concentration-time profiles are plotted together, while the values of the rate constants for the addition and fragmentation reactions leading to the best fitting are collected in *Table 1*.

Table 1. *Rate Constants Estimated for Some Addition and Fragmentation Reactions* (see *Scheme 4*) *when Allowing the Presence of* Pr*SC(S)P(O)(OEt)$_2$*

Addition reactions		Fragmentation reactions	
	k/M^{-1}s^{-1}		k/s^{-1}
k_6	$5.0\cdot10^7$	k_{15}	$3.0\cdot10^3$
k_7	$2.0\cdot10^8$	k_{16}	$3.0\cdot10^3$
k_8	$2.0\cdot10^7$	k_{17}	$1.0\cdot10^4$
k_9	$2.0\cdot10^7$	k_{18}	$2.0\cdot10^3$
k_{10}	$1.0\cdot10^8$	k_{19}	$2.0\cdot10^4$
k_{11}	$1.5\cdot10^7$	k_{20}	$2.0\cdot10^3$
k_{12}	$6.0\cdot10^6$	k_{21}	$3.0\cdot10^3$
k_{13}	$1.0\cdot10^7$	k_{22}	$5.0\cdot10^3$
k_{14}	$6.0\cdot10^6$	k_{23}	$1.0\cdot10^4$

Scheme 4. *Reactions Involved in the AIBN-Initiated Polymerization of Styrene Mediated by* **5** *as RAFT Agent*[4]). Termination reactions involving two $X\mathrm{S\dot{C}(S}Y\mathrm{)P(O)(OEt)}_2$ (X, $Y=Pr$, Bn, St[4])) radicals are not considered. $M=$Monomer.

$\mathrm{AIBN} \rightarrow 2\,Pr$ (1)

$3\,M \rightarrow 2\,St$ (2)

$Pr + M \rightarrow St$ (3)

$Bn + M \rightarrow St$ (4)

$St + M \rightarrow St$ (5)

$Pr + Bn\mathrm{SC(S)P(O)(OEt)}_2 \rightarrow Pr\mathrm{S\dot{C}(S}Bn\mathrm{)P(O)(OEt)}_2$ (6)

$Pr + Pr\mathrm{SC(S)P(O)(OEt)}_2 \rightarrow Pr\mathrm{S\dot{C}(S}Pr\mathrm{)P(O)(OEt)}_2$ (7)

$Pr + St\mathrm{SC(S)P(O)(OEt)}_2 \rightarrow Pr\mathrm{S\dot{C}(S}St\mathrm{)P(O)(OEt)}_2$ (8)

$Bn + Bn\mathrm{SC(S)P(O)(OEt)}_2 \rightarrow Bn\mathrm{S\dot{C}(S}Bn\mathrm{)P(O)(OEt)}_2$ (9)

$Bn + Pr\mathrm{SC(S)P(O)(OEt)}_2 \rightarrow Bn\mathrm{S\dot{C}(S}Pr\mathrm{)P(O)(OEt)}_2$ (10)

$Bn + St\mathrm{SC(S)P(O)(OEt)}_2 \rightarrow Bn\mathrm{S\dot{C}(S}St\mathrm{)P(O)(OEt)}_2$ (11)

$St + Bn\mathrm{SC(S)P(O)(OEt)}_2 \rightarrow St\mathrm{S\dot{C}(S}Bn\mathrm{)P(O)(OEt)}_2$ (12)

$St + Pr\mathrm{SC(S)P(O)(OEt)}_2 \rightarrow St\mathrm{S\dot{C}(S}Pr\mathrm{)P(O)(OEt)}_2$ (13)

$St + St\mathrm{SC(S)P(O)(OEt)}_2 \rightarrow St\mathrm{S\dot{C}(S}St\mathrm{)P(O)(OEt)}_2$ (14)

$Pr\mathrm{S\dot{C}(S}Bn\mathrm{)P(O)(OEt)}_2 \rightarrow Pr + Bn\mathrm{SC(S)P(O)(OEt)}_2$ (15)

$Pr\mathrm{S\dot{C}(S}Bn\mathrm{)P(O)(OEt)}_2 \rightarrow Bn + Pr\mathrm{SC(S)P(O)(OEt)}_2$ (16)

$Pr\mathrm{S\dot{C}(S}Pr\mathrm{)P(O)(OEt)}_2 \rightarrow Pr + Pr\mathrm{SC(S)P(O)(OEt)}_2$ (17)

$Pr\mathrm{S\dot{C}(S}St\mathrm{)P(O)(OEt)}_2 \rightarrow Pr + St\mathrm{SC(S)P(O)(OEt)}_2$ (18)

$Pr\mathrm{S\dot{C}(S}St\mathrm{)P(O)(OEt)}_2 \rightarrow St + Pr\mathrm{SC(S)P(O)(OEt)}_2$ (19)

$Bn\mathrm{S\dot{C}(S}Bn\mathrm{)P(O)(OEt)}_2 \rightarrow Bn + Bn\mathrm{SC(S)P(O)(OEt)}_2$ (20)

$Bn\mathrm{S\dot{C}(S}St\mathrm{)P(O)(OEt)}_2 \rightarrow Bn + St\mathrm{SC(S)P(O)(OEt)}_2$ (21)

$Bn\mathrm{S\dot{C}(S}St\mathrm{)P(O)(OEt)}_2 \rightarrow St + Bn\mathrm{SC(S)P(O)(OEt)}_2$ (22)

$St\mathrm{S\dot{C}(S}St\mathrm{)P(O)(OEt)}_2 \rightarrow St + St\mathrm{SC(S)P(O)(OEt)}_2$ (23)

$Pr + Pr \rightarrow \mathrm{Products}$ (24)

$Pr + Pr \rightarrow \mathrm{Products}$ (25)

$Bn + Bn \rightarrow \mathrm{Products}$ (26)

$Pr + St \rightarrow \mathrm{Products}$ (27)

$Bn + St \rightarrow \mathrm{Products}$ (28)

$St + St \rightarrow \mathrm{Products}$ (29)

$Pr + Pr\mathrm{S\dot{C}(S}Pr\mathrm{)P(O)(OEt)}_2 \rightarrow \mathrm{Products}$ (30)

$Pr + Pr\mathrm{S\dot{C}(S}Bn\mathrm{)P(O)(OEt)}_2 \rightarrow \mathrm{Products}$ (31)

$Pr + Pr\mathrm{S\dot{C}(S}St\mathrm{)P(O)(OEt)}_2 \rightarrow \mathrm{Products}$ (32)

$Pr + Bn\mathrm{S\dot{C}(S}Bn\mathrm{)P(O)(OEt)}_2 \rightarrow \mathrm{Products}$ (33)

$Pr + Bn\mathrm{S\dot{C}(S}St\mathrm{)P(O)(OEt)}_2 \rightarrow \mathrm{Products}$ (34)

$Pr + St\mathrm{S\dot{C}(S}St\mathrm{)P(O)(OEt)}_2 \rightarrow \mathrm{Products}$ (35)

$Bn + Pr\mathrm{S\dot{C}(S}Pr\mathrm{)P(O)(OEt)}_2 \rightarrow \mathrm{Products}$ (36)

$Bn + Pr\mathrm{S\dot{C}(S}Bn\mathrm{)P(O)(OEt)}_2 \rightarrow \mathrm{Products}$ (37)

$Bn + Pr\mathrm{S\dot{C}(S}St\mathrm{)P(O)(OEt)}_2 \rightarrow \mathrm{Products}$ (38)

$Bn + Bn\mathrm{S\dot{C}(S}Bn\mathrm{)P(O)(OEt)}_2 \rightarrow \mathrm{Products}$ (39)

$Bn + Bn\mathrm{S\dot{C}(S}St\mathrm{)P(O)(OEt)}_2 \rightarrow \mathrm{Products}$ (40)

$Bn + St\mathrm{S\dot{C}(S}St\mathrm{)P(O)(OEt)}_2 \rightarrow \mathrm{Products}$ (41)

$St + Pr\mathrm{S\dot{C}(S}Pr\mathrm{)P(O)(OEt)}_2 \rightarrow \mathrm{Products}$ (42)

$St + Pr\mathrm{S\dot{C}(S}Bn\mathrm{)P(O)(OEt)}_2 \rightarrow \mathrm{Products}$ (43)

$St + Pr\mathrm{S\dot{C}(S}St\mathrm{)P(O)(OEt)}_2 \rightarrow \mathrm{Products}$ (44)

$St + Bn\mathrm{S\dot{C}(S}Bn\mathrm{)P(O)(OEt)}_2 \rightarrow \mathrm{Products}$ (45)

$St + Bn\mathrm{S\dot{C}(S}St\mathrm{)P(O)(OEt)}_2 \rightarrow \mathrm{Products}$ (46)

$St + St\mathrm{S\dot{C}(S}St\mathrm{)P(O)(OEt)}_2 \rightarrow \mathrm{Products}$ (47)

The computed value of conversion (*ca.* 10%) was lower than the experimental one [12]. Conversely, the optimized model reproduced very well the consumption of $Bn\mathrm{SC(S)P(O)(OEt)}_2$ (**5**; *Fig. 3,b*) and indicated a loss of dithioester that might be possibly due to cross-termination between the radicals *Pr*, *Bn*, *St*, and the radicals $X\mathrm{S\dot{C}(S}Y\mathrm{)P(O)(OEt)}_2$ (X, $Y=Pr$, Bn, St) under the ESR experimental conditions (low styrene/**5** ratio). The reproduction of the concentration–time profiles of radicals **6**–**9**, although not as good, is nevertheless gratifying also in view of the complexity of the system. Actually, the more noticeable discrepancy between experimental and calculated curves is to be found in the time profile of the total radical concentration, although it is possible that this derives to some extent from intrinsic limitations of the ESR experiments. In particular, the homogeneous warming up of the ESR tube may take several minutes, so that experimental radical concentrations may be on the low side at early times. The calculated values lower than the experimental ones for the concentration of $St\mathrm{S\dot{C}(S}St\mathrm{)P(O)(OEt)}_2$ (**9**), on the other hand, are probably due

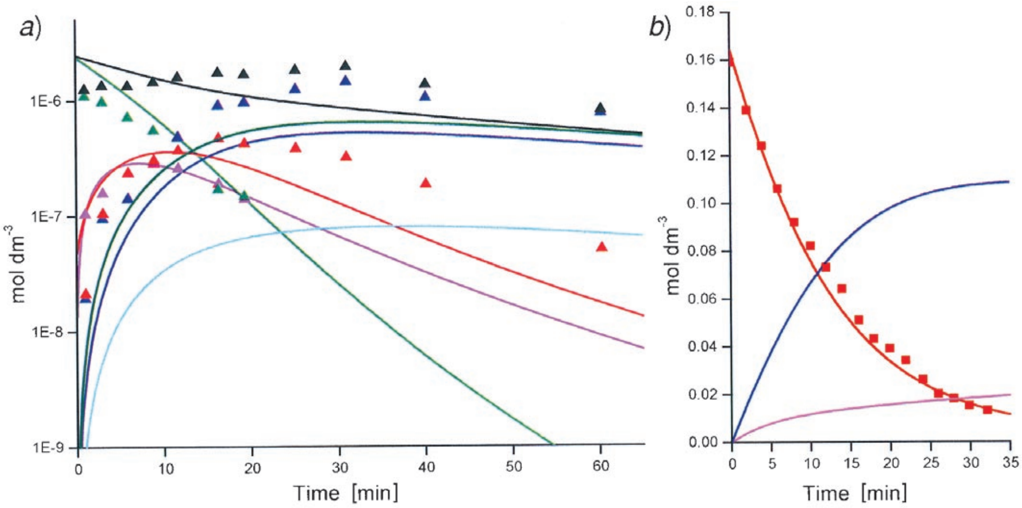


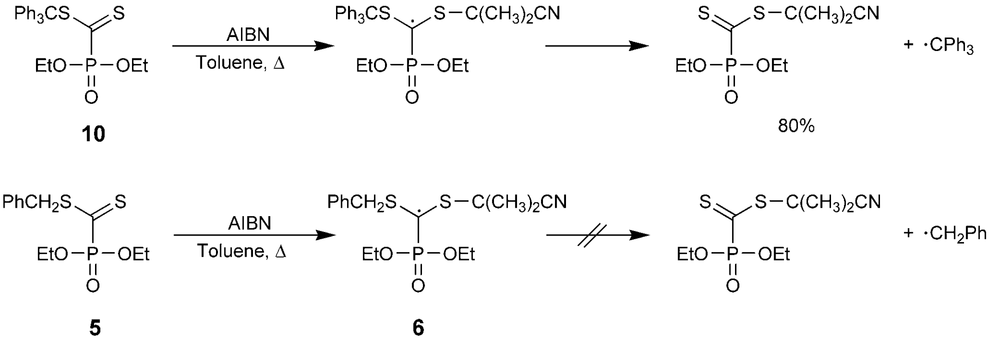
Fig. 3. *Experimental* (symbols) *and calculated (lines) concentration–time profiles of some of the species involved in the AIBN-initiated polymerization of styrene controlled by* **5** *at 90°.* a) *Pr*S$\dot{\mathrm{C}}$(S*Bn*)P(O)(OEt)$_2$ (**6**; ▲,▬), *Bn*S$\dot{\mathrm{C}}$(S*Bn*)P(O)(OEt)$_2$ (**7**; ▲,▬), *St*S$\dot{\mathrm{C}}$(S*Bn*)P(O)(OEt)$_2$ (**8**; ▲,▬), *St*S$\dot{\mathrm{C}}$(S*St*)P(O)(OEt)$_2$ (**9**; ▲,▬), *Pr*S$\dot{\mathrm{C}}$(S*St*)P(O)(OEt)$_2$ (▬), *St*S$\dot{\mathrm{C}}$(S*St*)P(O)(OEt)$_2$ + *Pr*S$\dot{\mathrm{C}}$(S*St*)P(O)(OEt)$_2$ (▬), and total radical concentration (▲,▬); b) *Bn*SC(S)P(O)(OEt)$_2$ (**5**; ■,▬), *St*SC(S)P(O)(OEt)$_2$ (▬), and *Pr*SC(S)P(O)(OEt)$_2$ (▬).

to a decrease of the rate constants of reactions involving termination of *St* and *St*S$\dot{\mathrm{C}}$(S*X*)P(O)(OEt)$_2$ (*X* = *Pr*, *Bn*, *St*) radicals with increasing chain length that was not taken into account. It might also be argued that having considered only the four radicals **6**–**9** in the simulations of the ESR spectra, whereas a species like *Pr*S$\dot{\mathrm{C}}$(S*St*)P(O)(OEt)$_2$ that could contribute to the *d* signal solely attributed to *St*S$\dot{\mathrm{C}}$(S*St*)P(O)(OEt)$_2$ (**9**) was disregarded, could have been too drastic an approximation. Yet, an examination of *Fig. 3,a*, suggests that this should not be the case, the predicted contribution of *Pr*S$\dot{\mathrm{C}}$(S*St*)P(O)(OEt)$_2$ being negligible with respect to that of *St*S$\dot{\mathrm{C}}$(S*St*)P(O)(OEt)$_2$ (**9**).

A major reason of concern when considering these results is instead to be found in the fact that the model takes into account all of the 47 reactions indicated in *Scheme 4* as actually occurring, whereas there is chemical evidence that it may not be so. In a recent paper, it has been reported that benzyl dithiobenzoate is an ineffective RAFT agent in methyl methacrylate (= methyl 2-methylprop-2-enoate; MMA) polymerization [22], due to its very low transfer coefficient ($c_{\mathrm{tr}} \leq 0.03$). This means that *tert*-alkyl radicals are incapable of bringing about the formal displacement of benzyl radicals *via* addition–elimination to *Bn*SC(S)Ph. Extrapolating to the present case, this would mean that the radical intermediates *Pr*S$\dot{\mathrm{C}}$(S*Bn*)P(O)(OEt)$_2$ (**6**) and *Pr*S$\dot{\mathrm{C}}$(S*St*)P(O)(OEt)$_2$ formed in *Eqn. 6* and *8*, respectively, do not fragment to *Pr*SC(S)P(O)(OEt)$_2$ and *Bn* or *St*.

Also, some of us have previously shown that while the thermal reaction of AIBN with either triphenylmethyl (diethoxyphosphoryl)dithioformate (**10**) or its fluorenyl analogue affords *Pr*SC(S)P(O)(OEt)$_2$ in good yields (*Scheme 5*), in the similar reaction

Scheme 5. *Thermal Reactions of Triphenylmethyl (Diethoxyphosphoryl)dithioformate* (**10**), *and of* **5** *with AIBN*



of AIBN with **5**, the latter is recovered virtually unchanged [23], thus further substantiating that the *Pr*S$\dot{C}$(S*Bn*)P(O)(OEt)$_2$ (**6**) radical intermediate does not fragment to *Pr*SC(S)P(O)(OEt)$_2$ and *Bn*. These results imply that in the AIBN-initiated polymerization of styrene controlled by *Bn*SC(S)P(O)(OEt)$_2$ (**5**) as RAFT agent, the adventitious dithioester *Pr*SC(S)P(O)(OEt)$_2$ should not be present at any stage.

In this light, we remodelled the polymerization process by excluding from the list in *Scheme 4* all the reactions involving either the dithioester *Pr*SC(S)P(O)(OEt)$_2$ or the intermediate radical *Pr*S$\dot{C}$(S*Pr*)P(O)(OEt)$_2$ which can only derive from addition of *Pr* to *Pr*SC(S)P(O)(OEt)$_2$. This was achieved by setting equal to zero the values of the rate constants k_7, k_{10}, k_{13}, k_{16}, k_{17}, k_{19}, k_{30}, k_{36}, and k_{42}. The resulting concentration–time profiles are represented in *Fig. 4*, and the rate constants estimated for the addition and fragmentation reactions are collected in *Table 2*. The plot shows a considerably improved fitting for radical *Bn*S$\dot{C}$(S*Bn*)P(O)(OEt)$_2$ (**7**) at the initial stages, and only a slight improvement of the correlation for radical *St*S$\dot{C}$(S*St*)P(O)(OEt)$_2$ (**9**), the total radical concentration, and possibly radical *St*S$\dot{C}$(S*Bn*)P(O)(OEt)$_2$ (**8**). On the other hand, a principal deficiency occurs for radical *Pr*S$\dot{C}$(S*Bn*)P(O)(OEt)$_2$ (**6**) that seems to be formed much faster in the simulation than in the ESR experiment. A further problem is that radical *Pr*S$\dot{C}$(S*St*)P(O)(OEt)$_2$ is now predicted to be present after *ca.* 5 minutes in a concentration greater than 10^{-7} M, a value that should make it detectable in the ESR experiment, whereas its presence was not taken into account in the simulations that have led to the experimentally derived concentration/time profiles of radicals **6**–**9**.

It should also be noted that the values of the addition (k_{14}) and fragmentation (k_{23}) rate constants, although now larger and smaller, respectively, do not show a dramatic change in the two models.

Returning to the afore mentioned debate about the magnitude of the rate constant for the fragmentation reactions, the order of magnitude of k_{23} reported in *Tables 1* and *2* is substantially higher than those on the low side estimated in some studies [8][17][18][24][25], and appears instead to be more consistent with the higher values reported in other works [11][14][15][26][27].

The rate constants for the addition and fragmentation reactions are bound to be critically affected by the stability of the intermediate *X*S$\dot{C}$(S*Y*)Z radicals (where

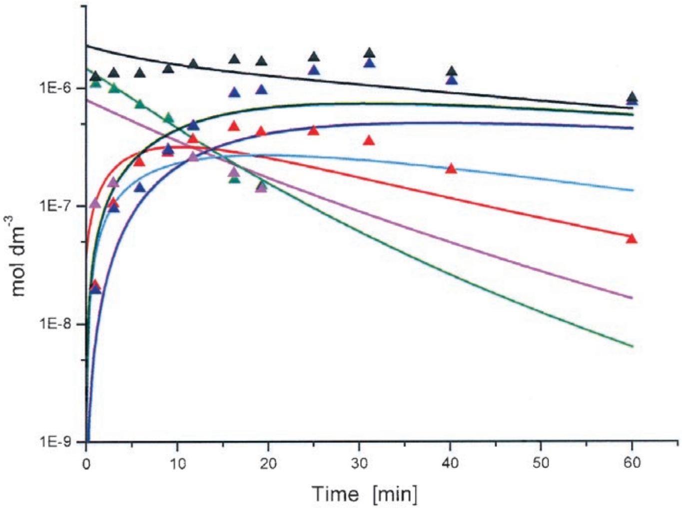


Fig. 4. *Experimental* (symbols) *and estimated* (lines) *concentration–time profiles of some of the species involved in the AIBN-initiated polymerization of styrene controlled by* **5** *at 90°.* *Pr*SĊ(S*Bn*)P(O)(OEt)$_2$ (**6**; ▲,▬), *Bn*SĊ(S*Bn*)P(O)(OEt)$_2$ (**7**; ▲,▬), *St*SĊ(S*Bn*)P(O)(OEt)$_2$ (**8**; ▲,▬), *St*SĊ(S*St*)P(O)(OEt)$_2$ (**9**; ▲,▬), *Pr*SĊ(S*St*)P(O)(OEt)$_2$ (▬), *St*SĊ(S*St*)P(O)(OEt)$_2$ + *Pr*SĊ(S*St*)P(O)(OEt)$_2$ (▬), and total radical concentration (▲,▬).

Table 2. *Rate Constants Estimated for Some Addition and Fragmentation Reactions (*see *Scheme 4) when Not Allowing for the Presence of* Pr*SC(S)P(O)(OEt)$_2$*

Addition reactions		Fragmentation reactions	
	k/M^{-1}s^{-1}		k/s^{-1}
k_6	$3.0 \cdot 10^7$	k_{15}	$2.0 \cdot 10^3$
k_8	$4.0 \cdot 10^7$	k_{18}	$2.0 \cdot 10^3$
k_9	$3.0 \cdot 10^7$	k_{20}	$4.0 \cdot 10^3$
k_{11}	$2.5 \cdot 10^7$	k_{21}	$4.0 \cdot 10^3$
k_{12}	$2.0 \cdot 10^7$	k_{22}	$5.0 \cdot 10^3$
k_{14}	$2.0 \cdot 10^7$	k_{23}	$5.0 \cdot 10^3$

Z = P(O)(OEt)$_2$, Ph and *X*, *Y* = *Pr*, *Bn*, *St*). *X*SĊ(S*Y*)Z Radicals contain two electron-donating thioether functions (S*X* and S*Y*) bound to the radical center: thus, electron-withdrawing Z groups should stabilize *X*SĊ(S*Y*)Z through the captodative effect [28][29], the stabilization becoming more pronounced with the increasing accepting character of Z, whereas electron-donating Z groups should exert a lower, if any, stabilizing action. The relative electron-withdrawing ability of Z residues can be estimated from the reduction potentials of compounds having the same structure but for the Z group; although the reduction potentials of *St*SC(S)P(O)(OEt)$_2$ and *St*SC(S)Ph are not available, those of *Bn*SC(S)P(O)(OEt)$_2$ (**5**) and of *Bn*SC(S)Ph are known to be −1.03 V [30] and −1.32 V [31] *vs.* SCE. These values indicate that the diethoxyphosphoryl group is a stronger electron acceptor than phenyl, and that, therefore, *X*SĊ(S*Y*)P(O)(OEt)$_2$ radicals should be more stable than *X*SĊ(S*Y*)Ph radicals. As a consequence, the rate of addition of *St* radicals to *St*SC(S)P(O)(OEt)$_2$ (*i.e.*, k_{14}) and that of fragmentation of the spin adduct *St*S$\dot{\text{C}}$(S*St*)P(O)(OEt)$_2$ (**9**) (*i.e.*, k_{23}) are foreseen to be larger and smaller, respectively, than those for the corresponding reactions of *St* with *St*SC(S)Ph.

These expectations were supported by density-functional-theory (DFT) calculations. At the HMDFT-BB1K level of theory, radicals *St*S$\dot{\text{C}}$(S*St*)P(O)(OEt)$_2$ (**9**) and *St*S$\dot{\text{C}}$(S*St*)Ph (**1**) are computed to be less stable than the Me radical, taken as reference, by 26.6 and 30.9 kcal mol^{-1}, respectively. That is, *St*S$\dot{\text{C}}$(S*St*)P(O)(OEt)$_2$ (**9**) is computed to be more stable than *St*S$\dot{\text{C}}$(S*St*)Ph (**1**) by 4.3 kcal mol^{-1}, in accordance with what is expected on the basis of the captodative effect. Accordingly, the activation energy E_a (including ZPVE (zero-point vibrational energy) correction) for β-elimination of the styryl radical from *St*S$\dot{\text{C}}$(S*St*)P(O)(OEt)$_2$ (**9**; 16.4 kcal mol^{-1}) is computed to be 0.3 kcal mol^{-1} higher than that for *St* elimination from *St*S$\dot{\text{C}}$(S*St*)Ph (**1**; 16.1 kcal mol^{-1}), while E_a for the addition (reverse reaction) of the styryl radical to *St*SC(S)P(O)(OEt)$_2$ (3.3 kcal mol^{-1}) is computed to be 0.6 kcal mol^{-1} smaller than that for addition of *St* to *St*SC(S)Ph (3.9 kcal mol^{-1}).

Theoretical rate constants for the addition of the styryl radical to the CTAs *St*SC(S)P(O)(OEt)$_2$ and *St*SC(S)Ph and for the β-fragmentation of the resulting adduct radicals *St*S$\dot{\text{C}}$(S*St*)P(O)(OEt)$_2$ (**9**) and *St*S$\dot{\text{C}}$(S*St*)Ph (**1**) were evaluated from the free-energy barriers computed by estimating the enthalpy and entropy contributions from frequency calculations at 90°. The free-energy barriers computed for the β-fragmentation reactions (ΔG (**9**) = 17.0 kcal mol^{-1} and $\Delta G^{\ddagger}_{\text{fr}}$(**1**) = 16.5 kcal mol^{-1}) are slightly smaller than those computed for the addition reactions ($\Delta G^{\ddagger}_{\text{ad}}$(*St*SC(S)P(O)(OEt)$_2$) = 19.1 kcal mol^{-1} and $\Delta G^{\ddagger}_{\text{ad}}$(*St*SC(S)Ph) = 19.8 kcal mol^{-1}). From the transition-state theory, the rate constants are computed to be k_{fr}(**9**) = $0.4 \cdot 10^3$ s^{-1}, k_{fr}(**1**) = $0.9 \cdot 10^3$ s^{-1}, k_{ad}(*St*SC(S)P(O)(OEt)$_2$) = $0.7 \cdot 10^3$ M^{-1} s^{-1}, k_{ad}(*St*SC(S)Ph) = $0.3 \cdot 10^3$ M^{-1} s^{-1}. In accordance with experimental findings, the computed rate constant for addition of the styryl radical to *St*SC(S)P(O)(OEt)$_2$ is twice that for addition to *St*SC(S)Ph, while the rate constant for β-fragmentation of the RAFT adduct leading to *St*SC(S)P(O)(OEt)$_2$ is half that leading to *St*SC(S)Ph.

In contrast with experiments, comparable values were calculated for the fragmentation and addition rate constants. In particular, the absolute rate constant computed for addition of the styryl radical to *St*SC(S)P(O)(OEt)$_2$ is largely underestimated with respect to the values estimated modelling the ESR results and reported in *Tables 1* and *2*, while the rate constant for β-fragmentation is only slightly underestimated. The fragmentation enthalpy should be overestimated by *ca.* 2 kcal mol^{-1} in line with the error estimated for the BB1K method (see the computational details in the *Exper. Part*). The large discrepancy observed for the addition reactions can be explained considering that, in solution, part of the translational and rotational entropy of the reactants and of the transition-state complex is lost. Thus, the large decrease of entropy computed in the gas-phase in a bimolecular process on going from the reagents to the transition state is usually substantially overestimated. Indeed, a similar discrepancy between theory and experiment has been observed in computing the addition/fragmentation rate constants involving a thiyl radical and an alkene C=C bond [32]. The harmonic-oscillator approximation employed to compute the vibrational contributions to enthalpy and entropy causes one to slightly underestimate the addition rate.

For example, the rate constant for the benzyl-radical addition to the C=S bond of MeC(S)SMe is underestimated by a factor of 5.9 [33]. Using this correction factor for the addition of the styryl radical to a thiocarbonyl group, the agreement between theory and experiment slightly improves, although remaining very poor ($k_{ad}(St\text{SC(S)P(O)(OEt)}_2) = 4.1 \cdot 10^3\ \text{M}^{-1}\ \text{s}^{-1}$ as compared to $k_{14} = 2.0 \cdot 10^7\ \text{M}^{-1}\ \text{s}^{-1}$ from *Table 2*). Hence, we used an alternative approach to compute reliable rate constants from MO calculations. The rate constants for radical fragmentations and radical additions can be estimated through the *Arrhenius* equation by using the computed activation energies E_a and reliable experimental frequency factors (see the computational details in the *Exper. Part*). The trend of the values estimated in this way ($k_{fr}(\mathbf{9}) = 7.4 \cdot 10^3\ \text{s}^{-1}$, $k_{fr}(\mathbf{1}) = 1.1 \cdot 10^4\ \text{s}^{-1}$, $k_{ad}(St\text{SC(S)P(O)(OEt)}_2) = 4.6 \cdot 10^6\ \text{M}^{-1}\ \text{s}^{-1}$, $k_{ad}(St\text{SC(S)Ph}) = 2.0 \cdot 10^6\ \text{M}^{-1}\ \text{s}^{-1}$) does not change, but the addition rate constants increase by three orders of magnitude. Interestingly, the values calculated for the CTA $St\text{SC(S)P(O)(OEt)}_2$ (($k_{fr}(\mathbf{9})$) and $k_{ad}(St\text{SC(S)P(O)(OEt)}_2)$) are now in fairly good accord with those estimated from ESR experiments (k_{23} and k_{14} in *Tables 1* and *2*).

Conclusions. – Our modelling of the time evolution of the concentration of a number of radical species detected during the AIBN-initiated polymerization of styrene by using benzyl (diethoxyphosphoryl)dithioformate (**5**) as RAFT agent indicates that the rate constant for the thiophilic addition of the propagating radical to give species **9** (k_{ad}) should be in the range of 10^6 to $10^7\ \text{M}^{-1}\ \text{s}^{-1}$, whereas that for the release of the propagating radical from **9** (k_{fr}) should be in the range of 10^3 to $10^4\ \text{s}^{-1}$. These results are supported by DFT calculations at the HMDFT-BB1K level.

Although these rate-constant values are strictly related to the actual RAFT agent **5** used in this study, the DFT calculations also suggest that the addition and fragmentation rates in RAFT processes involving more conventional CTAs, *e.g.*, dithiobenzoates, should not differ largely from those determined in the present study.

Prof. *Fischer*'s pioneering ESR studies of the kinetics of radical reactions greatly contributed to the development of radical chemistry. We consider ourselves lucky for having had the privilege to collaborate with him and to enjoy his friendship. The authors wish to thank *E. Rizzardo* (*CSIRO*, Au) for helpful discussions and suggestions.

Experimental Part

Materials. Compound **5** was prepared according to established procedures [34]. Styrene (99%; *Aldrich*) was distilled *in vacuo* just before use, while AIBN (98%; *Fluka*), DPPH (95%; *Aldrich*), and all solvents (*Aldrich*) were used as received.

Polystyryl Bromide. A soln. comprising styrene (5.68 ml, 0.049 mol), copper(I) bromide (70.6 mg, 0.53 mmol), 4,4′-dinonyl-2,2′-bipyridine (403.6 mg, 1 mmol), and 1-phenylethyl bromide (0.34 ml, 2.5 mmol), was prepared and transferred to an ampoule that was degassed by three freeze-evacuate-thaw cycles, sealed, and heated at 110° for 7 h in a thermostatted oil bath. The conversion, by NMR, was estimated to be 67.7%. The soln. was diluted with CHCl_3 and treated with MeOH, and the precipitate filtered. GPC analysis: M_n 1205, $PD = 1.1$.

ESR Apparatus and Methods. ESR Spectra: upgraded *Bruker-ER-200D/ESP-300* spectrometer, equipped with a standard variable-temperature device, an NMR gaussmeter for field calibration, and a frequency counter for the determination of g-factors. The g-factors were corrected with respect to that of perylene radical cation in conc. H_2SO_4 soln. Spectra were stored and manipulated on a dedicated *Bruker-ESP-3220* data system. Computer simulations of the spectra were obtained by using a software based on a Monte Carlo minimization procedure [35].

ESR Polymerization Studies. A master batch of 5.0 ml (44 mmol) of styrene, 72.0 mg (0.438 mmol) of AIBN, and 266.0 mg (0.874 mmol) of **5** was prepared. A sample of the soln. (300 μl) was placed in a *Pyrex* tube and carefully degassed through repeated freeze and thaw cycles; the tube was flushed with Ar, sealed, and then placed in the cavity of the ESR spectrometer heated at 90°. Spectra were recorded repeatedly until the spectral pattern did not show any further change. The amount of radicals present in the sample at a given time was estimated by comparing the double integral of each individual spectrum with the double integral of the spectrum of a DPPH soln. of known concentration (a synthetic ruby crystal was used as an internal standard for the cavity sensitivity).

Computational Details. Hybrid meta DFT calculations with the BB1K (Becke88 [36]-Becke95 [37] 1-parameter model for kinetics) functional [38] were carried out by using the Gaussian 03 system of programs [39] to compute theoretically the addition and fragmentation kinetic constants from the calculated free energies. Unrestricted wave function was used for radical species. Total energies were obtained employing the valence double-ζ basis set supplemented with polarization functions [40][41]. Standard diffuse functions were added on heavy atoms [42][43]. This HMDFT model (BB1K/6-31+G**) was very recently tailored to give good reaction-barrier heights [38]. Unfortunately, the test used in the parameterization of the BB1K method consists of only H-abstraction reactions. However, preliminary calculations show that the BB1K method performs slightly better than the G3(MP2)-RAD and RMP2/6-311+G(3df,2p)//B3LYP/6-31G(d) methods that were validated to study RAFT processes [44]. The addition enthalpy $\Delta H^{\ddagger}_{\mathrm{ad}}$ and fragmentation enthalpy $\Delta H^{\ddagger}_{\mathrm{fr}}$ at 0 K (*i.e.*, total energies plus ZPVE) for the model RAFT system $Me^{\bullet}+S{=}CHMe \rightarrow MeS\dot{C}HMe$ are computed to be 2.5 and 30.2 kcal mol^{-1}, resp. These values are comparable to those computed with the G3(MP2)-RAD method ($\Delta H^{\ddagger}_{\mathrm{ad}}=1.1$ kcal mol^{-1} and $\Delta H^{\ddagger}_{\mathrm{fr}}=23.9$ kcal mol^{-1}) and with the RMP2/6-311+G(3df,2p)//B3LYP/6-31G(d) method ($\Delta H^{\ddagger}_{\mathrm{ad}}=0.8$ kcal mol^{-1} and $\Delta H^{\ddagger}_{\mathrm{fr}}=25.1$ kcal mol^{-1}) [44]. Indeed, the deviations (0.2 and 2.4 kcal mol^{-1}) of the BB1K values from those obtained with the high-level composite method W1//CC ($\Delta H^{\ddagger}_{\mathrm{ad}}=2.3$ kcal mol^{-1}, $\Delta H^{\ddagger}_{\mathrm{fr}}=27.8$) [44] are slightly smaller than the corresponding deviations for the G3(MP2)-RAD method (-1.2 and -3.9 kcal mol^{-1}) and for the RMP2/6-311+G(3df,2p)// B3LYP/6-31G(d) method (-1.5 and -2.7 kcal mol^{-1}).

A thorough conformational screening was carried out as previously suggested [45]. First, local minima were determined at the HF/6-31G* level. Then, the optimized geometries were reoptimized at the BB1K/6-31+G** level to determine the true global minimum. Indeed, the global minimum determined at the HF/6-31G* level [45] was later found to be a local minimum at the B3LYP/6-31G* level even if this local minimum lies only 0.1 kcal mol^{-1} higher in energy above the true global minimum [33]. In the present case, HF and B3LYP optimizations lead to the same global minimum. Radical-stabilization energies were estimated computing the C−H bond dissociation energy relative to that computed for methane. Free energy barriers at 90° and 1 atm were computed from frequency calculations using a scaling factor of 0.9561 to account for anharmonicity [38] and the harmonic-oscillator approximation. The nature of the transition states was verified by frequency calculations (one imaginary frequency).

Rate constants $k(T)$ were evaluated from the computed free energies by using the transition-state theory as $k(T)=k_{\mathrm{B}}T(hc^{\circ})^{-1}\exp(-\Delta G/RT)$ where the concentration c° is equal to 1 for β-fragmentation reactions (unimolecular process) and to 0.033558 mol dm^{-3} (the inverse of molar volume at 90° and 1 atm) for addition reactions (bimolecular process). As an alternative, rate constants $k(T)$ were also estimated from the computed activation energies E_{a} by using reliable experimental frequency factors A in the *Arrhenius* equation $k(T)=A\exp(-E_{\mathrm{a}}/RT)$. A values were assumed to be $10^{8.65}$ M^{-1} s^{-1} for radical additions and $10^{13.74}$ s^{-1} for radical fragmentations. These values were estimated adding to reliable experimental A values for addition/fragmentation of alkyl radicals to a C=C bond ($10^{8.22}$ M^{-1} s^{-1} and $10^{12.97}$ s^{-1}, resp.) [46] the average increase ($10^{0.43}$ M^{-1} s^{-1} and $10^{0.77}$ s^{-1}, resp.) of the frequency factors computed with a high level *ab initio* method on going from C=C to C=S bonds for the model systems $Me^{\bullet}+Z{=}CXY \rightarrow MeZ\dot{C}XY$ (X,Y = H, Me; Z = CH_2, S) attributed to reduced steric hindrance [47].

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Received January 26, 2006