Direct ESR Detection of Free Radicals in the RAFT Polymerization of Styrene

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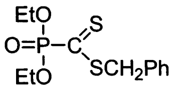
ABSTRACT: Benzyl (diethoxyphosphoryl)dithioformate (**1**) has been used to control the AIBN initiated radical polymerization of styrene. In a comparative study with the more popular RAFT transfer agent benzyl dithiobenzoate (**2**), compound **1** led to higher molecular weight polymers, although with a slightly worse polydispersity. During the polymerization process mediated by **1** a few radicals have been intercepted and characterized by means of ESR spectroscopy. The nature and relative amount of the various radical species varied as the polymerization proceeded, matching expectations based on the generally accepted RAFT mechanism. The present ESR results induce a reassessment of the identity of a radical species observed in a previous preliminary study.

Introduction

Controlled radical polymerization has rapidly progressed since its introduction, and several methods have been devised for its realization. In all cases the control of molar mass and of polydispersity is achieved by converting the chain propagating radicals into a "dormant form" in equilibrium with the "active" form, thus keeping very low the concentration of the latter species and minimizing the termination by self-reaction. In SFRP (stable free radical polymerization) stable nitroxide radicals[1−4] or their related alkoxyamines[5] control the polymerization. Transition metal complexes are instead used[6−8] in ATRP (atom transfer radical polymerization). In the RAFT (reversible addition fragmentation transfer) polymerization the process is mediated by compounds containing the dithioester function,[9−13] and in a recent paper, we described the controlled radical polymerization of styrene using benzyl (diethoxyphosphoryl)dithioformate (**1**) as RAFT agent.[14] In both the thermally initiated and AIBN-initiated systems the molar mass increased linearly with time, as expected for a controlled polymerization process, while the molar mass distribution progressively increased. This last finding together with repolymerization data suggested that the rate constant of radical formation was not large enough to ensure a fast start of the polymerization process in comparison to the overall monomer conversion time. In addition, the rate of bond dissociation and re-formation appeared to be low relative to the propagation rate.

To gain further insight into the RAFT characteristics of α-phosphorus-substituted dithioformates, we have investigated by means of ESR spectroscopy the AIBN-initiated polymerization of styrene mediated by compound **1**; in addition, we have compared the polymerization controlling capacity of **1** with that of benzyl dithiobenzoate (**2**), a compound known to be a very efficient RAFT transfer agent.[9]



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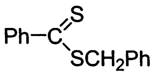

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Experimental Section

Materials. Compounds **1**[14] and **2**[9] were prepared according to established procedures. 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.

AIBN-Initiated RAFT Styrene Polymerization. The AIBN-initiated polymerization of styrene in the presence of either **1** or **2** was carried out using styrene:RAFT:AIBN ratios of either 922:1:0.18 (method a) or 50:1:0.5 (method b) according to the following procedures. *Method a*. A master batch of 19.0 mL (166 mmol) of styrene, 5.4 mg (33 μmol) of AIBN, and 54.7 mg (0.180 mmol) of **1** or 43.9 mg (0.180 mmol) of **2** was prepared, and aliquots of 3.0 mL were placed in polymerization ampules that were degassed by freeze and thaw cycles and sealed under nitrogen. The polymerization reaction was performed at 333 K. At the end of the reaction, each ampule was quenched in cold water and the reaction mixture diluted with methylene chloride. The polymer was then precipitated into methanol, washed with methanol, and purified by precipitation from methylene chloride solution into methanol. The polymer was dried in vacuo for several hours. Conversion of styrene was estimated gravimetrically. In a typical run, 3.0 mL (26 mmol) of styrene were reacted with 8.6 mg (28 μmol) of **1** and 0.85 mg (5.1 μmol) of AIBN at 333 K for 20 h with a conversion of 13.9%. The number-average molar mass and polydispersity index resulted $M_n = 25\,900$ and $M_w/M_n = 1.24$. *Method b*. 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 **1** or 213.0 mg (0.874 mmol) of **2** was prepared, and samples were used for the ESR studies. Aliquots of 4.0 mL were placed in polymerization ampules that were degassed by freeze and thaw cycles and sealed under nitrogen. The polymerization reaction was performed at 333 K for 20 h. At the end of the reaction, each ampule was quenched in cold water and the reaction mixture diluted with methylene chloride. The polymer was then precipitated into methanol, washed with methanol, and purified by precipitation from methylene chloride solution into

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methanol. The polymer was dried in vacuo for several hours. Conversion of styrene was estimated gravimetrically.

ESR Experiments. ESR spectra were recorded on an upgraded Bruker ER 200/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 that were corrected with respect to that of perylene radical cation in concentrated sulfuric acid. Spectra were stored and manipulated on a dedicated Bruker ESP 3220 data system. Computer simulations of the spectra were obtained using a software[15] based on a Monte Carlo minimization procedure.[16] In a typical ESR experiment, 300 μL of a solution of styrene, **1**, and AIBN prepared according to method b was placed in a Pyrex ESR tube (i.d. 3.8 mm). The solution was carefully degassed through repeated freeze and thaw cycles; the tube was saturated with argon, sealed, and then placed in the cavity of the ESR spectrometer heated at either 333 or 363 K. Spectra were recorded repeatedly until the spectral pattern did not show any further change. The amount of radical 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 solution of known concentration (a synthetic ruby crystal was used as an internal standard for the cavity sensitivity).

Results and Discussion

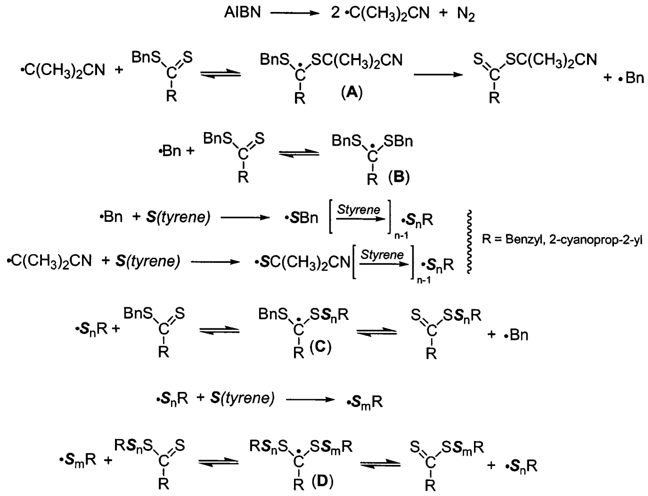
ESR Study. The general mechanism of the polymerization of styrene (**S**) controlled by dithioesters as RAFT transfer agents involves the formation of polymer-bound dithioesters [RC(S)S**S**$_x$] resulting from addition of a growing polymer radical $^{\bullet}$**S**$_x$ to the RAFT agent followed by expulsion of a $^{\bullet}$R′ radical. This in turn reacts with the monomer, providing new propagating radicals that react with the dormant polymer-bound dithioesters in a dynamic equilibrium between the propagating and the dormant species.

Several attempts have been made to evidence by means of ESR spectroscopy the presence of free radicals in this process, and indeed the detection of signals attributed to radical **D** has been reported on three different occasions.[17−19] In all instances, R was a phenyl ring, 2-cyanoprop-2-yl dithiobenzoate having been used as RAFT agent. The concentration of the observed radical as determined by double integration of the ESR signal, which was normally poorly resolved, was on the order of 10^{-7} M, and its time profile[18] was found to be fairly constant from an early stage of polymerization.

On the other hand, an examination of the detailed outline of the RAFT styrene polymerization as represented in Scheme 1 reveals that several radical species structurally related to **D** are involved in the process, i.e., radicals **A**, **B**, and **C**. It may therefore be erroneous attributing the observed ESR signal to a single radical species. In the case of dithiobenzoates species **A**−**D** will have rather complex spectra resulting from coupling of the unpaired electron with the hydrogen atoms of the aromatic ring and, possibly, additional hyperfine structure due to the attacking radicals; in all cases the spectra would be characterized by closely related ESR spectral parameters, and under the poor resolution conditions typical of polymerization experiments, the observed spectrum will most likely be the sum of the signals from different radicals. Double integration of the signal would then provide the overall radical concentration rather than the amount of an individual species.

In a recent study[14] we have shown that, as initially suggested by other authors,[11] also phosphoryl dithioesters can be satisfactorily used to control the styrene radical polymerization and have evidenced that benzyl (diethoxyphosphoryl)dithioformate (**1**) is a well-performing RAFT agent. On that occasion we also reported the detection of a weak ESR signal that was tentatively attributed to the intermediate radical **D**, where R is a diethoxyphosphoryl group. For ESR purposes benzyl (diethoxyphosphoryl)dithioformate (**1**) is much more suitable than 2-cyanoprop-2-yl dithiobenzoate or its benzyl analogue **2** because the spectra of the adducts resulting from thiophilic addition of alkyl radicals to the thiocarbonyl function are simpler and structurally more informative. Actually, the spectra of the alkyl adducts of phosphoryl dithioformates consist of a simple 1:1 doublet with a separation of ca. 2.0 mT exhibiting an additional hyperfine structure that varies with the nature of the estereal residue and of the attacking alkyl radical.

Scheme 1. Detailed Outline of the Mechanism of the Radical Polymerization of Styrene Controlled by a Benzyl Dithioester; Termination Reactions Are Not Included



We have now reinvestigated the AIBN-initiated polymerization of styrene in the presence of compound **1** at 333 and 363 K under conditions more suitable for an ESR investigation, that is, using a molar ratio styrene:**1**:AIBN of 50:1:0.5 rather than that normally used for preparative purposes (i.e., 920:1:0.18). Under these conditions the ESR spectra were much more intense than those observed in an earlier investigation[14] and revealed a much more complex situation where several radicals rather than just one could be identified. Figure 1a shows the spectra observed when heating at 363 K the above mixture inside the cavity of an ESR spectrometer over a time interval of ca. 30 min. The drastic variation of the spectral pattern with time is evident. Because the spectra clearly indicated the presence of more than one paramagnetic species, attempts were made to simulate them by assuming the simultaneous presence of two, three, or all of the radicals appearing in Scheme 1. Eventually, the experimental spectra at different times could be well reproduced (see Figure 1b) by admitting the interplay of four different radicals, the concentration of which varies with time as the polymerization process proceeds. Relying on the experience that we have gained in our previous studies on the addition of free radicals to a large variety of dialkoxyphosphoryl dithioformates,[20−24] and on the basis of the hyperfine spectral parameters used for the simulations (see Table 1), we identify the four radicals as species **A**−**D** (see Scheme 1), where R is a diethoxyphosphoryl group.

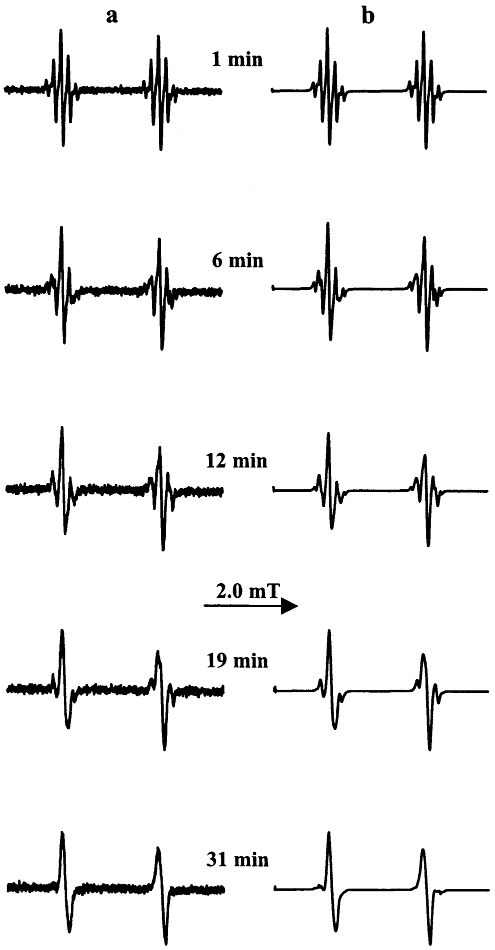


Figure 1. Experimental (**a**) and computer simulated (**b**) ESR spectra observed at different times during the AIBN-initiated polymerization of styrene in the presence of **1** at 363 K (**S**:**1**:AIBN = 50:1:0.5). The spectra result from the superimposition of the signals of the fours radicals **A**−**D** (see Table 1) in different proportions (see Figure 2) with the exception of the bottom one (31 min) that was reproduced by assuming the presence of radicals **D** and **C** only.

Table 1. ESR Spectral Parameters for Radicals A−D[a] **at 363 K**

radical	$a(^{31}P)$/mT	a(other)/mT	g
A	2.226	0.250 (2H)	2.0057_1
B	2.235	0.168 (4H)	2.0057_3
C	2.197	0.229 (2H)	2.0057_4
D	2.172		2.0058_5

[a] R = $P(O)(OEt)_2$.

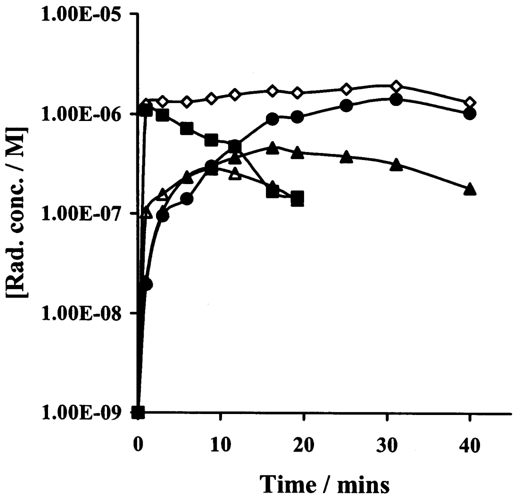


Figure 2. Time profile of the ESR determined overall radical concentration (◇) and of the concentration of radical species **A** (△), **B** (■), **C** (▲), and **D** (●) during the AIBN initiated polymerization of styrene in the presence of the RAFT agent **1** (**S**:**1**:AIBN = 50:1:0.5) at 363 K.

The identity of species **A** and **B** could be confirmed in separate studies generating the authentic radicals by photolysis of benzene solutions of **1** containing either AIBN or dibenzyl mercury. The spectrum of radical **A**, resulting from addition of the 2-cyanoprop-2-yl radical to the RAFT transfer agent **1,** is a 1:1 doublet (one ^{31}P atom) of 1:2:1 triplets (two equivalent ^{1}H atoms of the benzyl moiety) and is mostly present in the early polymerization stage. Radical **B**, resulting from addition of benzyl radicals to compound **1**, is instead responsible for a 1:1 doublet (one ^{31}P atom) of 1:4:6:4:1 quintets (four equivalent ^{1}H atoms of the two benzyl moieties): its concentration should be high in the initial stage of polymerization and become negligibly small toward the end of the process. Radical **C** results from the addition of the growing polymer radical $^{\bullet}\mathbf{S}_n$ to **1** and, rather than a single species, is more likely to represent a bunch of species with slightly different n values. Its spectrum is again a 1:1 doublet (one ^{31}P atom) of 1:2:1 triplets (two equivalent ^{1}H atoms of the benzyl moiety). In principle, the spectrum of **C** should also exhibit an additional 1:1 doublet splitting due to the tertiary hydrogen of the propagating radical [$^{\bullet}CH(C_6H_5)CH_2\mathbf{S}$]. On the other hand, the splitting of β-tertiary hydrogen atoms in these kinds of adducts is normally small,[20−23] and in the present case it is most likely hidden within the rather large line width. For the same reason we associate the broad 1:1 doublet signal (one ^{31}P atom) with radical **D**, the radical bearing a growing polymer fragment ($^{\bullet}\mathbf{S}_n$ and $^{\bullet}\mathbf{S}_m$) bound to each sulfur atom. In line with expectations, this species largely dominates the late stages of the polymerization. As it was the case for **C**, **D** is not a single radical species but again a number of closely related species with slightly different n and m values. Radicals **D** would then have somewhat different ^{31}P splittings, which satisfactorily accounts for the asymmetry of the lines of the spectra observed toward the end of the experiments. Figure 2 shows the time profile of the overall radical concentration as well as that of the concentration of radicals **A**−**D** determined through computer simulation at different polymerization stages.

It is evident from Figure 2 that the overall radical concentration [R$^{\bullet}$] remains fairly constant over the considered time interval. We determined the radical concentration to be ca. 10^{-6} M, a value slightly larger but still in substantial agreement with that previously reported for the radical detected during the polymerization of styrene mediated by a polystyryl dithiobenzoate at 333 K[18] and also consistent with that measured in the polymerization of styrene controlled by cumyl dithiobenzoate at 363 K.[17] In both cases the radical was identified as $\mathbf{S}_n S\dot{C}(C_6H_5)S\mathbf{S}_m$, but on the basis of our results we believe that also in these previous instances, what was considered as the ESR signal of a single species must in fact have been the superimposition of signals from different radicals structurally related to **A**−**D**. As mentioned above, in the case of the dithiobenzoate derivatives the spectral parameters do not allow the identification of the different species that we have been able to observe thanks to the uniquely favorable spectral properties of the radical adducts derived from the RAFT agent **1**. The traces shown in Figure 2 confirm that while in the late stages of the polymerization the signal is indeed virtually due to radical **D**, the early stages of the process are dominated by radicals **A** and **B** that are later on replaced by radical **C**. On this basis we feel that previous kinetic studies should be reconsidered, being inappropriate to assume that the value derived from integration of the observed ESR signal when using dithiobenzoates represents the concentration of $\mathbf{S}_n\mathrm{S\dot{C}}(\mathrm{C_6H_5})\mathrm{S}\mathbf{S}_m$.

The participation of radicals **A**−**D** in the polymerization of styrene was further substantiated when the process was carried out at 333 K. Also, in this case the four radical species were observed, and their concentration was found to evolve with a similar profile although stretched over a longer time interval.

We believe it sensible to assume that despite the different composition in terms of [monomer]:[RAFT agent]:[initiator] used in the ESR study, the radical species intervening in the polymerization process are the same that are formed during the product studies. At the same time, we are aware that the relative ESR intensities of the different species will be typical of the actual composition used in the ESR study. Nevertheless, the present results, obtained by carrying out the polymerization under conditions more appropriate for ESR studies, are a valuable mechanistic tool for the study of the RAFT polymerization. Of particular interest is the clear identification of the four radical species **A**−**D**, and the profile of their evolution in time is currently the object of a detailed kinetic analysis aimed to shed further light into the mechanism of this process and to find conditions for its optimization. The identification of radicals **A**−**D** has also led us to reassess as radical **C** the identity of the species mainly responsible for the weak doublet of triplet that we had detected in a previous study[14] and that we then erroneously attributed to species **D**.

It has been pointed out that phosphoryl dithioesters are not as good RAFT transfer agents as dithiobenzoates. On the other hand, the choice of compound **1** for the present ESR investigation was almost compulsory because dithiobenzoates would have been useless due to intrinsic spectroscopic reasons that would make their identification and quantification impossible.

Product Study. To compare the radical control efficiency of RAFT agents **1** and **2,** AIBN-initiated styrene polymerizations were performed at 333 K using either compounds as controlling agent. The molar ratio of styrene and the RAFT agent was kept constant at 930 in all of the polymerizations, and that between the RAFT agent and AIBN was fixed at 5.4. These conditions are quite different from those employed in our previous paper[14] but equal to those suggested in the original patent by Rizzardo.[9]

The relevant results are collected in Table 2, while Figure 3 collectively reports the trend of M_n and M_w/M_n as a function of time for the polystyrene samples prepared using **1** and **2**. In both cases, the molar mass increased regularly with time and conversion, as expected in a controlled polymerization, although the molar masses of samples prepared with **1** were systematically higher than those of the corresponding samples prepared with **2**. However, a perfectly linear increase was observed only for **2**. Besides, in the case of **2** the polydispersity index decreased regularly with time or conversion whereas in the case of **1** a definite broadening of the molar mass distribution is observed with increasing conversion, M_w/M_n increasing from 1.17 (conversion, 0.6%) to 1.36 (conversion, 28%).

Table 2. Molar Mass and Conversion Data for Polystyrene Samples Prepared via AIBN-Initiated RAFT Polymerization with 1 or 2 as RAFT Agents

RAFT	time/h	M_n	M_w/M_n	conv[c]/%
1[a]	4	4100	1.17	0.6
1[a]	8	11500	1.20	3.4
1[a]	15	20000	1.25	10.0
1[a]	20	25900	1.24	13.9
1[a]	30	31300	1.32	22.4
1[a]	40	38200	1.36	28.0
2[a]	4	3550	1.22	2.8
2[a]	8	4550	1.20	4.2
2[a]	15	12400	1.18	11.5
2[a]	20	16600	1.10	15.6
2[a]	30	22600	1.14	24.0
1[b]	20	6200	1.40	21.5
2[b]	20	2950	1.37	28.4

[a] Each sample was prepared in bulk by reacting 3.0 mL (26 mmol) of styrene with [AIBN] = 1.7×10^{-3} M and [RAFT agent] = 9.3×10^{-3} M, using a molar ratio between styrene and **1** or **2** of 930 mol/mol. [b] Samples were prepared in bulk by reacting 4.0 mL (35 mmol) of styrene with [AIBN] = 8.8×10^{-2} M and [RAFT agent] = 17.5×10^{-2} M, using a molar ratio between styrene and **1** or **2** of 50 mol/mol and a molar ratio between **1** or **2** and AIBN of 2 mol/mol. [c] Conversions were determined gravimetrically.

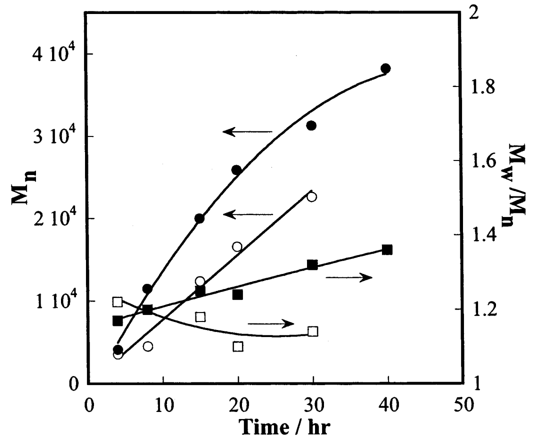


Figure 3. Trend of the number-average molar mass (circles) and polydispersity index (squares) as a function of time for AIBN-initiated polymerization of styrene with RAFT agent **1** (●, ■) and RAFT agent **2** (○, □).

The different behavior of RAFT agents **1** and **2** becomes even more evident when the ratio between M_n and the conversion X_a is plotted as a function of time (see Figure 4). In the case of **1**, M_n/X_a, which represents the maximum attainable molar mass, decreased monotonically with time, steeply at first and then more gradually until a limiting value of about 100 000 is reached. This limiting value corresponds to a degree of polymerization of 1000, which is similar to the molar ratio between the styrene monomer and the RAFT agent used in the various polymerizations. In the case of **2**, M_n/X_a was instead nearly constant in the proximity of the same limiting molar mass.

These findings indicate that the rate of primary radical addition and the subsequent primary fragmentation of **2**, that is, the elementary reactions taking place while the benzyl group is still attached to the RAFT agent or is involved in the reaction as the leaving radical, were sufficiently fast relative to the overall monomer conversion time, thus ensuring a fast initiation process.

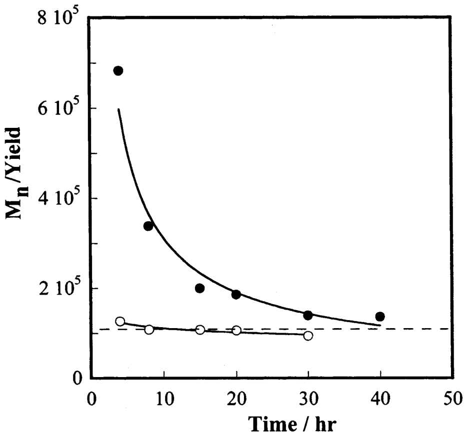


Figure 4. Trend of the ratio between M_n and the conversion X_a as a function of time for AIBN-initiated RAFT polystyrenes with RAFT agent **1** (●) and RAFT agent **2** (○). The dashed line indicates the theoretical limiting.

In the case of **1** these reactions were definitely slower, thus spreading the initiation process over longer time intervals and increasing the polydispersity value. In addition, the trend of M_w/M_n with time suggests that the rate of bond dissociation and re-formation for the steady-state adduct from **2** is fast with respect to the propagation rate, leading to a progressive decrease of the polydispersity with time, but relatively slow for steady-state adduct from **1**, thus resulting in the opposite effect. A slower fragmentation of the dithioformates than of the dithiobenzoates adducts **C** and **D** may reflect a greater stability of these radicals in the former case. Actually in radicals **C** and **D** two electron-donating SR substituents are bound to the radical center simultaneously with the electron-withdrawing phosphoryl group in the case of **1** or with the phenyl group in the case of **2**. In the former case captodative stabilization of the radicals may occur,[25,26] thus making their fragmentation more difficult.

The polymerization of styrene was also repeated using a ratio **S**:**1**(or **2**):AIBN = 50:1:0.5, that is, the same value used for the ESR studies. The last two entries in Table 2 indicate that for both compounds the number-average molar mass of the obtained polymer was, according to expectation, lower than that of the polymer obtained with a ratio **S**:**1**(or **2**):AIBN = 930:1:0.2 and again higher in the case of **1** than in the case of **2**. In both instances there was also an increase of the polydispersity value that can be tentatively attributed to the presence of a larger amount of initiator in the system; this effect was more relevant for **2** than for **1**, and as a result under a lower styrene:RAFT ratio the polydispersity of the polymer obtained using either **1** or **2** were virtually the same.

Concluding Remarks

Although it behaves in a different way with respect to the more popular dithiobenzoates, benzyl (diethoxyphosphoryl)dithioformate (**1**) is an efficient RAFT transfer agent in the polymerization of styrene. The unprecedented detection of several radical species during the polymerization of styrene controlled by **1** is in agreement with the generally accepted mechanism of the process and has led us to the reassessment of a previous erroneous identification by our group. It seems sensible to infer that structurally related radicals are formed when using dithiobenzoates as transfer agent, and in this light it is advisable that previous kinetics studies based on the radical concentrations as determined by ESR spectroscopy be reconsidered.

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