Controlled Radical Polymerization of Styrene with Phosphoryl- and (Thiophosphoryl)dithioformates as RAFT Agents

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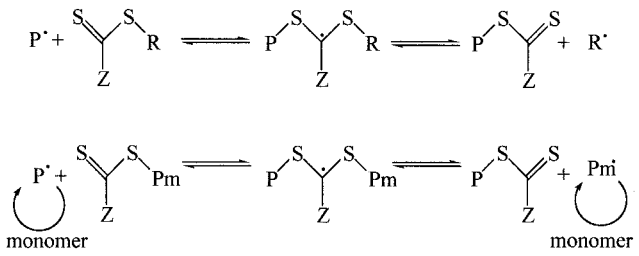
ABSTRACT: Benzyl (diethoxyphosphoryl)dithioformate (**1**) and benzyl (diethoxythiophosphoryl)dithioformate (**2**) were studied as RAFT agents in the polymerization of styrene. The reactive intermediates involved in the process were identified by electron spin resonance spectroscopy as the species deriving from the addition of the polymer propagating radical to the chain transfer agent, in agreement with the RAFT mechanism. Both thermally and AIBN-initiated RAFT styrene polymerizations were performed at different temperatures. In general, the molar mass increased with time as expected for a controlled polymerization process. The molar mass distribution also progressively increased. Inefficient control of the molar mass distribution appears to be related to the rate of radical formation, which is not sufficiently fast compared to the overall monomer conversion, as well as to the rate of bond dissociation and reformation with respect to the propagation rate. As a result, both **1** and **2** behave as RAFT agents but, at relatively high conversion, afford polymers endowed with polydispersities as large as in conventional radical polymerizations.

Introduction

The achievement of controlled radical polymerizations is one of the most important goals in precision polymerization because of the versatility and applicability of the radical polymerizations in terms of both monomer structures and simplicity in handling.[1,2] Since the introduction of the concept of reversible termination of growing chains to form dormant species that can be reactivated as polymer radicals, controlled radical polymerization systems have rapidly progressed. Several controlled radical polymerizations were developed, including stable free radical polymerization (SFRP) using stable nitroxyl radicals[3−5] or alkoxyamine[6] initiators and atom transfer radical polymerization (ATPR) mediated by transition metal complexes.[7−9] In these systems, suppression of irreversible polymer chain terminations allowed control of molar mass and molar mass distribution. The molar mass usually increased linearly with conversion, as expected for a controlled polymerization process, leading to polymers with predicted molar masses and narrow polydispersities. In addition, these polymers further grow whenever additional monomer is supplied, and novel materials have therefore been designed with highly differentiated structures, including block,[10] hyperbranched,[11] star, and comb[12] polymers starting from well-known monomers able to undergo free radical polymerization. However, both SFRP and ATPR are successful only for a limited number of monomers and suffer from a number of disadvantages, such as high reaction temperatures and expensive reagents that are sometimes difficult to remove.

Recently, the reversible addition−fragmentation chain transfer process[13−21] (RAFT) was described. The elementary reactions of RAFT (Scheme 1), as elucidated by Rizzardo,[19,21] involve a reversible chain transfer in which a dithioester behaves as a transfer agent reacting with initiating and propagating radicals to give a transfer agent and a species that is able to initiate

Scheme 1. Elementary Reactions in a RAFT Polymerization



polymerization. The dithioester is transferred between the active and dormant chains, thus maintaining the living character of the polymerization. In this respect, Z should activate the C═S double bond to radical addition. To obtain polymers with predetermined molar mass and narrow molar mass distribution, both the rate of addition and fragmentation must be fast relative to the rate of propagation, and the leaving radical (R•) must be able to reinitiate propagation. The former requirement allows rapid consumption of the RAFT agent and fast equilibration of the dormant and active species, while the latter allows the chain reaction to proceed. Not all thiocarbonylthio compounds are effective as RAFT agents. Their efficiency depends on subtle details of the molecular structure.[13] For example, dithiocarbamate derivatives with a nonbonded electron pair of nitrogen included as part of an aromatic system are highly effective, whereas simple *N*,*N*′-dialkyl dithiocarbamates are ineffective as RAFT agents.

Among thiocarbonylthio derivatives, those bearing a phosphoryl or thiophosphoryl function at the thiocarbonyl carbon are of special interest. Indeed, these compounds have long since been known, but after having been employed in agriculture for some time as pesticides,[22] their popularity declined owing to their rather unfriendly environmental impact.

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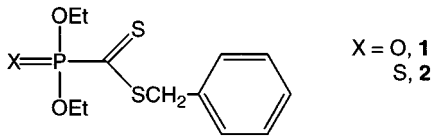
In recent years, we widely investigated the reactivity of phosphoryl and thiophosphoryl dithioesters $(R'O)_2P(O)C(S)SR$ and $(R'O)_2P(S)C(S)SR$ toward free radicals.[23−25] These derivatives are effective traps for radicals, ranging from nucleophilic alkyl radicals (e.g., *tert*-butyl) to electrophilic alkoxy and thiyl radicals (e.g., *tert*-butoxyl and *tert*-butylthiyl), as well as to metal-centered radicals. The trapping process occurred in all cases via thiophilic addition of the radical with formation of spin adducts whose persistence, although closely related to the nature of the substituents R and R′, was in most cases unusually high. Owing to their ability to readily undergo radical addition and to the remarkable persistence of the resulting adducts, these compounds were successfully exploited as stabilizers in the processing of polypropylene.[26]

In this paper, we provide evidence of the effectiveness of benzyl (diethoxyphosphoryl)dithioformate (**1**) and benzyl (diethoxythiophosphoryl)dithioformate (**2**) as RAFT agents in the polymerization of styrene and describe their use in both thermally and AIBN-initiated styrene RAFT polymerizations under different conditions. Indeed, compound **1** is included in the original patent of Rizzardo,[13] but few details were reported.



Experimental Section

Materials. NaH (dry in powder 95%) was purchased from Aldrich, and diethyl phosphite (95%) and Lawesson's reagent (98%) were purchased from Fluka. CS_2 (99% from Carlo Erba) was kept over molecular sieves (0.4 nm), while THF was dried by distillation from $LiAlH_4$. AIBN (98%) was purchased from Fluka and used as received. All solvents were used as received from Aldrich. Styrene (99%) was purchased from Aldrich and washed with 3 × 100 mL of 2.0 M sodium hydroxide and 3 × 100 mL of water, dried with anhydrous sodium sulfate, and stored at 5 °C. Styrene was distilled under vacuum before use.

Benzyl (Diethoxyphosphoryl)dithioformate (1). A solution of diethyl phosphite (1.25 mL, 9.7 mmol) in THF (5 mL) was added dropwise under nitrogen to a suspension of NaH (0.23 g, 9.7 mmol) in THF (10 mL) in a 50 mL two-necked flask equipped with a condenser and a magnetic stirrer. When the evolution of hydrogen was over, the reaction mixture was heated and refluxed for 5 min. After cooling the flask in an acetone−CO_2 bath, dry CS_2 (2.9 mL, 48 mmol) was added. At the end of the addition, the bath was removed and the temperature was allowed to rise to 25 °C. The reaction mixture was then stirred for 30 min, and benzyl bromide (1.3 mL, 11 mmol) was added dropwise. After stirring for an additional 30 min, 30 mL of hexane was added, the mixture was filtered, and the solvent evaporated. The residue was quickly chromatographed over silica gel in a short column (7 cm) using first cycloexane as eluent to remove impurities and then diethyl ether to collect the red fraction (2.3 g, 78% yield). ^{1}H NMR: 1.36 (t, 6H, J = 7.6 Hz, C**H**$_3$CH$_2$O), 4.26 (m, 4H, CH$_3$C**H**$_2$O), 4.46 (s, 2H, SC**H**$_2$Ph), 7.30 (s, 5H, CH$_2$**Ph**). ^{13}C NMR: 16.20 (d, J_{CP} = 6.34 **C**H$_3$CH$_2$O), 40.63 (d, J_{CP} = 2.72 S**C**H$_2$Ph), 64.70 (d, J_{CP} = 6.94 CH$_3$**C**H$_2$O), 128.00, 128.77, 129.26, 133.53 (s, s, s, s, **Ph**), 228.16 (d, J_{CP} = 174.54 P**C**(S)S). ^{31}P NMR: −4.57. Mass spectrometry (+EI) *m*/*z*: 304, 276, 248, 182, 121, 91.

Benzyl (Diethoxythiophosphoryl)dithioformate (2). A mixture of benzyl (diethoxyphosphoryl)dithioformate (2.00 g, 6.58 mmol) and Lawesson's reagent (2.66 g, 6.58 mmol) in dry toluene (20 mL) was refluxed under nitrogen in a flask equipped with a condenser and a magnetic stirrer until the reagent disappeared (checking with TLC, hexane: CH_2Cl_2 7:3 as eluent). At the end of the reaction, the solid Lawesson's reagent was completely dissolved. The crude reaction mixture was filtered after cooling, the solvent evaporated, and cyclohexane was added to the residue that was filtered again. After Kugel−Rohr distillation (175 °C, 0.05 mTorr), pure product was obtained (1.36 g), 65% yield. ^{1}H NMR: 1.36 (t, 6H J = 6.8 Hz C**H**$_3$CH$_2$O), 4.27 (m, 4H CH$_3$C**H**$_2$O), 4.43 (s, 2H SC**H**$_2$-Ph), 7.32 (s, 5H CH$_2$**Ph**). ^{13}C NMR: 15.99 (d, J_{CP} = 7.24 **C**H$_3$-CH$_2$O), 41.59 (d, J_{CP} = 1.61 S**C**H$_2$Ph), 65.01 (d, J_{CP} = 7.24 CH$_3$**C**H$_2$O), 128.05, 128.84, 129.37, 133.67 (s, s, s, s, **Ph**), 231.38 (d, J_{CP} = 132.49 P**C**(S)S).^{31}P NMR: 63.38. Mass spectrometry (+EI) *m*/*z*: 320, 287, 274, 244, 153, 125, 97, 65.

Thermally Initiated RAFT Styrene Polymerizations. A master batch of 20 mL (173.4 mmol) of styrene, 143.9 mg (0.4734 mmol) of **1**, or 150.8 mg (0.4734 mmol) of **2** was prepared, and aliquots of 2.0 mL were placed in polymerization ampules. The content was degassed by freeze and thaw cycles and sealed under nitrogen. The polymerization reaction was performed at the appropriate temperature. 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 on silica gel in vacuo for several hours. Conversion of styrene was estimated gravimetrically. As a typical example, 2.0 mL (17 mmol) of styrene was reacted with 14.9 mg (46.0 μmol) of **2** at 90 °C for 24 h, giving sample PS12 with a yield of 28.6%. Number-average molar mass and polydispersity index resulted in M_n = 25 000 and M_w/M_n 1.38. Following the above procedure, several polystyrene samples were synthesized by performing the polymerizations for different reaction times at 90 and 100 °C. The reaction yields and molar mass values are collected in Table 1.

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

sample[a]	dithio compd	temp (°C)	time (h)	$M_n \times 10^{-3}$	M_w/M_n	conv[b] (%)
PS1	**1**	90	6	5.30	1.12	1.1
PS2	**1**	90	10	10.9	1.14	4.3
PS3	**1**	90	24	20.3	1.89	19.1
PS4	**1**	90	30	24.5	2.19	30.3
PS5	**1**	90	48	34.6	3.43	32.6
PS6	**1**	100	6	3.70	1.12	1.4
PS7	**1**	100	10	9.30	1.39	3.5
PS8	**1**	100	24	21.6	2.43	34.0
PS9	**1**	100	48	70.3	2.96	59.0
PS10	**2**	90	6	8.10	1.09	1.1
PS11	**2**	90	10	14.0	1.10	13.6
PS12	**2**	90	24	25.0	1.38	28.6
PS13	**2**	90	30	27.0	1.54	31.0
PS14	**2**	90	48	38.3	1.79	36.0
PS15	**2**	100	6	5.60	1.09	1.0
PS16	**2**	100	10	13.8	1.08	14.9
PS17	**2**	100	24	35.8	2.17	59.8
PS18	**2**	100	30	38.1	2.32	69.7

[a] Each sample was prepared in bulk by reacting 2.0 mL (17 mmol) of styrene using a molar ratio between styrene and **1** or **2** of 370 mol/mol. [b] Conversions were determined gravimetrically.

AIBN-Initiated RAFT Styrene Polymerization. A master batch of 25 mL (218 mmol) of styrene, 13.7 mg of AIBN, 76.3 mg (0.251 mmol) of **1**, or 80.2 mg (0.251) of **2** was prepared, and aliquots of 2 mL were placed in polymerization ampules. The content was degassed by freeze and thaw cycles and sealed under nitrogen. The polymerization reaction was performed at the appropriate temperature. 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 on silica gel in vacuo for several hours. Conversion of styrene was estimated by

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

sample[a]	dithio compd	temp (°C)	time (h)	$M_n \times 10^{-3}$	M_w/M_n	conv[b] (%)
PS19	**1**	60	13	29.3	1.50	1.2
PS20	**1**	60	18	33.1	1.66	8.4
PS21	**1**	60	24	38.6	1.93	14.2
PS22	**1**	60	48	60.2	2.22	25.7
PS23	**1**	90	3	33.8	1.60	16.1
PS24	**1**	90	6	42.3	2.21	28.7
PS25	**1**	90	18	46.0	2.16	34.5
PS26	**1**	90	24	50.0	2.36	39.2
PS27	**1**	90	48	74.3	2.50	42.8
PS28	**2**	60	6	6.40	1.24	1.1
PS29	**2**	60	18	23.5	1.61	12.4
PS30	**2**	60	24	32.2	2.33	12.2
PS31	**2**	60	30	42.7	2.49	31.8
PS32	**2**	90	3	19.8	1.89	19.7
PS33	**2**	90	6	26.1	1.99	25.0
PS34	**2**	90	18	41.9	2.27	44.0
PS35	**2**	90	24	47.3	2.57	52.0
PS36	**2**	90	30	53.0	2.85	55.7

[a] Each sample was prepared in bulk by reacting 2.0 mL (17 mmol) of styrene with [AIBN] = 3.3×10^{-3} M and **1** or **2**, using a molar ratio between styrene and **1** or **2** of 865 mol/mol. [b] Conversions were determined gravimetrically.

Table 3. Molar Mass and Conversion Data for Polystyrene Samples Prepared via Repolymerization of Styrene in Bulk

sample[a]	original polymeric sample	polymer (g)	styrene (mL)	$M_n \times 10^{-3}$	M_w/M_n	conv[b] (%)
PS37	PS3	0.190	5.0	256	2.01	38.7
PS38	PS11	0.120	5.0	116	1.90	12.8
PS39	PS20	0.178	5.0	190	2.12	18.2
PS40	PS29	0.202	5.0	220	1.53	22.8

[a] Each sample was prepared in bulk by reacting the original polystirene sample with styrene, without any initiator, at 100 °C for 14 h. [b] Conversions were determined gravimetrically.

weighting the obtained polymer. As a typical example, 2.0 mL (17 mmol) of styrene was reacted with 6.1 mg (20 μmol) of **1** and 1.1 mg (6.7 μmol) of AIBN at 90 °C for 6 h, giving sample PS24 with an yield of 29.7%. Number-average molar mass and polydispersity index resulted in M_n = 42 300 and M_w/M_n 2.21.

Following the above procedure, several polystyrene samples were synthesized by performing the polymerizations for different reaction times at 60 and 90 °C. The reaction yields and molar mass values are collected in Table 2.

RAFT Repolymerization of Styrene in Bulk. About 0.20 g of a polystyrene sample, prepared either by thermally initiated or AIBN-initiated RAFT styrene polymerization as above-described, and 5.0 mL (4.5 g, 44 mmol) of styrene were placed in a polymerization ampule. The content was degassed by freeze and thaw cycles and sealed under nitrogen. The polymerization reaction was performed at 100 °C. The resulting polymer was then precipitated into methanol, washed with methanol, and purified as reported for the polystyrene samples. As a typical example, 0.190 g of sample PS3 was reacted with 5.0 mL (44 mmol) of styrene at 100 °C for 14 h, giving sample PS37 with an yield of 38.7%. Number-average molar mass and polydispersity index resulted in M_n = 256 000 and M_w/M_n 2.01. Molar mass and conversion data for prepared samples are listed in Table 3.

Characterization. ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ on a Varian Mercury 400 NMR spectrometer. δ values are given in ppm from TMS. ^{31}P NMR spectra were measured in $CDCl_3$ on a Varian VXR-200 NMR spectrometer. δ values are given in ppm from H_3PO_4 30% in H_2O. Mass spectra were obtained using a Finnigan Mat GCQ ion trap mass spectrometer.

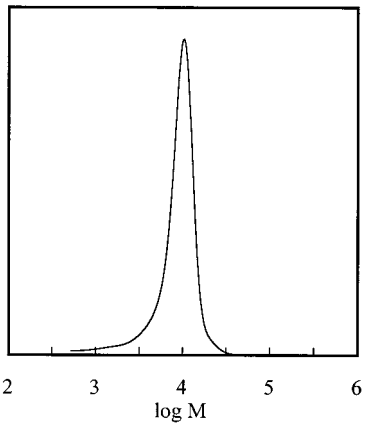


Figure 1. SEC curve of a polystyrene sample prepared at 90 °C for 6 h using **2** as the RAFT agent.

EPR spectra were recorded on an upgraded Bruker ER200D/ESP300 spectrometer equipped with an NMR gauss meter for magnetic field calibration. A Systron Donner 6245A frequency counter was used to determine the *g* factors that were corrected with respect to that of the perylene radical cation in concentrated sulfuric acid. The temperature inside the EPR cavity was controlled using a standard variable temperature accessory.

Average molar masses were determined by SEC of THF solutions with a 590 Waters chromatograph equipped with refractive index and ultraviolet detectors, using PLgel 10^3, 10^4, and 10^5 Å columns calibrated with polystyrene standard samples. The molar mass calculations performed using the refractive index detector gave rise to quite different and systematically lower molar mass values than those obtained with the ultraviolet detector. This was attributed to the presence of the strongly UV-absorbing end group which imparts a molar mass dependence to the UV detection. Accordingly, the molar mass data were determined using the refractive index detector only.

Results and Discussion

To check the effectiveness of benzyl (diethoxyphosphoryl)dithioformate (**1**) or benzyl (diethoxythiophosphoryl)dithioformate (**2**) as RAFT agents, some scouting experiments were performed. Figure 1 shows the SEC curve of a polystyrene sample prepared at 100 °C for 6 h using **2** as the RAFT agent and employing a styrene/**2** molar ratio of 300. The resulting polymer sample, obtained in 14% yield, showed a number-average molar mass of M_n = 5500 with polydispersity index of M_w/M_n = 1.17. From the analysis of the ^{1}H NMR spectrum of this polymer sample, a number-average molar mass of M_n = 5600 was evaluated by comparing the integral of the methylene groups of the ethoxy end group (4.2 ppm) and the phenyl groups (7.3−6.2 ppm) of the polystyrene chain, assuming that only one fragment deriving from the RAFT agent is present per polymer chain. The close agreement between the M_n determined by SEC and by NMR end group analysis confirms that only one fragment is present per polymer chain, as expected in a reversible addition−fragmentation chain transfer mechanism. Similar results could be obtained using **1**.

Further evidence supporting the RAFT mechanism was obtained by electron spin resonance spectroscopy, the technique of choice for investigating free radicals that can often provide direct information on the reactive intermediates. Indeed, when argon-saturated tubes containing styrene and either **1** or **2** (0.0275 M) were heated at 90 °C inside the cavity of an ESR spectrom-

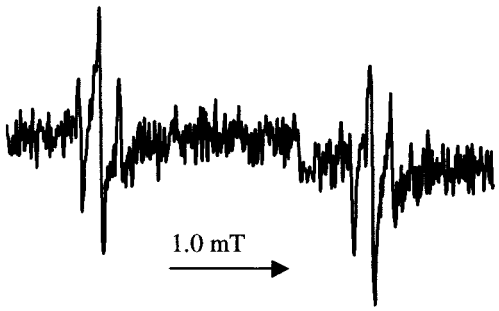
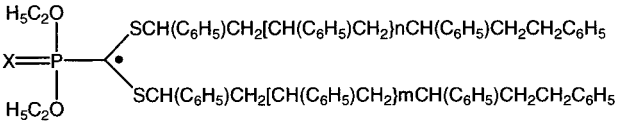
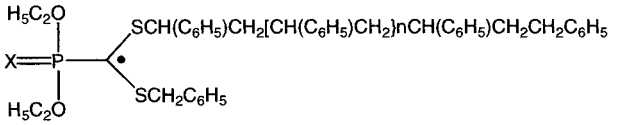


Figure 2. ESR spectrum observed by heating a thoroughly deoxygenated sample of styrene containing a small amount of **1** (0.0275 M).

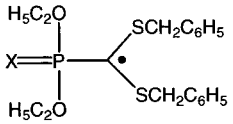
eter, spectra were observed (Figure 2). The spectra were similar in both cases, consisting of a doublet (1:1, 2.15 to 2.25 mT) of triplets (1:2:1, ca. 0.16 mT) with very close *g*-factors (ca. 2.0058). These hyperfine spectral parameters are inconsistent with either the $^{\bullet}CH_2C_6H_5$ benzyl radical[27] or the propagating radical $^{\bullet}CH(C_6H_5)CH_2[CH(C_6H_5)CH_2]_xCH(C_6H_5)CH_2CH_2C_6H_5$ and indicate that the species responsible for the observed spectra are radicals having the general structure **3** and **4**, where the phosphorus atom is responsible for the doublet and the two CH groups for the smaller triplets. It is believed that the propagating radicals resulting from the thermal self-initiated polymerization of styrene add to a chain transfer agent leading to adducts **5**/**6** (not detected). These latter species quickly suffer displacement of the benzyl moiety, leading to new dithioformates that undergo further addition by propagating radicals with formation of radical adducts **3**/**4**. Radicals **3**/**4** cannot be mistaken with either the dibenzyl self-adducts **7**/**8** or the monobenzyl adducts **5**/**6**. Indeed, both species exhibit different ESR spectra, namely a doublet of quintets in the case of the dibenzyl self-adducts (one phosphorus and two + one nearly equivalent hydrogen atoms) for **5**/**6**.



3, X = O; **4**, X = S



5, X = O; **6**, X = S



7, X = O; **8**, X = S

The identification of radicals **3**/**4** is also substantiated by the similarity of their spectral parameters with those previously reported for a large variety of structurally related radicals[24,25] and with those of the authentic dibenzyl self-adducts **7**/**8** obtained by photoreacting compounds **1**/**2** with dibenzyl mercury. In control experiments, compounds **1**/**2** did not exhibit any decomposition at the temperature used for the polymerization (90 °C): thus, prolonged heating of argon-purged *tert*-butylbenzene solution of **1**/**2** did not result in the observation of the ESR spectra of **7**/**8** or in any sensible variation of their NMR spectra.

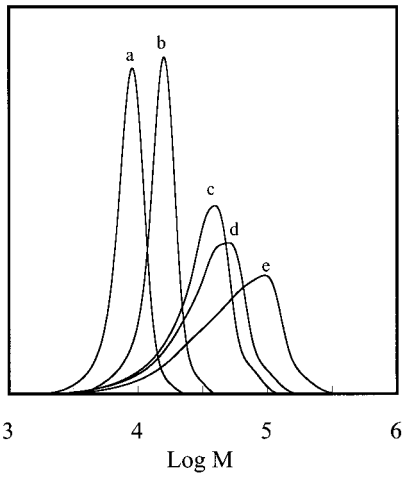


Figure 3. SEC curves of thermally initiated RAFT polystyrene samples prepared at 90 °C using **2** as the RAFT agent at different reaction times: a, 6 h; b, 10 h; c, 24 h; d, 30 h; e, 48 h.

We polymerized styrene with benzyl (diethoxyphosphoryl)dithioformate (**1**) or benzyl (diethoxythiophosphoryl)dithioformate (**2**) as RAFT agents using both a purely thermal initiation and in the presence of a conventional free radical initiator (AIBN). The results will be discussed separately.

Thermally Initiated RAFT Styrene Polymerizations. The thermally initiated RAFT styrene polymerizations were performed at 90 and 100 °C. The molar ratio between styrene and the raft agents was kept constant at 370 in all of the polymerizations. Several polymerizations were performed, and the conversion and the molar mass evolution were studied as a function of time. The molar mass characteristics of the polymers were determined by size exclusion chromatography (SEC). Figure 3 shows the SEC curves of the polystyrene samples prepared at 90 °C using **2** as the RAFT agent. The SEC curves are shifted toward higher values along the molar mass scale with increasing the reaction time, as expected for a controlled polymerization. In addition, the conversion increased monotonically up to around 33% conversion. However, the SEC curves become progressively broader with time. Parts a and b of Figure 4 illustrate the trend of M_n and M_w/M_n as a function of time for the polystyrene samples prepared using **1** and **2**, respectively, at 90 and 100 °C. In all cases, M_n increases linearly with time, and the increase is more pronounced for the reactions performed at higher temperature. At both temperatures, the reactions performed in the presence of the RAFT agent **2** are somewhat faster than those with **1**, and the products present comparatively smaller polydispersity indexes. A maximum reaction yield of 70% was obtained after 30 h at 100 °C using **2**. However, the polydispersity index increases with time from relatively low values (M_w/M_n = 1.1−1.3) after about 10 h to very high values (M_w/M_n > 2.5) at the end of the reaction. As the broadening of the molar mass distribution often indicates the presence of irreversible termination reactions, several polystyrene samples prepared with **1** and **2** and with narrow and broad molar mass distribution were further reacted with styrene at 100 °C for 14 h. The relevant data are collected in Table 3. As a typical example, Figure 5

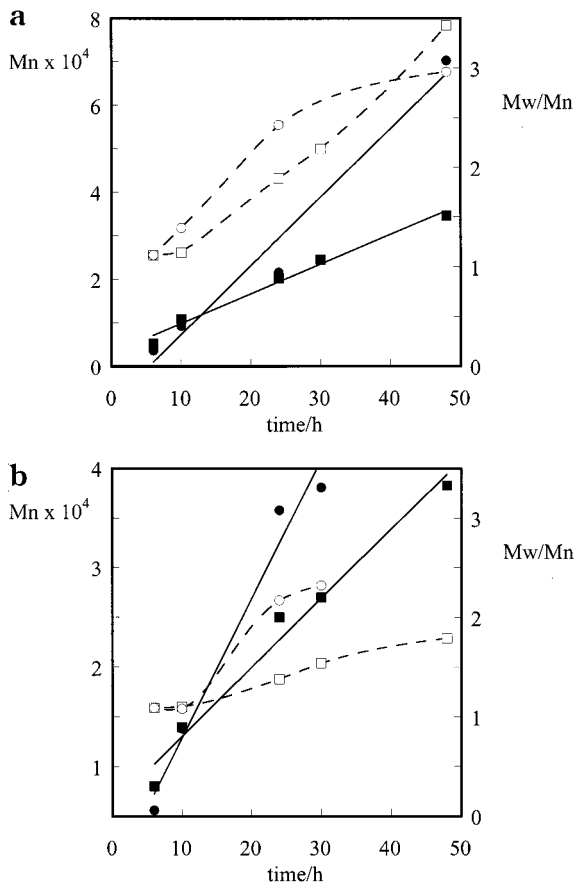


Figure 4. Trend of the number-average molar mass and polydispersity index of thermally initiated RAFT polystyrenes as a function of time. (a) RAFT agent **1**: 90 °C, M_n (■) and M_w/M_n (□); 100 °C, M_n (●) and M_w/M_n (○). (b) RAFT agent **2**: 90 °C, M_n (■) and M_w/M_n (□); 100 °C, M_n (●) and M_w/M_n (○).

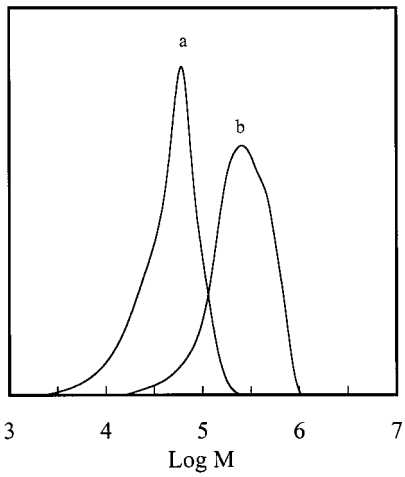


Figure 5. SEC curves of sample PS3 (a) and after repolymerization with styrene (b).

shows the SEC curves of sample PS3 and after repolymerization with styrene. Irrespective of the width of the molar mass distribution and of the RAFT agent employed, the polystyrene samples obtained after repolymerization display a monomodal SEC curve which is shifted toward higher values along the molar mass scale. Although there was no trace of the original polystyrene sample, the molar mass distribution of the samples after repolymerization are broader than that of the original polystyrene sample. These data indicate that the thermally initiated RAFT styrene polymerizations with **1** and **2** are not accompanied by irreversible termination reactions. The origin of the substantial broadening of the molar mass distribution with time becomes evident when the ratio between M_n and the conversion X_a is plotted as a function of time (Figure 6). M_n/X_a, which represents the maximum attainable molar mass, decreases monotonically with time steeply at first and then more gradually until a limiting value of about 40 000 is reached. This limiting value is the same in all systems, irrespective of the RAFT agent and polymerization temperature, and corresponds to a degree of polymerization of 400, which is similar to the molar ratio between the styrene monomer and the RAFT agent used in the various polymerizations. These data clearly indicate that the rate constant of radical formation in the thermally initiated RAFT styrene polymerizations with the RAFT agents **1** and **2** is not large enough to ensure a fast start of the polymerization process in comparison to the overall monomer conversion time by reaction. In addition, the increasing width of the molar mass distribution upon successive repolymerizations indicates that the rate of bond dissociation and re-formation is low relative to the propagation rate. Under these conditions, the polydispersities are as large as in conventional radical polymerizations although the polymer is still able to initiate the polymerization of monomers.

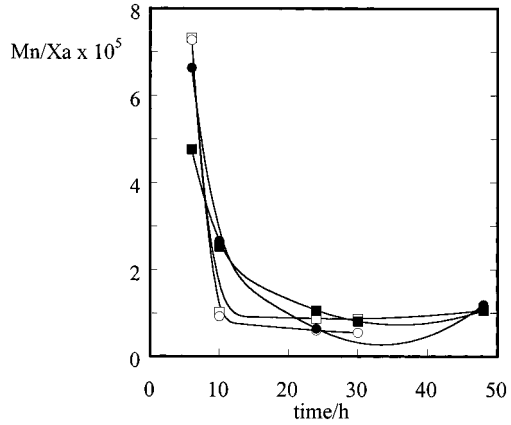


Figure 6. Trend of the ratio between M_n and the conversion X_a as a function of time for thermally initiated RAFT styrene polymerizations: 90 °C and RAFT agent **1** (■); 100 °C and RAFT agent **1** (●); 90 °C and RAFT agent **2** (□); 100 °C and RAFT agent **2** (○).

AIBN-Initiated RAFT Styrene Polymerization. The AIBN-initiated RAFT styrene polymerizations were performed at 60 and 90 °C. The molar ratio of styrene and the RAFT agents was kept constant at 870 in all of the polymerizations, and the ratio of the RAFT agent and AIBN was fixed at 3. Figure 7 shows the SEC curves of the polystyrene samples prepared with AIBN at 60 °C using **2** as the RAFT agent; Figures 8 and 9 report the trend of M_n and M_w/M_n as a function of time for the samples prepared with **1** and **2,** respectively, at 60 and 90 °C. Although M_n progressively increases with time, the width of the molar mass distribution also increases. The widening of the molar mass distribution is more pronounced when the reaction is performed at 90 °C but also occurs at 60 °C. To get information about the incidence and occurrence of irreversible termination reactions in these AIBN-initiated RAFT system, some polystyrene samples with relatively narrow or broad molar mass distribution were further reacted with styrene at 100 °C for 5 h. Irrespective of the width of

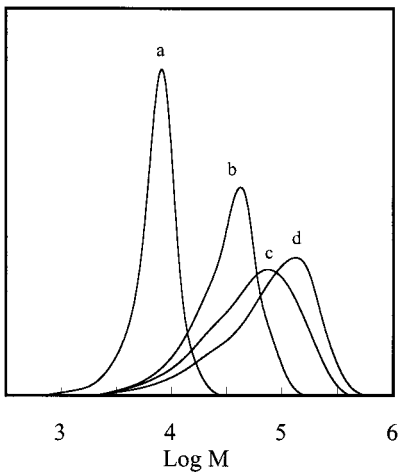


Figure 7. SEC curves of AIBN-initiated RAFT polystyrene samples prepared at 60 °C using **2** as the RAFT agent at different reaction time: a, 6 h; b, 18 h; c, 24 h; d, 30 h.

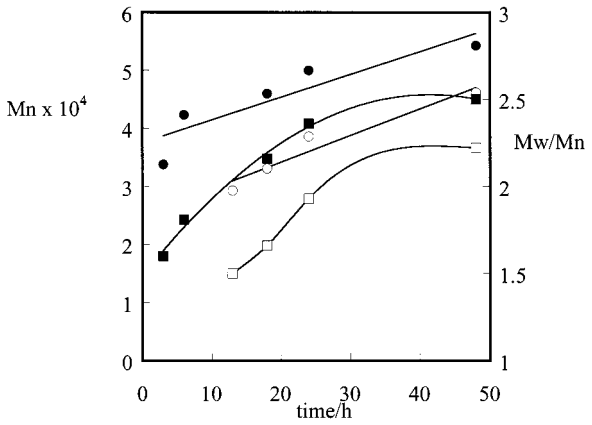


Figure 8. Trend of the number-average molar mass and first polydispersity index of AIBN-initiated RAFT polystyrenes using the RAFT agent **1** as a function of time: 60 °C: M_n (○), M_w/M_n (□); 90 °C: M_n (●), M_w/M_n (■).

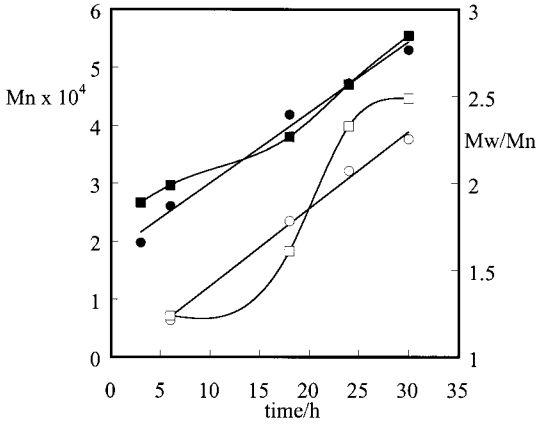


Figure 9. Trend of the number-average molar mass and first polydispersity index of AIBN-initiated RAFT polystyrenes using the RAFT agent **2** as a function of time: 60 °C: M_n (○), M_w/M_n (□); 90 °C: M_n (●), M_w/M_n (■).

the molar mass distribution and of the RAFT agent employed, the polystyrene samples obtained after repolymerization present a molar mass distribution centered at higher molar mass values than the original polystyrene sample with little or no trace of it. In addition, the molar mass distribution of the samples after repolymerization are broader than the one of the original polystyrene sample.

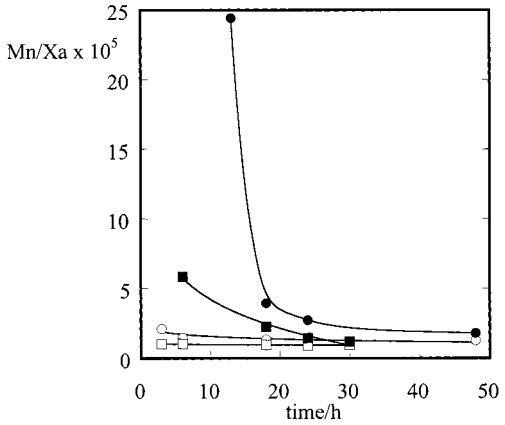


Figure 10. Trend of M_n/X_a as a function of time for AIBN-initiated RAFT styrene polymerizations: 60 °C and RAFT agent **1** (●); 90 °C and RAFT agent **1** (○); 60 °C and RAFT agent **2** (■); 90 °C and RAFT agent **2** (□).

Figure 10 reports M_n/X_a as a function of time. At 60 °C, M_n/X_a decreases with time until a limiting value of about 100 000 is reached, which corresponds to the expected limiting molar mass. For the samples prepared at 90 °C, M_n/X_a is constant and corresponds to the same limiting molar mass. These findings indicate that at 60 °C the rate constant of radical formation in the AIBN-initiated RAFT styrene polymerizations is not sufficiently fast relative to the overall monomer conversion time, thus possibly contributing to the large polydispersities. However, the constancy of M_n/X_a at 90 °C indicates a fast start of the process. In this case, the inefficient control of the molar mass distribution is probably related to the rate of bond dissociation and reformation with respect to the propagation rate, in agreement with the results obtained in the thermally initiated RAFT polymerizations.

Concluding Remarks

Benzyl (diethoxyphosphoryl)dithioformate (**1**) and benzyl (diethoxythiophosphoryl)dithioformate (**2**) were employed in the controlled radical polymerization of styrene. The reactive intermediates involved in the process were identified by electron spin resonance spectroscopy as those derived from addition of the polymer propagating radical to the chain transfer agent, in agreement with the RAFT mechanism. Thermally initiated and AIBN-initiated RAFT styrene polymerizations were performed. In the thermally initiated systems, the molar mass increased linearly with time as expected for a controlled polymerization process. However, the molar mass distribution progressively increased. Repolymerization data suggested that the rate constant of radical formation is 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 appears to be low relative to the propagation rate.

In the AIBN-initiated systems, M_n progressively increases with time, and the width of the molar mass distribution also increases. Repolymerization experiments indicated that at 60 °C the rate of radical formation is not sufficiently fast in comparison to the overall monomer conversion, whereas at 90 °C a fast start of the process occurs. At both temperatures, the inefficient control of the molar mass distribution appears to be also related to the rate of bond dissociation and re-formation with respect to the propagation rate.

In conclusion, both benzyl (diethoxyphosphoryl)-dithioformate (**1**) and benzyl (diethoxythiophosphoryl)-dithioformate (**2**) behave as RAFT agents in styrene radical polymerization. On the other hand, the increase of the polydispersity value with conversion is a puzzling finding. Thermal decomposition of **1**/**2** during the process might account for the increase in molar mass distribution, but control experiments suggest that this should not be the case. If, as we have suggested above, the addition fragmentation rate is slower than the propagation, the growing polymer molecules tend to terminate by themselves, the phenomenon becoming more important at high conversion owing to the increased viscosity. On the other hand, we do not have any evidence of the formation of products coming from direct coupling of two radicals **3**/**4** or of radicals **3**/**4** with the propagating chain.[28] The estimation of the functionality of the high conversion polymer would provide information in this respect. Consequently, this investigation is being undertaken in order to obtain a better insight into the polymerization of styrene in the presence of **1**/**2**. These new studies will also include ESR experiments aimed at measuring the steady-state concentration of the propagating radicals under different conditions (molar ratio styrene: **1**/**2**, temperature, etc.) and possibly at determining the rates of radical addition to **1**/**2** and of fragmentation of radicals **3**/**4**. The results of these studies are beyond the scope of the present paper and will be reported elsewhere.

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