Searching for More Effective Agents and Conditions for the RAFT Polymerization of MMA: Influence of Dithioester Substituents, Solvent, and Temperature

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ABSTRACT: A series of tertiary dithiobenzoates differently substituted on the phenyl group (Z) were synthesized in order to investigate the RAFT-mediated polymerization of MMA. The chain-transfer agent 2-cyanoprop-2-yl dithiobenzoate, although an excellent RAFT agent for polymerization of MMA, does not yield a very narrow polydispersed polymer at low conversion. The introduction of electron-withdrawing substituents on the dithiobenzoate aromatic ring improves the activity of the chain-transfer agent narrowing the molecular weight distribution, especially in the first 2 h of the process; conversely, electrondonating substituents deteriorate the performance of the process in the early stages. Substituents on the dithiobenzoate that, for reasons of steric hindrance reduce the conjugation of the phenyl with the C=S double bond of the dithiogroup, diminish the effectiveness of the chain-transfer agent. The nature of the leaving group (R) also has a strong influence on the process: the substitution of 2-cyanoprop-2-yl with the bulkier 2-cyano-4-methylpent-2-yl as leaving group improves remarkably the MMA polymerization, especially in the early stages. The solvent effect on MMA RAFT polymerization using benzene, acetonitrile, and DMF was also investigated. The lower propagation rate constant of MMA in benzene gives rise to reduced rates of polymerization but narrower polydispersities of the polymer, especially at low conversions. The RAFT polymerizations of MMA were carried out at 60 and 90 °C to assess the temperature dependence of the process. The higher temperature increases both the rate of polymerization and the transfer constant of the RAFT agent, resulting in lower polydispersities at a given conversion. Ab initio calculations confirmed the observed experimental results.

Introduction

The reversible addition fragmentation chain-transfer process (RAFT) has been intensively investigated since its first reports.¹⁻³ The reason for the great interest in this methodology resides in its applicability to a wide variety of monomers, ability to afford polymers of low polydispersity, ability to finely control the molecular weight,^{4,5} and ability to allow for the generation of complex macromolecular architectures such as gradient or block copolymers^{2,3} and star polymers.^{4,6,7} By choosing the appropriate RAFT agent, it is possible to fit the different monomer requirements.^{2,8–11} Among the more common monomers, MMA, whose polymeric growing chain is a tertiary radical, is one of the most demanding with regard to the chain-transfer agent (CTA). Thus, in the dithioester 2 (Scheme 1),¹² R must be an excellent leaving group but, at the same time, a good reinitiating radical. Indeed, the tertiary cumyl and 2-cyanoprop-2yl are appropriate for MMA polymerization because they suit both of the essential requirements, whereas the triphenylmethyl radical, being too stable, cannot initiate a new radical chain and the benzyl group does not have an adequate leaving ability.^{5,13} Recently a polymerization of MMA controlled by a CTA which has a secondary leaving R group (methoxycarbonylphenylmethyl) was reported.¹⁴ This radical appears to be sufficiently stable for replacement by the PMMA growing chain and, at the same time, reactive enough toward MMA to re-

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initiate the radical process. However, the polydispersity of the polymer obtained at low conversion is higher than that observed using CTAs characterized by higher transfer constant (e.g., bearing 2-cyanoprop-2-yl as leaving group). The group Z in dithioesters 2 influences the stability of the intermediate radicals and modifies the reactivity of C=S double bond toward radical addition.^{5,8,15} The group Z plays an important role especially in MMA polymerization and, for instance, a phenyl as a stabilizing Z group is preferable in order to narrow the polydispersity and to prevent a bimodal molecular weight distribution.¹⁶ The faster consumption of the initial RAFT agent 2 is due to the role of the phenyl group which increases the stability of the intermediate radicals 3 and 4 and thereby increases the addition rate of the growing radical chains to the C=S double bond.⁵ However, even 2-cyanoprop-2-yl dithiobenzoate (2a), considered one of the best CTAs for MMA polymerization, does not give a very narrow polydispersed polymer at low conversion.

In the present work, new RAFT agents were synthesized varying the substituents on the phenyl of the dithiobenzoate in order to probe steric, polar, and resonance effects on the RAFT process. To achieve this, methyl-, methoxy-, fluoro-, cyano-, trifluoromethyl-, and phenyl-substituted dithiobenzoates were investigated as MMA polymerization mediators. Aromatic Z groups such as pyridine and naphthalene were also considered. The effects of different substituent groups on the molecular weight distribution of the polymer, especially in the first 2 h of the polymerization were observed. The influence of the substitution position on the aromatic Z

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Scheme 1. Steps Involving the Dithioester Functionality in the RAFT Polymerization Mechanism

$$(\underbrace{\overset{P_{n}}{M}}_{M} + \underbrace{\overset{S}{\sum}}_{Z} \underbrace{(2)}_{Z} \underbrace{\overset{P_{n}}{\longrightarrow}}_{Z} \underbrace{\overset{S}{\otimes}}_{Z} \underbrace{\overset{R_{n}}{\leftrightarrow}}_{Z} \underbrace{\overset{P_{n}}{\sum}}_{Z} \underbrace{\overset{P_{n}}{\longrightarrow}}_{Z} \underbrace{\overset{P_{m}}{\longrightarrow}}_{-P_{m}} \underbrace{\overset{P_{m}}{\longrightarrow}}_{(4)} \underbrace{\overset{S}{Z}}_{Z} \underbrace{\overset{P_{m}}{\longrightarrow}}_{Z} \underbrace{$$

group was also studied, as well as that of the bulkiness of the leaving group. The solvent and temperature dependence of the process were also investigated. The most representative intermediate radical models were subjected to ab initio calculations, and the calculated enthalpy barrier of the addition and the fragmentation reactions of the intermediate radicals were compared with the experimental results.

Experimental Section

Chemicals. 2-Bromo-m-xylene (Aldrich, 98%), 4-bromo-mxylene (Aldrich, 97%), 4-bromoanisole (Aldrich, 99%), 1-bromo-2,4-dimethoxybenzene (Aldrich, 97%), 1-bromo-4-fluorobenzene (Aldrich, 99%), 1-bromo-2,4-difluorobenzene (Aldrich, 98%), α-bromo-p-tolunitrile (Aldrich, 98%), 5-methylisophthalonitrile (Lancaster, 97%), 3,5-bis(trifluoromethyl)benzyl bromide (Aldrich, 97%), 2,3,4,5,6-pentafluorobenzyl chloride (Lancaster, 97%), 4-bromobiphenyl (Aldrich, 98%), 2-bromonaphthalene (Aldrich, 97%), 1-(bromomethyl)naphthalene (Aldrich, 98%), 4-(chloromethyl)pyridine hydrochloride (Fluka, 97%), 1 N iodine solution (Aldrich, 0.96N in water), sodium methoxide solution (Aldrich, 25% in methanol), carbon disulfide (Fluka, 99%), and 2,2'-azobis(2,4-dimethylpentanenitrile) (VAZO52, Du Pont, 99%) were used as received. Azobis(isobutirronitrile) (AIBN, Aldrich 98%) was crystallized from methanol. p-Toluenesulfonic acid monohydrate (Aldrich, 98.5%) was anhydrified in a Dean-Stark apparatus using toluene as azeotropic solvent. Methyl methacrylate (MMA, Aldrich, 99%) was purified by filtration through alumina, fractionated under reduced pressure, and flash distilled immediately prior to use. THF for synthesis was freshly distilled from LiAlH₄. Silica gel (Kieselgel 60, Merck, 230-400 mesh) was used for flash chromatography purification.

Analytical Techniques. NMR analysis were performed on a Brüker AC200 (¹H = 200 MHz, ¹³C = 50 MHz), Brüker DRX500 (¹H = 500 MHz, ¹³C = 125.6 MHz), or Varian Mercury 400 (¹H = 400 MHz, ¹³C = 100 MHz) spectrometers in CDCl₃ (δ , ppm from TMS). Mass Spectroscopy data were collected on a ThermoQuest MAT95XL high-resolution mass spectrometer. Size exclusion chromatography (SEC) was performed on a Waters Associates liquid chromatograph equipped with a differential refractometer and with three PLgel, 5 μ m, mixed C columns (MW range 200–2 000 000) and one PLgel, 3 μ m, mixed E column (MW range up to 30 000) at 22 °C with THF as eluent (flow rate 1 mL/min) calibrated with Polymer Laboratories polystyrene standards.

Bis(thiobenzoyl) Disulfide (1a). (Method A). A THF solution (10 mL) of bromobenzene (1.05 mL, 10 mmol) was added dropwise to a mixture of Mg (0.25 g, 10 mg atom) in THF (40 mL) and a crystal of I_2 in a two-necked round-bottom flask equipped with condenser and a magnetic stirrer with a nitrogen atmosphere. To initiate the reaction, the mixture was gently heated during the initial stages of the addition. After 3 h, carbon disulfide (1 mL, 16.7 mmol) was added dropwise and the solution was stirred for further 3 h. The solvent was then removed under vacuum and the resulting deep red viscous liquid was dissolved in a diluted K₂CO₃ solution (100 mL), filtered, washed with ethyl ether $(2 \times 50 \text{ mL})$, and poured in a round-bottom flask equipped with magnetic stirrer. An aqueous solution of iodine 0.96 N (10.42 mL, 10 mmol) was then added dropwise. During the addition, the solution started to change color from dark red to pink as the disulfide precipitated. After elimination of excess I₂ with few crystals of Na₂S₂O₃, the mixture was extracted with methylene chloride, dried over sodium sulfate, and evaporated. The crude product was used for the subsequent reaction without any further purification. A crystalline red solid (yield 90.2%) was obtained. ¹H NMR (400 MHz, CDCl₃), δ: 7.46 (m, m-ArH, 4H); 7.62 (m, *p*-Ar*H*, 2H); 8.09 (d, J = 8.6 Hz, *o*-Ar*H*, 4H). ¹³C NMR (100 MHz, CDCl₃), δ : 127.58 (Ar*C*-3); 128.66 (Ar*C*-2); 133.18 (Ar*C*-4); 143.66 (Ar*C*-1); 219.54 (*C*=S).

Bis(2,6-dimethylthiobenzoyl) Disulfide (1b). Following Method A using 2-bromo-*m*-xylene (1.33 mL) as starting material, the crude product was purified by flash chromatography (eluent, hexane/methylene chloride = 8:2). A crystalline red solid (yield 91.8%) was obtained. ¹H NMR (200 MHz, CDCl₃), δ : 2.33 (s, *CH*₃, 12H); 7.05–7.28 (m, Ar*H*, 6H). ¹³C NMR (50 MHz, CDCl₃), δ : 19.53 (*CH*₃); 128.01 (Ar*C*-3); 129.17 (Ar*C*-2); 133.87 (Ar*C*-4); 144.01 (Ar*C*-1); 229.05 (*C*=S).

Bis(2,4-dimethylthiobenzoyl) Disulfide (1c). Following Method A using 4-bromo-*m*-xylene (1.35 mL) as starting material, the crude product was purified by flash chromatography (eluent, hexane/methylene chloride = 8:2). A red liquid (yield 75.3%) was obtained. ¹H NMR (200 MHz, CDCl₃), δ : 2.38 (s, CH₃, 6H), 2.40 (s, CH₃, 6H); 7.04–7.38 (m, ArH, 6H). ¹³C NMR (50 MHz, CDCl₃), δ : 19.72 (*o*-CH₃); 21.30 (*p*-CH₃); [126.25; 126.89; 131.85; 134.46; 140.50; 142.13 (ArC)]; 222.78 (C=S).

Bis(4-methoxythiobenzoyl) Disulfide (1d). Following Method A using 4-bromoanisole (1.25 mL) as starting material, the crude product was purified by chromatography on alumina (eluent, methylene chloride). A deep red solid (yield 87%) was obtained. ¹H NMR (400 MHz, CDCl₃), δ : 3.90 (s, *CH*₃, 6H); 6.93 (d, *J* = 8.8 Hz, *m*-ArH, 4H); 8.19 (d, *J* = 8.8 Hz, *o*-ArH, 4H). ¹³C NMR (100 MHz, CDCl₃), δ : 55.67(*C*H₃); 113.84 (ArC-3); 130.06 (ArC-2); 136.91 (ArC-1); 164.23 (ArC-4); 217.56(*C*=S).

Bis(2,4-dimethoxythiobenzoyl) Disulfide (1e). Following Method A using 1-bromo-2,4-dimethoxybenzene (2.17 g) as starting material, the crude product (1.34 g) was not purified because of its instability toward cleaning procedures and was directly used for the subsequent reaction.

Bis(4-fuorothiobenzoyl) Disulfide (1f). Following Method A using 1-bromo-4-fluorobenzene (1.1 mL) as starting material, the crude product was purified by flash chromatography (eluent, hexane/methylene chloride = 8:2). A deep red solid (yield 45%) was obtained. ¹H NMR (200 MHz, CDCl₃), δ : 7.07–7.23 (m, *m*-ArH, 4H); 8.08–8.22 (m, *o*-ArH, 4H). ¹³C NMR (50 MHz, CDCl₃) δ : 115.77 (d, ²J_{CF} = 22 Hz, 3-ArC); 130.00 (d, ³J_{CF} = 9.3 Hz 2-ArC);139.84 (ArC-1); 165.96 (d, ¹J_{CF} = 255.5 Hz, 4-ArC); 217.20 (C=S).

Bis(2,4-difluorothiobenzoyl) disulfide (1g). Following Method A using 1-bromo-2,4-difluorobenzene (1.13 mL) as starting material, the crude product (0.66 g) was not purified because of its instability toward cleaning procedures and was directly used for the subsequent reaction.

Bis(4-cyanothiobenzoyl) Disulfide (1i). (Method B). A 25% solution of sodium methoxide in methanol (4.57 mL, 20 mmol) was added to a suspension of sulfur (0.64 g, 20 mmol) and α -bromo-*p*-tolunitrile (1.96 g, 10 mmol) in methanol (50 mL) in a round-bottom flask equipped with a condenser and magnetic stirring. After 3 h, the solvent was removed and the resulting dark brown crude product was dissolved in a diluted solution of NaHCO₃. After being washed with ethyl ether (2 \times 50 mL), an aqueous solution of iodine 0.96 N (10.42 mL, 10 mmol) was added dropwise. During the addition, the solution started to change color from dark brown to pink as the disulfide precipitated. After elimination of excess I2 with few crystals of Na₂S₂O₃, the mixture was extracted with ethyl ether and dried over sodium sulfate. After removal of the solvent, the brown solid crude product (yield 85.4%) was used for the subsequent reaction without any further purification. ¹H NMR (400 MHz, CDCl₃), δ : 7.76 (d, J = 8 Hz, o-ArH, 4H); 8.11 (d, J = 8 Hz, m-ArH, 4H). ¹³C NMR (100 MHz, CDCl₃) δ : 116.17 (ArC-4); 117.80 (CN); 127.89 (ArC-2); 132.50 (ArC-3); 146.11 (ArC-1); 216.23 (C=S).

Bis(3,5-dicyanothiobenzoyl) Disulfide (1j). Following Method B using 3,5-dicyano α -bromotoluene¹⁷ (2.07 g) as starting material, the crude product (0.44 g) was not purified because of its instability toward cleaning procedures and was directly used for the subsequent reaction.

Bis(3,5-bis(trifluoromethyl)thiobenzoyl) Disulfide (1k). Following Method B using 3,5-bis(trifluoromethyl)benzyl bromide (1.83 mL) as starting material, the crude product (0.87 g) was not purified because of its instability toward cleaning procedures and was directly used for the subsequent reaction.

Bis(2,3,4,5,6-pentafluorothiobenzoyl) **Disulfide** (11). Following Method B using 2,3,4,5,6-pentafluorobenzyl chloride (1.36 mL) as starting material, the crude product was not purified (yield 22.2%) and was directly used for the subsequent reaction. ¹³C NMR (100 MHz, CDCl₃) δ : 118.23 (tt, ²*J*_{CF} = 16.6 Hz, ³*J*_{CF} = 3.9 Hz, ArC-1); 137.72 (dm, ¹*J*_{CF} = 257.0 Hz, ArC-3); 142.34 (dm, ¹*J*_{CF} = 257.9 Hz, ArC-2); 146.58 (dm, ¹*J*_{CF} = 244.0 Hz, ArC-4); 209.67 (C=S).

Bis(4-phenylthiobenzoyl) Disulfide (1n). Following Method A using 4-bromobiphenyl (2.33 g) as starting material, after the addition of the iodine solution, the aqueous suspension was filtered and washed with water and then with methanol. A light brown solid (yield 92%) poorly soluble in cold solvents (ethyl acetate, chloroform) was obtained. ¹H NMR (400 MHz, CDCl₃/CS₂: 1/1), δ : [7.38–7.49 (m, 6H); 7.63–7.68 (m, 8H) (ArH)]; 8.20 (d, J = 8 Hz, 4H, p-ArH). ¹³C NMR (100 MHz, CDCl₃/CS₂: 1/1) δ : [126.92; 126.97; 128.20; 128.86; 139.36; 142.03; 145.65 (ArC)]; 217.29 (C=S).

Bis(2-naphthylthioyl) Disulfide (10). Following Method A using 2-bromo-naphthalene (2.07 g) as starting material, the crude product (0.86 g) was not purified because of its instability toward cleaning procedures and was directly used for the subsequent reaction.

Bis(1-naphthylthioyl) Disulfide (1p). Following Method B using 1-(bromomethyl)naphthalene (2.21 g) as starting material, the crude product (1.34 g) was not purified because of its instability toward cleaning procedures and was directly used for the subsequent reaction.

Triphenylmethyl Dithioisonicotinate (5h). A solution of 4-picolyl chloride hydrochloride (1.64 g, 10 mmol) in methanol (30 mL) was added to a suspension of sulfur (0.65 g, 20 mmol) and sodium methoxide 25% (6.5 mL, 30 mmol) in methanol (20 mL) in a round-bottom flask equipped with condenser and magnetic stirring. After 3 h, a solution of triphenyl bromomethane (3.23 g, 10 mmol) in ethyl ether (30 mL) was added dropwise to the dark-brown mixture that was stirred for an additional 2 h. The solvent was removed under vacuum, and the residue was dissolved with ethyl ether and then filtered. After the solvent was removed, the crude product was quickly passed through a small column filled with silica gel using ethyl ether as solvent to remove part of the impurities. A purple solid (1.7 g) was obtained, and it was used without further purification because of its instability.

2-Cyanoprop-2-yl Dithiobenzoate (2a). 2a was synthesized as previously reported. 12

2-Cyanoprop-2-yl(2,6-dimethyl) Dithiobenzoate (2b). The solution of 1b (0.508 g, 1.4 mmol) and the azo compound (AIBN) (0.266 g, 1.62 mmol) in ethyl acetate (120 mL) was degassed in a round-bottom flask equipped with condenser and magnetical stirring and then refluxed in nitrogen atmosphere for 16 h. The end of the reaction was checked by TLC. After the solvent was removed in a vacuum, the crude product was purified by flash chromatography (eluent, hexane/ethyl ether = 7:3) obtaining a crystalline pink solid (yield 96%). ¹H NMR (200 MHz, CDCl₃), δ : 1.95 (s, 6H, C(CH₃)₂CN); 2.34 (s, 6H, ArCH₃); 6.97–7.24 (m, 3H, ArH). ¹³C NMR (50 MHz, CDCl₃), δ : 18.93 (ArCH₃); 26.03 (C(CH₃)₂CN); 47.54 (C(CH₃)₂CN); 119.67 (CN); [128.01; 128.97; 133.32; 144.89 (ArC)]; 230.12 (C= S). Accurate Mass: 249.0652 (theoretical mass for C₁₃H₁₅-NS₂: 249.0646).

2-Cyanoprop-2-yl(2,4-dimethyl) Dithiobenzoate (2c). Following the procedure for compound **2b** using **1c** (0.508 g) and AIBN as azo compound, after flash chromatography (eluent, hexane/ethyl ether = 8:2), a crystalline red solid (yield 90.1%) was obtained. ¹H NMR (200 MHz, CDCl₃), δ : 1.91 (s,

6H, C(CH₃)₂CN); 2.33 (s, 3H, *o*-ArCH₃); 2.36(s, 3H, *p*-ArCH₃); 6.98–7.21 (m, 3H, ArH). ¹³C NMR (50 MHz, CDCl₃), δ : 19.40 (*o*-ArCH₃); 21.24 (*p*-ArCH₃); 26.09 (C(CH₃)₂CN); 41.97 (C(CH₃)₂CN); 119.81 (CN); [126.31; 127.71; 131.853; 133.75; 140.08; 143.19 (ArC)]; 228.05 (C=S). Accurate Mass: 249.0650 (theoretical mass for C₁₃H₁₅NS₂: 249.0646).

2-Cyanoprop-2-yl(4-methoxy) Dithiobenzoate (2d). Following the procedure for compound **2b** using **1d** (0.513 g) and AIBN as azo compound, after flash chromatography (eluent, methylene chloride), a crystalline red solid (yield 86%) was obtained. ¹H NMR (200 MHz, CDCl₃), δ : 1.94 (s, 6H, C(CH₃)₂-CN); 3.87 (s, 3H, OCH₃); 6.88 (d, J = 8.95 Hz, 2H, *m*-ArH); 8.00 (d, J = 8.95, 2H, *o*-ArH). ¹³C NMR (50 MHz, CDCl₃), δ : 26.66 (C(CH₃)₂CN); 41.50 (C(CH₃)₂CN); 55.61 (OCH₃); 120.29 (CN); 113.66 (ArC-3); 128.77 (ArC-2); 137.66 (ArC-1); 164.02 (ArC-4); 220.40 (C=S). Accurate Mass: 251.0441 (theoretical mass for C₁₂H₁₂NOS₂: 251.0439).

2-Cyanoprop-2-yl(2,4-dimethoxy) Dithiobenzoate (2e). Following the procedure for compound **2b** using **1e** (0.597 g) and AIBN as azo compound, after flash chromatography (eluent, ethyl ether), a red solid (yield 79.8%) was obtained. ¹H NMR (200 MHz, CDCl₃), δ : 1.87 (s, 6H, C(CH₃)₂CN); [3.80 (s, 3H); 3.82 (s, 3H) (OCH₃)]; 6.35-6.53 (m, 2H, *m*-ArH); 7.69 (d, J = 8.6, 1H, *o*-ArH). ¹³C NMR (50 MHz, CDCl₃), δ : 26.16 (C(CH₃)₂CN); 41.48 (C(CH₃)₂CN); [55.40; 55.64 (OCH₃)]; 120.37 (CN); [98.27; 105.14; 128.03; 131.93; 156.92; 163.53 (ArC)]; 221.05 (*C*=S). Accurate Mass: 281.0541 (theoretical mass for C₁₃H₁₅NO₂S₂: 281.0544).

2-Cyanoprop-2-yl(4-fluoro) Dithiobenzoate (2f). Following the procedure for compound **2b** using **1f** (0.479 g) and AIBN as azo compound, after flash chromatography (eluent, hexane/ethyl ether = 7:3), a deep pink crystalline solid (yield 92%) was obtained. ¹H NMR (200 MHz, CDCl₃), δ : 1.94 (s, 6H, C(CH₃)₂CN); 7.08 (t, $J_{\rm HF}$ = 8.55 Hz, 2H, *m*-ArH); 7.97 (m, 2H, o-ArH). ¹³C NMR (50 MHz, CDCl₃), δ : 26.47 (C(CH₃)₂CN); 45.85 (C(CH₃)₂CN); 115.60 (d, ² $J_{\rm CF}$ = 22 Hz, ArC-3); 119.85 (d, ¹ $J_{\rm CF}$ = 254.2 Hz, ArC-4); 220.80 (CN). Accurate Mass: 239.0238 (theoretical mass for C₁₁H₁₀FNS₂: 239.0239).

2-Cyanoprop-2-yl(2,4-difluoro) Dithiobenzoate (2g). Following the procedure for compound **2b** using **1g** (0.530 g) and AIBN as azo compound, after flash chromatography (eluent, petroleum spirit/ethyl ether: 8:2), a red oil (yield 31.6%) was obtained. ¹H NMR (500 MHz, CDCl₃), δ : 1.92 (s, 6H, C(CH₃)₂CN); 6.80–6.96 (m, 2H, *m*-ArH); 7.60–7.69 (m, 1H, *o*-ArH). ¹³C NMR (125.6 MHz, CDCl₃), δ : 26.23 (C(CH₃)₂CN); 42.24 (*C*(CH₃)₂CN); 104.79 (dd, ²J_{CF} = ²J_{CF} = 25.9 Hz, ArC-3); 111.80 (dd, ²J_{CF} = 21.7 Hz, ⁴J_{CF} = 3.7 Hz, ArC-5); 115.10 (dd, ²J_{CF} = 24.0 Hz, ⁴J_{CF} = 7.9 Hz, ArC-1); 119.52 (CN); 131.38 (dd, ³J_{CF} = 10.3 Hz, ³J_{CF} = 2.4 Hz, ArC-6); 158.21 (dd, ¹J_{CF} = 257.4 Hz, ³J_{CF} = 12.8 Hz, ArC-2); 164.46 (dd, ¹J_{CF} = 255.8 Hz, ³J_{CF} = 11.8 Hz, ArC-4); 216.95 (d, ³J_{CF} = 3.0 Hz, *C*=S). Accurate Mass: 257.0136 (theoretical mass for C₁₁H₉F₂NS₂: 257.0144).

2-Cyanoprop-2-yl Dithioisonicotinate (2h). The solution of **5h** (1.702 g, 4.28 mmol) and AIBN (0.913 g, 5.56 mmol) in ethyl acetate (120 mL) was degassed in a round-bottom flask equipped with condenser and magnetic stirring and then refluxed for 16 h. The end of the reaction was checked by TLC. After the solvent was removed under vacuum, the crude product was purified by flash chromatography (eluent, ethyl ether). 0.69 g of a red oil (yield 72.3%) were obtained. ¹H NMR (200 MHz, CDCl₃), δ : 1.92 (s, 6H, C(CH₃)₂CN); 7.64 (d, J = 4.48 Hz, 2H, *o*-ArH); 8.70 (d, J = 4.48 Hz, 2H, *m*-ArH). ¹³C NMR (50 MHz, CDCl₃), δ : 26.14 (C(CH₃)₂CN); 41.91 (C(CH₃)₂-CN); 119.12 (CN); 119.69 (ArC-2); 149.50 (ArC-1); 150.34 (ArC-3); 220.62 (C=S). Accurate Mass: 222.0288 (theoretical mass for C₁₁H₁₀N₂S₂: 222.0285).

2-Cyanoprop-2-yl 4-Cyanodithiobenzoate (2i). Following the procedure for compound **2b** using **1i** (0.499 g) and AIBN as azo compound, the crude product was first purified by sublimation to remove the AIBN decomposition byproduct (tetramethyl succinonitrile) and then by flash chromatography (eluent, hexane/ethyl acetate = 8:2). A purple crystalline solid (yield 35%) was obtained. ¹H NMR (200 MHz, CDCl₃), δ : 1.97

(s, 6H, C(CH₃)₂CN); 7.72 (d, J = 8.38 Hz, 2H, o-ArH); 7.97 (d, J = 8.38 Hz, 2H, m-ArH). ¹³C NMR (50 MHz, CDCl₃), δ : 26.28 (C(CH₃)₂CN); 42.18 (C(CH₃)₂CN); 115.71 (ArC-4); 117.85 (ArCN); 119.28 (C(CH₃)₂CN); 127.07 (ArC-3); 132.32 (ArC-2); 146.97 (ArC-1); 220.54 (C=S). Accurate Mass: 246.0280 (theoretical mass for C₁₂H₁₀N₂S₂: 246.0285).

2-Cyanoprop-2-yl 3,5-Dicyanodithiobenzoate (2j). Following the procedure for compound **2b** using **1j** (0.569 g) and AIBN as azo compound, after flash chromatography (eluent, methylene chloride), a crystalline red solid (yield 25%) was obtained. ¹H NMR (400 MHz, CDCl₃), δ : 1.96 (s, 6H, C(CH₃)₂-CN); 8.08 (t, J = 1.47 Hz, 1H, p-ArH); 8.34 (d, J = 1.47 Hz, 2H, o-ArH). ¹³C NMR (100 MHz, CDCl₃), δ : 26.23 (C(CH₃)₂-CN); 42.74 (C(CH₃)₂CN); 114.67 (ArC-3); 115.67 (ArCN); 118.71 (C(CH₃)₂CN); 133.49 (ArC-2); 137.56 (ArC-4); 145.31 (ArC-1); 216.43 (C=S). Accurate Mass: 271.0242 (theoretical mass for C₁₃H₉N₃S₂: 271.0238).

2-Cyanoprop-2-yl 3,5-Bis(trifluoromethyl) Dithiobenzoate (2k). Following the procedure for compound **2b** using **1k** (0.810 g) and AIBN as azo compound, after flash chromatography (eluent, cyclohexane/ethyl ether = 8:2), a red-purple solid (yield 50.4%) was obtained. ¹H NMR (200 MHz, CDCl₃): δ : 1.97 (s, 6H, C(CH₃)₂CN); 8.04 (s, 1H, *p*-ArH); 8.29 (s, 2H, *o*-ArH). ¹³C NMR (50 MHz, CDCl₃), δ : 26.28 (C(CH₃)₂CN); 42.49 (C(CH₃)₂CN); 119.07 (CN); 122.71 (q, ¹J_{CF} = 271.6 Hz, CF₃); 125.42 (ArC-2); 126.58 (ArC-4); 132.14 (q, ²J_{CF} = 33.8 Hz, ArC-3); 145.28 (ArC-1); 218.64 (C=S). Accurate Mass: 357.0080 (theoretical mass for C₁₃H₉F₆NS₂: 357.0081).

2-Cyanoprop-2-yl 2,3,4,5,6-Pentafluoro Dithiobenzoate (21). Following the procedure for compound 2b using 1l (0.681 g) and AIBN as azo compound, after flash chromatography (eluent, methylene chloride), a red oil (yield 52%) was obtained. ¹H NMR (400 MHz, CDCl₃): δ : 1.93 (s, 6H, C(CH₃)₂CN). ¹³C NMR (100 MHz, CDCl₃), δ : 25.90 (C(CH₃)₂CN); 42.75 (C(CH₃)₂CN); 118.60 (CN); 119.52 (t, ²J_{CF} = 17.0 Hz, ArC-1); 137.53 (dm, ¹J_{CF} = 255.7 Hz, ArC-3); 142.03 (dm, ¹J_{CF} = 256.6 Hz, ArC-4); 142.29 (dm, ¹J_{CF} = 249.0 Hz, ArC-2); 206.36 (C=S). Accurate Mass: 310.9867 (theoretical mass for C₁₁H₆F₅NS₂: 310.9862).

2-Cyanoprop-2-yl-4-pyridiniumdithiocarboxate 4-Toluenesulfonate Salt (2m). 2m was obtained by dissolving 2h and an equimolar amount of anhydrous 4-methylbenzenesulfonic acid in situ when preparing the MMA stock solution.

2-Cyanoprop-2-yl(4-phenyl) Dithiobenzoate (2n). Following the procedure for compound **2b** using **1n** (0.642 g) and AIBN as azo compound, after flash chromatography (eluent, hexane/ethyl ether = 8:2), a pink crystalline product (yield 76%) was obtained. ¹H NMR (200 MHz, CDCl₃), δ : 1.97 (s, 6H, C(CH₃)₂CN); [7.35–7.57 (m, 3H); 7.57–769 (m, 4H); 8.03 (d, J = 8.22 Hz, 2H) (ArH)]. ¹³C NMR (50 MHz, CDCl₃), δ : 26.55 (C(CH₃)₂CN); 41.71 (C(CH₃)₂CN); 120.04 (CN); [127.12; 127.21; 128.34; 128.99; 139.59; 143.19; 145.736 (ArC)]; 221.97 (C=S). Accurate Mass: 297.0648 (theoretical mass for C₁₈H₁₅-NS₂: 297.0646).

2-Cyanoprop-2-yl-2-naphthyl Dithiolate (20). Following the procedure for compound **2b** using **10** (0.569 g) and AIBN as azo compound, after flash chromatography (eluent, cyclohexane/toluene/methylene chloride = 5:4:1) and crystallization from methanol, a pale red solid (yield 64%) was obtainined. ¹H NMR (200 MHz, CDCl₃), δ : 1.98 (s, 6H, C(CH₃)₂CN); [7.12–7.32 (m, 1H); 7.45–7.68 (m, 2H); 7.77–8.08 (m, 4H) (ArH)]. ¹³C NMR (50 MHz, CDCl₃), δ : 26.34 (C(CH₃)₂CN); 41.64 (C(CH₃)₂CN); 119.95 (CN); [123.88; 126.39; 127.03; 127.61; 128.24; 128.35; 129.56; 132.06; 135.26; 141.46 (ArC)]; 222.41 (C=S). Accurate Mass: 271.0496 (theoretical mass for C₁₈H₁₅-NS₂: 271.0489).

2-Cyanoprop-2-yl-1-naphthyl Dithiolate (2p). Following the procedure for compound **2b** using **1p** (0.569 g) and AIBN as azo compound, after flash chromatography (eluent, cyclohexane/toluene/methylene chloride = 5:4:1), a red, viscous liquid (yield 85%) was obtained. ¹H NMR (200 MHz, CDCl₃), δ : 1.97 (s, 6H, C(CH₃)₂CN); [7.38–7.65 (m, 4H); 7.80–7.98 (m, 2H); 8.12–8.27 (m, 1H) (ArH)]. ¹³C NMR (50 MHz, CDCl₃), δ : 26.00 (C(CH₃)₂CN); 42.22 (C(CH₃)₂CN); 119.67 (CN); [124.32; 124.48; 126.53; 127.26; 128.20; 129.18; 130.56; 133.62; 143.34

(ArC)]; 226.38 (C=S). Accurate Mass: 271.0492 (theoretical mass for $C_{18}H_{15}NS_2$: 271.0489).

2-Cyano-4-methylpent-2-yl dithiobenzoate (2q) Following the procedure for compound 2b using 1a (0.429 g) and 2,2'azobis(2,4-dimethylpentanenitrile) (0.402 g) as azo compound, after flash chromatography (eluent, hexane/ethyl acetate = 8:2), a red oil (yield 95%) was obtained. ¹H NMR (400 MHz, CDCl₃), δ : [1.07 (d, J = 6.8 Hz, 3H); 1.12 (d, J = 7.8 Hz, 3H) $(CH(CH_3)_2]$; [1.88 (dd, ${}^{1}J = 14.1$ Hz, ${}^{2}J = 5.6$ Hz, 1H); 2.24 $(dd, {}^{1}J = 14.1 \text{ Hz}, {}^{2}J = 6.6 \text{ Hz}, 1\text{H}) (CH_2)]; 1.95 (s, 3\text{H}, C(CH_3)-$ CN); 2.08 (m, 1H, CH_2CHMe_2);7.39 (dd, J = 7.8 Hz, J = 7.4Hz, 2H, *m*-ArH); 7.53 (t, J = 7.4 Hz, 1H, *p*-ArH); 7.89 (d, J =7.8 Hz, 2H, o-ArH). ¹³C NMR (100 MHz, CDCl₃), δ: [23.56; 24.00 (CH(CH₃)₂)]; 24.70 (C(CH₃)CN); 25.74 (CH₂CHMe₂); 45.81 (CMeCN); 46.64 (CH2); 119.39 (CMeCN); 126.59 (ArC-3); 128.45 (ArC-2); 132.73 (ArC-4); 144.74 (ArC-1); 222.98 (C= S). Accurate Mass: 263.0807 (theoretical mass for C14H17-NS₂: 263.0802).

2-Cyano-4-methylpent-2-yl-4-cyano Dithiobenzoate (2r). Following the procedure for compound **2b** using **1i** (0.499 g) and 2,2'-azobis(2,4-dimethylpentanenitrile) (0.402 g) as azo compound, after flash chromatography (eluent, hexane/ethyl acetate = 8:2), a purple oil (yield 48%) was obtained. ¹H NMR (400 MHz, CDCl₃), δ : [1.08 (d, J = 6.4 Hz, 3H); 1.12 (d, J = 6.8 Hz, 3H) (CH(CH₃)₂)]; [1.88 (dd, ¹J = 14.2 Hz, ²J = 5.8 Hz, 1H); 2.21 (dd, ¹J = 14.2 Hz, ²J = 6.6 Hz, 1H) (CH₂)]; 2.07 (m, 1H, CH₂CHMe₂); 1.96 (s, 3H, C(CH₃)CN); 7.67 (d, J = 8.4 Hz, 2H, *o*-ArH); 7.92 (d, J = 8.4 Hz, 2H, *m*-ArH). ¹³C NMR (100 MHz, CDCl₃), δ : [23.51; 23.98 (CH(CH₃)₂)]; 24.57 (C(CH₃)CN); 25.77 (CH₂CHMe₂); 46.37 (CMeCN); 127.11 (ArC-2); 132.31 (ArC-3); 147.30 (ArC-1); 220.41 (C=S). Accurate Mass: 288.0746 (theoretical mass for C₁₅H₁₆N₂S₂: 288.0755).

2-Cyano-4-methylpent-2-yl 3,5-bistrifluoromethyldithiobenzoate (2s). Following the procedure for compound 2b using **1k** (0.810 g) and 2,2'-azobis(2,4-dimethylpentanenitrile) (0.402 g) as azo compound, after flash chromatography (eluent, cyclohexane/ethyl ether = 8:2), a red-purple oil (yield 52%) was obtained. ¹H NMR (400 MHz, CDCl₃), δ : [1.09 (d, J = 6.8 Hz, 3H); 1.14 (d, J = 6.8 Hz, 3H) (CH(CH₃)₂)]; [1.90 (dd, ${}^{1}J = 14.1$ Hz, ${}^{2}J = 5.6$ Hz, 1H); 2.24 (dd, ${}^{1}J = 14.1$ Hz, ${}^{2}J = 6.2$ Hz, 1H) (CH₂)]; 2.08 (m, 1H, CH₂CHMe₂);1.98 (s, 3H, C(CH₃)CN); 8.03 (s, 1H, p-ArH); 8.27 (s, 2H, o-ArH). ¹³C NMR (100 MHz, CDCl₃), *δ*: [23.49; 24.00 (CH(CH₃)₂)]; 24.55 (C(CH₃)CN); 25.84 (CH₂CHMe₂); 46.62 (CH₂); 46.65 (CMeCN); 118.63 (CMeCN); 122.73 (q, ${}^{1}J_{CF} = 272$ Hz, CF_{3});125.41 (ArC-4); 126.62 (ArC-2); 132.11 (q, ${}^{2}J_{CF}$ =33.8 Hz, ArC-3); 145.58 (ArC-1); 218.51 (C= S). Accurate Mass: 399.0544 (theoretical mass for $C_{16}H_{15}F_{6}$ -NS₂: 399.0550).

2-Cyano-4-methylpent-2-yl-4-methoxyl Dithiobenzoate (2t). Following the procedure for compound 2b using 1d (0.513 g) and 2,2'-azobis(2,4-dimethylpentanenitrile) (0.402 g) as azo compound, after flash chromatography (eluent, toluene), a red oil (yield 22.8%) was obtained. ¹H NMR (400 MHz, CDCl₃), δ : [1.07 (d, J = 6.8 Hz, 3H); 1.11 (d, J = 6.4 Hz, 3H) (CH(CH_3)₂)]; [1.87 (dd, ¹J = 14.2 Hz, ²J = 6.8 Hz, 1H); 2.25 (dd, ¹J = 14.2 Hz, ²J = 6.2 Hz, 1H) (CH₂)]; 2.07 (m, 1H, CH₂CHMe₂); 1.95 (s, 3H, C(CH_3)CN); 3.86 (s, 3H, OCH₃); 6.87 (d, J = 9 Hz, 2H, m-ArH); 7.98 (d, J = 9 Hz, 2H, o-ArH). ¹³C NMR (100 MHz, CDCl₃), δ : [23.57; 24.02 (CH(CH_3)₂)]; 24.94 (C(CH_3)CN); 25.76 (CH₂CHMe₂); 45.63 (CMeCN); 128.72 (ArC-2); 137.86 (ArC-1); 163.88 (ArC-4); 220.35 (C=S). Accurate Mass: 293.0913 (theoretical mass for C₁₅H₁₉NOS₂: 293.0908).

MMA Polymerizations at 60 °C. A stock solution of MMA (7.01 M), AIBN (6.3×10^{-3} M), and RAFT agent (1.12×10^{-2} M) in benzene (or a different solvent when specified) was prepared. Aliquots (2 mL) were transferred to four ampules, degassed with three freeze–evacuate–thaw cycles, and sealed. The ampules were heated at 60 ± 1 °C in a thermostated water bath for 1, 2, 4, and 16 h. The conversions were estimated by analyzing a portion of the obtained mixtures by ¹H NMR (400 MHz) weighting the $-C(O)OCH_3$ integral of MMA (3.75 ppm) and PMMA (3.59 ppm). The excess monomer and solvent were

Scheme 2. General Synthetic Strategy for Tertiary Dithiobenzoates



removed by evaporation at ambient temperature under vacuum, and the residues were analyzed directly by GPC.

MMA Polymerizations at 90 °C. A stock solution of MMA (6.55 M), 1,1-azobis(cyclohexanecarbonitrile) (1.18×10^{-3} M) and RAFT agent (1.13×10^{-2} M) in benzene was prepared. Aliquots (2 mL) were transferred to four ampules, degassed with three freeze-evacuate-thaw cycles, and sealed. The ampules were heated at 90 ± 1 °C in a thermostated oil bath for 1, 2, 4, and 16 h and then treated as described for experiments at 60 °C.

Computational Details. DFT calculations were carried out with the Gaussian 98 system of programs¹⁸ employing the B3LYP functional^{19,20} and the valence double- ζ basis set supplemented with polarization d functions on heavy atoms²¹ (B3LYP/6-31G*). The unrestricted wave function was used for radical species. Energies (*E*) were corrected for the zero point vibrational energies (ZPVE) computed at the B3LYP/6-31G* level from frequency calculations using a scaling factor of 0.9806 to account for anharmonicity.²² Enthalpies (*H*) in the gas phase at 333 °K were calculated from eq 1 using the rigidrotor and harmonic-oscillator approximation.

$$H_{333} = E + \text{ZPVE} + \Delta H_{0 \to 333} \tag{1}$$

Results and Discussion

Synthesis of Chain-Transfer Agents. Tertiary dithio esters were synthesized by the radical reaction of bis(thiocarbonyl) disulfide 1 with a tertiary azo compound^{23,24} (Scheme 2). Thiocarbonyl disulfides having an unsubstituted phenyl ring (1a) (Table 1) or a phenyl ring substituted with methyl (1b, 1c), methoxy (1d, 1e), fluoro (1f, 1g) and phenyl (1n), or 2-naphthalene (10) as Z group were synthesized by reacting the appropriate Grignard reagent with carbon disulfide and subsequent oxidation of the dithiocarboxylate salt with aqueous iodine. The aryl Grignard reagents bearing strongly electron-withdrawing substituents do not react easily with carbon disulfide to give the corresponding dithiocarboxylate salt; thus, phenyl derivatives substituted with cyano (1i, 1j), trifluoromethyl (1k), and the pentafluorophenyl derivative (11) were obtained by the oxidation of the appropriate benzyl bromide or chloride precursors with sodium methoxide in the presence of sulfur²⁵ followed by oxidation of the dithiocarboxylate salt with iodine. Also, 2-cyanoprop-2-yl 1-naphthyldithioate (2p) was obtained in better yields by oxidation of 1-chloromethylnaphthalene in the presence of sulfur and subsequent reaction of the disulfide product with AIBN.

It was also difficult to obtain the 4-pyridine derivative (2-cyanoprop-2-yl dithioisonicotinate) **2h** (Table 1) from the related bis(thiocarboxy) disulfide because the oxidation of the corresponding sodium dithiocarboxylate failed to occur. Thus, triphenylmethyl dithioisonicotinate was synthesized by reaction of sodium dithioisonicotinate, obtained by the oxidation of 4-picolyl chloride in the presence of sulfur, with triphenylmethyl chloride followed by a radical reaction with AIBN (Scheme 3).²⁶ Some of the most significant dithiobenzoates were synthesized with 2-cyano-4-methylpent-2-yl as leaving group by reacting disulfides 1 (Scheme 2) with 2,2'-azobis(2,4-dimethylpentanenitrile) (VAZO-52).

Conformational Effects of the Group Z. Previous studies of the RAFT process demonstrated that best results on MMA polymerization are achieved with an activating Z group. Barner-Kowollik et al. evidenced the bimodal behavior of the MMA polymerization using cumyl phenyldithioacetate (CPDA) as a RAFT agent¹⁶ and suggested that, at low monomer conversion, CPDA acts as a "conventional" chain-transfer agent working in nonliving mode, whereas at higher monomer conversion, it works in living mode. Similarly, this hybrid behavior was also observed in MMA polymerization mediated by S-methoxycarbonylphenylmethyl methyltrithiocarbonate (MCPMT), which has a nonactivated Z group (-SMe), whereas, S-methoxycarbonylphenylmethyl dithiobenzoate (MCPDB), which has phenyl as Z, provided a more uniform polymerization.¹⁴ In this work, we found that methyl groups in ortho positions diminish the performance of the CTA with respect to the parent compound 2-cyanoprop-2-yl dithiobenzoate (2a). Indeed, MMA polymerization mediated by the 2,6dimethyldithiobenzoate derivative (2b) showed a trend from no control in the first 2 h to a low control at the end of the process (PD_{1h} 1.67, PD_{2h} 1.70, PD_{4h} 1.62, PD_{16h} 1.46) in comparison to the polymerization of MMA in absence of CTA (PD_{1h} 1.61, PD_{2h} 1.65, PD_{4h} 2.05, PD_{16h} 2.32) (Table 2). The SEC molecular weight distribution reproduced in Figure 1 clearly shows a bimodal behavior recalling that of MMA polymerizations mediated by CTAs not carrying a phenyl as group Z.

Thus, in the case of **2b**, the phenyl does not act as a stabilizing Z group showing a behavior similar to alkyl or thioalkyl substituents. The steric hindrance of the two methyl groups in ortho positions reduces the conjugation of the aromatic system with the dithiocarboxyl group by preventing its free rotation. On the other hand, the 2,4-dimethyl-substituted dithiobenzoate derivative 2c leads to a living RAFT polymerization of MMA, as evidenced in the SEC plot shown in Figure 2. Nevertheless, the polydispersity at low conversion is inferior to that obtained with the parent compound 2a (PD_{1h} 1.58, PD_{2h} 1.42, PD_{4h} 1.22, PD_{16h} 1.12) (Table 2). The plots of molecular weight versus conversion for the polymerizations mediated by compounds 2a, 2b, and 2c are linear for 2a, quasi-linear for 2c, and nonlinear for 2b, whose trend highlights the nonliving character of the MMA polymerization (Figure 3). (In a clean living polymerization, the plot of M_n versus conversion should pass through the zero point.)

This behavior suggests that the methyl in the 2-position of the dithiobenzoate hampers the rotation of the phenyl group, reducing its conjugation with the dithiocarboxyl group and thereby deactivates the C=S double bond. Similarly, the position of the dithiocarboxyl group in naphthalene-derivatized CTAs influences the degree of control of MMA polymerizations. Thus, the different polydispersity of the polymer obtained using the 1-naphthyldithioate derivative 2p (PD_{1h} 1.47, PD_{2h} 1.29) or the 2-naphthyldithioate **20** (PD_{1h} 1.30, PD_{2h} 1.19) (Table 2), evidences that the isomer substituted in position 1, which is less free to rotate, has a lower transfer constant. Recent studies have led to similar results in the MMA polymerization mediated by 2-cyanoprop-2yl 1-dithionaphthalenate²⁷ and 2-cyanoprop-2-yl 1-dithiophenanthrenate.²⁸

Electronic Effects of the Group Z. Since the first studies on RAFT polymerization, it has been reported that by changing the nature of the Z group it is possible

Table 1. Synthesized Chain-Transfer Agents and Their Precursors							
z	-s z	z	`s´ ^R	z z	S ^{CPh3}		
Disul	tude 1	Dithioe	ester 2	Iriphenylme	7	2	R
1a		2 2a	ş{−CN	1k	F ₃ C F ₃ C	2 2k	}CN
1b		2b	ξ ←CN	11	F F F F	21	} ————————————————————————————————————
1c		2c	}————————————————————————————————————		H ⁺ N	2m	}————————————————————————————————————
1d	МеО	2d	}————————————————————————————————————	1n	Ph-	2n	}———← CN
1e	MeO	2e	}————————————————————————————————————	10	C C C C C C C C C C C C C C C C C C C	20	ξ CN
1f	F	2f	ξ _ CN	1р		2р	ξ _ CN
1g	F	2g	ξ	1a		2q	} ────────────────────────────────────
5h	N	2h	ξ (CN	1i	NC	2r	}CN
1i	NC-	2i	ξ	1k	F ₃ C F ₃ C	2s	È ⊂N
1j	NC NC	2j	} ————————————————————————————————————	1d	MeO	2t	} ────────────────────────────────────





to tune the CTA characteristics in order to satisfy the different monomer requirements^{2,8-11} and that all of the different Z groups primarily influence the reactivity of the C=S double bond toward radical addition. In this work, we found that by varying the electronic properties of the Z group via substitution of the phenyl with electron-withdrawing or electron-donating substituents or by replacing the phenyl with an electron-withdrawing heteroaromatic residue (4-pyridinyl) the efficiency of the CTA in MMA polymerization is affected. Precisely, the

electron-donating substituents (e.g., 4-methoxy derivative **2d**) reduce the control of the polymerization, as shown by higher polydispersity values relative to those observed with the unsubstituted derivative 2a (Table 2), with the effect being more evident in the first 2 h of the process. The introduction of a second methoxy group (2e) leads to a further deterioration of the performance as reported in Table 2: PD_{1h} : 1.40 (2d), 1.47 (2e); PD_{2h}: 1.28 (2d), 1.33 (2e). The 2,4-dimethoxy derivative $(\mathbf{2e})~(PD_{1h}~1.47)$ allows a better control of the polymerization than the 2,4 dimethyl derivative (2c) (PD_{1h} 1.58). This difference is not attributed to the electron-donating properties of the methyl group, whose inductive effect is smaller than the mesomeric effect of methoxy group, but is likely to reflect the bulkier nature of methyl which leads to a reduced conjugation between the Z group and

Table 2. Number-Average Molecular Weight (M_n) , Polydispersity Index (PDI), and Conversion Data for Polymerization ^a
of MMA at 60 °C in the Presence of 2-Cvanoprop-2-vl Dithioesters 2 (CTA)

CTA	time (h)	$M_{ m n} \; 10^{-3}$	PDI	% conv	CTA	time (h)	$M_{ m n} \; 10^{-3}$	PDI	% conv
control set	1	275	1.61	13.8	2i	1	5.0	1.26	7.7
	2	259	1.65	21.5		2	8.7	1.13	16.9
	4	315	2.05	37.9		4	17	1.07	36.0
	16	575	2.32	99.9		16	45	1.08	99.9
2a	1	7.0	1.34	7.1	2j	1	4.3	1.24	6.8
	2	11	1.20	16.2	-	2	8.8	1.11	16.0
	4	20	1.12	32.0		4	17	1.06	31.0
	16	55	1.06	92.6		16	59	1.06	99.1
2b	1	32	1.67	9.1	2k	1	5.4	1.20	6.6
	2	31	1.70	16.1		2	10	1.11	15.0
	4	34	1.62	31.4		4	21	1.06	27.2
	16	45	1.46	97.0		16	59	1.07	96.2
2c	1	9.3	1.58	8.2	21	1	4.2	1.24	6.8
	2	13	1.42	15.0		2	7.9	1.13	14.8
	4	21	1.22	28.4		4	15	1.07	28.7
	16	49	1.12	96.1		16	52	1.06	99.9
2d	1	6.8	1.40	7.1	2m	1	2.6	1.19	5.5
	2	10	1.28	14.8		2	5.8	1.13	9.6
	4	18	1.15	30.5		4	14	1.14	23.7
	16	51	1.08	94.7		16	39	1.30	59.1
2e	1	9.2	1.47	8.0	2n	1	6.1	1.29	7.2
	2	10	1.33	13.8		2	10	1.17	14.9
	4	19	1.20	30.6		4	19	1.09	29.6
	16	53	1.08	97.7		16	53	1.07	99.8
2f	1	6.2	1.31	8.2	2o	1	6.3	1.30	7.7
	2	10	1.22	11.8		2	11	1.19	11.5
	4	19	1.11	32.3		4	20	1.10	31.5
	16	54	1.06	97.3		16	55	1.07	99.8
$2\mathbf{g}$	1	8.7	1.32	7.7	2p	1	9.1	1.47	8.2
	2	14	1.18	15.5	_	2	14	1.29	17.2
	4	26	1.11	30.3		4	23	1.17	32.5
	16	69	1.08	97.3		16	62	1.09	99.9
2h	1	6.9	1.26	5.3					
	2	15	1.11	14.6					

75 a MMA 7.01 M, CTA 1.12 \times 10^{-2} M, AIBN 6.1 \times 10^{-3} M in benzene

28

1.06

1.07

31.9

98.6

4

16





Figure 1. SEC distribution time evolution during polymerization of MMA (7.01 M) mediated by 2-cyanoprop-2-yl 2,6-dimethyldithiobenzoate (**2b**) $(1.12 \times 10^{-2} \text{ M})$ and initiated by AIBN (6.1×10^{-3} M) at 60 °C in benzene. Each plot is scaled relative to monomer conversions (9, 16, 31, and 97% respectively).

the dithiocarboxy moiety (see above). Conversely, the presence of electron-withdrawing substituents (fluoro, cyano, and trifluoromethyl) on the phenyl increases the control of the polymerization in the early stages of the

Figure 2. SEC distribution time evolution during polymerization of MMA (7.01 M) mediated by 2-cyanoprop-2-yl 2,4-dimethyldithiobenzoate (2c) $(1.12 \times 10^{-2} \text{ M})$ and initiated by AIBN (6.1×10^{-3} M) in benzene at 60 °C.

process compared to the parent CTA 2a (Table 2). The polymerization was also more controlled when the phenyl was replaced with a 4-pyridinyl residue (2h) and even more so with its salified derivative (2m) as Z group. Thus, compounds 4-fluorophenyl (2f) (PD_{1h} 1.31, PD_{2h} 1.22), 2,4-difluorophenyl (2g) (PD_{1h} 1.26, PD_{2h} 1.13), 4-cyanophenyl (2i) (PD_{1h} 1.26, PD_{2h} 1.13), 4-pyridine



Figure 3. Molecular weight evolution with monomer conversion for MMA (7.01 M) polymerization mediated by 2-cyanoprop-2-yl dithiobenzoate (**2a**), 2-cyanoprop-2-yl 2,6-dimethyldithiobenzoate (**2b**), or 2-cyanoprop-2-yl 2,4-dimethyldithiobenzoate (**2c**) (1.12×10^{-2} M) and initiated by AIBN (6.1×10^{-3} M) in benzene at 60 °C.



Figure 4. SEC traces after 1 h polymerization of MMA (7.01 M) mediated by 2-cyanoprop-2-yl dithiocarboxylate derivatives $(1.12 \times 10^{-2} \text{ M})$ phenyl (**2a**), 2,4-dimethoxyphenyl (**2e**), 3,5-bis(trifluoromethyl)phenyl (**2k**), and 4-pyridinium 4-toluene-sulfonate salt (**2m**) and initiated by AIBN (6.1 × 10⁻³ M) at 60 °C in benzene. Traces normalized by height.

(2h) (PD_{1h} 1.26, PD_{2h} 1.11), 3,5-dicyanophenyl (2j) (PD_{1h} 1.24, PD_{2h} 1.11), 2,3,4,5,6-pentafluorophenyl (2l) (PD_{1h} 1.24, PD_{2h} 1.13), 3,5-bis(trifluoromethyl)phenyl (2k) (PD_{1h} 1.20, PD_{2h} 1.11), and 4-pyridinium *p*-toluensulfonic salt (2m) (PD_{1h} 1.19, PD_{2h} 1.13) (Table 2) represent a series of CTAs with increasing efficiency in MMA polymerization, although not strictly in the above order. As shown in Figure 4, there is a progressive narrowing of the molecular weight distribution of the polymer after 1 h at 60 °C when switching from electron-donating to electron-withdrawing substituents.

The addition rate of the mildly nucleophilic PMMA propagating radical to the RAFT agent increases with the electrophilicity of the sulfur. Thus, the transfer constant is higher in CTAs bearing electron-withdrawing Z groups. A generally larger molecular weight was obtained in the first 2 h of polymerization compared to the calculated values (eq 2) (Figure 5), indicating a slow

$$M_{n\text{theor}} = \left(\frac{[\text{MMA}]}{[\text{CTA}]} \text{MW}_{\text{MMA}} \cdot \text{conversion}\right) + \text{MW}_{\text{CTA}} \quad (2)$$



Figure 5. Molecular weight obtained by GPC (M_n) after 1 h polymerization of MMA (7.01 M) mediated by different CTAs $(1.12 \times 10^{-2} \text{ M})$ initiated by AIBN $(6.1 \times 10^{-3} \text{ M})$ at 60 °C in benzene (empty bars) and calculated molecular weight (solid bars) arranged by decreasing percentage difference.

consumption of the initial RAFT agent in the early stages of the process, especially for those with electrondonating substituents on the phenyl. The difference between the found and the calculated M_n decreases as the CTA efficiency increases, although the arrangement obtained following this parameter is not perfectly coincident with that derived from the polydispersity values, possibly because of experimental errors affecting the evaluation of conversion and the very close polydispersity values found. When the CTA is particularly efficient, the calculated M_n is instead equal to or larger than the observed one. This is likely due to the fact that the experimental PMMA molecular weight values, having been obtained by GPC calibrated with polystyrene standards, are ca. 10% smaller than the real ones.

Electron-withdrawing Z groups, particularly the more effective ones such as those present in compounds 2k, 2l, 2m, increase to some extent the polymerization retardation, suggesting that the stability of the intermediate radicals is slightly enhanced. Also, when the Z group is a 4-biphenyl (2n) or a 2-naphthyl (2o), the performance is slightly better relative to the parent compound (2a). The higher transfer constants of the former CTAs are reflected in their faster consumption and smaller differences between the found and the calculated molecular weight (Figure 5).

Solvent Effect. The solubility of 2-cyanoprop-2-yl 4-pyridiniumdithiocarboxate 4-toluenesulfonate salt (**2m**) in the MMA/benzene stock solution is low at ambient temperature but is complete at 60 °C. Although the polydispersity of the polymers obtained in the first 2 h is very good (Table 2), it starts to increase after the fourth hour resulting, after 16 h, in a broad and complex SEC trace. The polymerization is also strongly retarded. Acetonitrile and dimethylformamide (DMF) are much better solvents and were used to improve the CTA solubility while performing the polymerizations at the same molar ratios used for benzene. The SEC traces of the polymers obtained (Figure 6) evidence that also in acetonitrile there is a good response in the first 2 h but after 16 h the molecular weight distribution becomes broad and complex. On the other hand, better results are obtained in DMF at the end of the process, although the SEC profile of the polymer obtained after 16 h is still complex and the polydispersity is not as low as that of polymers obtained with other CTAs.



Figure 6. SEC traces of PMMA resulting from MMA (7.01 M) polymerization mediated by 2-cyanoprop-2-yl 4-pyridinium dithiocarboxate 4-toluenesulfonate salt (**2m**) (1.12×10^{-2} M) and initiated by AIBN (6.1×10^{-3} M) at 60 °C in benzene (a), acetonitrile (b), and dimethylformamide (c).

Table 3. Number-Average Molecular Weight (M_n) , Polydispersity Index (PDI), and Conversion Data for Polymerization of MMA (7.01 M) at 60 °C in the Presence of Dithioesters 2 (CTA) $(1.12 \times 10^{-2} \text{ M})$ and Initiated by AIBN $(6.1 \times 10^{-3} \text{ M})$ Using Benzene, Acetonitrile, and DMF as Solvent

			0	,	,				
CTA	time (h)	$M_{ m n}~10^{-3}$	PDI	conv (%)	CTA	time (h)	$M_{ m n}~10^{-3}$	PDI	conv (%)
$2\mathbf{a}^a$	1	7.0	1.34	7.1	$2\mathbf{m}^a$	1	2.6	1.19	5.5
	2	11	1.20	16.2		2	5.8	1.13	9.6
	4	20	1.12	32.0		4	14	1.14	23.7
	16	55	1.06	92.6		16	39	1.30	59.1
$\mathbf{2a}^{b}$	1	7.0	1.40	10.9	$2\mathbf{m}^b$	1	3.9	1.12	8.7
	2	11	1.27	22.5		2	10	1.07	18.4
	4	19	1.15	38.8		4	20	1.08	31.0
	16	52	1.12	99.9		16	52	1.21	83.1
$\mathbf{2a}^{c}$	1	9.0	1.39	9.3	$2\mathbf{m}^c$	1	2.8	1.26	3.5
	2	14	1.28	19.1		2	6.7	1.14	8.8
	4	25	1.13	39.3		4	21	1.09	26.8
	16	64	1.07	99.9		16	59	1.14	72.4

^a Polymerization conducted in benzene. ^b Polymerization conducted in acetonitrile. ^c Polymerization conducted in dimethylformamide.

(II)

Scheme 4. Possible Termination Reactions in RAFT Polymerization

$$(III) P_{0^{\bullet}} + Z \xrightarrow{SP_{n}} Z \xrightarrow{SP_{n}} Z \xrightarrow{SP_{n}} (IV) P_{0^{\bullet}} + Z \xrightarrow{SP_{n}} P_{0-1} = CH_{2} + Z \xrightarrow{SP_{n}} = CH_{2} + Z \xrightarrow{SP_{n}} P_{0-1} = CH_{2} + Z \xrightarrow{SP_{n}} = CH_{2} + Z \xrightarrow{SP_{n}} P_{0-1} = CH_{2} + Z \xrightarrow{SP_{n}} = CH_{2} + Z \xrightarrow{SP$$

For the sake of comparison, polymerization experiments using the parent CTA 2-cyanoprop-2-yl dithiobenzoate (2a) were also performed in acetonitrile and DMF. These polymerizations resulted in higher conversions but increased polydispersities of the polymers with respect to the polymerization carried out in benzene (Table 3). These findings can be explained by the somewhat lower propagation rate constant (k_p) for the polymerization of MMA in benzene compared to acetonitrile and DMF.²⁹ In the absence of other effects, a higher $k_{\rm p}$ would give higher conversions but would also reduce the chain-transfer constant (k_{tr}/k_p) of the RAFT agent. In the case of 2-cyanoprop-2-yl 4-pyridiniumdithiocarboxate 4-toluenesulfonate salt (2m), the situation is more complex (Table 3). While there is evidence of a higher overall rate of polymerization in acetonitrile and DMF when compared to benzene, there is no indication of increased polydispersities (lower chaintransfer constants) in the former solvents. The out-

(I) $P_n + P_m - P_n - P_m$

standing features of the RAFT polymerizations with **2m** in all three solvents are rapid attainment of narrow polydispersity, retardation of polymerization, and complex molecular weight distributions at the higher conversions (Table 3 and Figure 6).

 $P_m + P_n \rightarrow P_m H + P_{n-1} = CH_2$

These observations suggest a high transfer constant accompanied by an increase in the level of termination reactions of the intermediate radicals **3** and **4** (Scheme 1). Indeed, DFT calculations (see below) indicate that electron-withdrawing Z groups enhance the rate of addition of radicals to the RAFT agent and decrease the rate of fragmentation of the intermediate radical. These effects would result in higher concentrations of radicals **3** and **4** and hence increase the probability of their reaction with other radicals. The possible side reactions for intermediate radical **4** are outlined in Scheme 4. Aside from the termination reactions of the propagating radicals (steps I and II), other possible termination reactions involve combination of the intermediate radi-

CTA	time (h)	$M_{ m n} \ 10^{-3}$	PDI	conv (%)	CTA	time (h)	$M_{ m n} \ 10^{-3}$	PDI	conv (%)
2q	1	4.7	1.18	8.3	2s	1	2.5	1.13	3.9
_	2	12	1.10	18.9		2	7.4	1.06	12.8
	4	24	1.08	31.7		4	16	1.04	28.2
	16	65	1.09	99.9		16	56	1.06	99.9
2r	1	4.6	1.15	7.0	2t	1	3.0	1.24	4.4
	2	10	1.07	14.7		2	7.0	1.13	12.0
	4	21	1.06	32.0		4	16	1.06	25.4
	16	58	1.09	99.9		16	55	1.06	99.9

Table 4. Number-Average Molecular Weight (M_n), Polydispersity Index (PDI), and Conversion Data for the Polymerization^a of MMA at 60 °C in the Presence of 2-Cyano-4-methylpent-2-yl Dithioesters (CTA)

 a MMA 7.01 M, CTA 1.12 \times 10^{-2} M, AIBN 6.1 \times 10^{-3} M in benzene.

 Table 5. Number-Average Molecular Weight (M_n), Polydispersity Index (PDI), and Conversion Data for Polymerization^a of MMA at 90 °C in the Presence Dithioesters 2 (CTA) Initiated by 1,1-Azobis(cyclohexanecarbonitrile)

CTA	time (h)	$M_{ m n} \ 10^{-3}$	PDI	conv (%)	CTA	time (h)	$M_{ m n} \ 10^{-3}$	PDI	conv (%)
2a	1	9.4	1.28	18.2	2q	1	9.1	1.13	16.0
	2	16	1.15	27.6	-	2	17	1.08	25.0
	4	24	1.11	47.3		4	30	1.08	44.6
	16	53	1.09	97.6		16	58	1.09	88.8
2i	1	7.3	1.19	15.0	$2\mathbf{r}$	1	4.2	1.14	8.6
	2	15	1.09	25.9		2	12	1.08	18.9
	4	27	1.06	45.6		4	22	1.07	32.0
	16	48	1.08	95.5		16	49	1.09	83.8
$2\mathbf{k}$	1	5.0	1.21	9.8	2s	1	11	1.09	17.8
	2	9.1	1.15	15.0		2	13	1.10	22.5
	4	27	1.11	34.7		4	25	1.09	37.4
	16	33	1.10	81.7		16	45	1.11	80.7

 a MMA 6.55 M, CTA 1.13 \times 10^{-2} M, initiator 1.8 \times 10^{-3} M in benzene.

cal 4 and the growing radical chain to form the threearmed star³⁰⁻³³ (step III) or disproportionation to yield a vinyl-ended chain and the reduced form of the intermediate radical (step IV). The intermediate radical 4 can also react with 2-cyanoprop-2-yl radical derived from the initiator decomposition (step V) (these two radicals could also disproportionate) and dimerize to form the four-armed star (step VI). The termination reactions are expected to be more competitive with chain propagation at high conversion when the monomer concentration is lower. This could explain the greater broadening of the molecular weight distribution toward the end of the process.

Influence of the Leaving Group R. In the course of this study, it was found that for all the CTAs carrying 2-cyanoprop-2-yl as the leaving group (R) and independently from the nature of Z, it was not possible to reach at low conversion the same narrow molecular weight distribution obtained at higher conversion. The use of a bulkier and better leaving group as 2-cyano-4-methylpent-2-yl confirmed that R plays a key role in the early stages of polymerization.¹³ The higher stability of the radical leaving group shifts the equilibrium from the intermediate radical 3 (Scheme 1) to the macroCTA (PMMA-RAFT agent) and thereby increases the chaintransfer constant of the initial CTA. Thus, while the group Z influences the whole process, the leaving group R only affects the initial stages when there is more need for improvement. The narrower molecular weight distribution of polymers obtained using 2-cyano-4-methylpent-2-yl dithiobenzoate (2q), 2-cyano-4-methylpent-2-yl 4-cyanodithiobenzoate (2r), 2-cyano-4-methylpent-2-yl 3,5-bistrifluoromethyldithiobenzoate (2s), or 2-cyano-4-methylpent-2-yl 4-methoxydithiobenzoate (2t) as CTA demonstrates a remarkably improved performance in the first 2 h of the polymerization (Table 4). The good leaving ability of the R group in the CTA 2-cyano-4methylpent-2-yl 4-methoxydithiobenzoate (2t) leads to





polymers of lower polydispersity than those obtained with the parent compound 2a, despite the presence of the deactivating methoxy group. Best results are obtained when the favorable effect of a bulky R group is combined with the favorable effect of electron-withdrawing substituents on Z, for example, as in RAFT agent 2s (Table 4).

Effect of Temperature in the RAFT-Mediated MMA Polymerization. Some of the more representative chain-transfer agents were used in the polymerization of MMA at 90 °C initiated by 1,1-azobis-(cyclohexanecarbonitrile). The results (Table 5) show a general improvement in performance in comparison to the polymerizations conducted at 60 °C.

The higher polymerization temperature appears to increase the propagation rate constant and the chaintransfer constant, allowing for very narrow polidispersities from the beginning of the process, and furthermore, this is achieved at lower rates of initiation. Following the same trend for experiments at 60 °C, electron-withdrawing substituents on the phenyl improved the performance of the CTAs at 90 °C. A further improvement was achieved using 2-cyano-4-methylpent-2-yl as leaving group.

DFT Calculations. Enthalpy barriers for the addition and fragmentation reactions involved in the RAFT process were calculated for the model intermediate radicals **5** (Scheme 5) using the group CMe₂COOMe (X) to mimic the fragment derived from MMA and either

Table 6. Enthalpy Barriers for the Addition and Fragmentation Reactions Modeling the RAFT Polymerization of MMA in the Presence CTAs 2 Computed at the B3LYP/6-31G* Level at 333 K

CTA	$\Delta H^{\#}_{ m Xadd}$	$\Delta H^{\#}_{\mathrm{Xfrag}}$	$\Delta H^{\#}_{ m Yadd}$	$\Delta H^{\rm \#}{}_{\rm Yfrag}$
2a	5.3	10.6	7.2	8.6
2q	5.3	10.6	7.7	6.4
2d	5.4	10.2	7.3	8.5
2f	5.2	10.4	7.2	8.5
2i	4.5	11.6	6.4	9.3
$2\mathbf{k}$	4.3	10.9	6.1	8.6

 Table 7. Radical Stabilization Energy^a (kcal/mol)

 Computed at the B3LYP/6-31G* level

•R	BDE (kcal/mol)
•CHMeCOOMe •CMe ₂ COOMe (X•)	9.6 20.6
$^{\bullet}CMe_{2}CN (Y'^{\bullet})$ $^{\bullet}CMe(CH_{2}CHMe_{2})CN (Y''^{\bullet})$	21.5 22.6

 $^a\,\mathrm{C-H}$ bond dissociation energy relative to the C–H BDE computed for methane.

 CMe_2CN (Y') or $CMe(CH_2CHMe_2)CN$ (Y'') as leaving group. Also, electron-donating or electron-withdrawing moieties were used as Z group.

The calculated enthalpy barrier for the addition of the radical X[•] to the C=S double bond of the CTA ($\Delta H^{\#}_{Xadd}$) is small and decreases with the increasing electronwithdrawing ability of the Z group along the series: 3,5bistrifluoromethylphenyl (**2k**) > 4-cyanophenyl (**2i**) > 4-fluorophenyl (**2f**) > phenyl (**2a**) > 4-methoxyphenyl (**2d**) (Table 6). Conversely, the enthalpy barrier for the fragmentation of S–X bond ($\Delta H^{\#}_{Xfrag}$) of radicals **5** is higher and displays an opposite trend, that is, $\Delta H^{\#}_{Xfrag}$ increases with the electron-withdrawing ability of the Z group.

Radical 2-cyanoprop-2-yl (Y') is computed to be more stable than the radical CMe₂COOMe (X) by ca. 1 kcal/ mol (Table 7). As a consequence, although similar trends are computed for the reversible addition fragmentation reactions of the group Y', $\Delta H^{\#}_{Yfrag}$ and $\Delta H^{\#}_{Yadd}$ are, respectively, computed to be about 2 kcal/mol smaller and 1.5 kcal/mol larger than $\Delta H^{\#}_{Xfrag}$ and $\Delta H^{\#}_{Xadd}$, and thus, the transfer constant of CTAs **2**, which affects the polydispersity mainly in the early stages of the process (eq 3),⁵ is expected to be high since the fragmentation rate of 2-cyanoprop-2-yl (Y) is predicted to be high.

$$k_{\rm tr} = k_{\rm Xadd} \frac{k_{\rm Xfrag}}{k_{\rm Xfrag} + k_{\rm vfrag}} \tag{3}$$

The stability of the radical group is also expected to increase with steric hindrance. Indeed, the radical 2-cyano-4-methylpent-2-yl (Y'') has a calculated stabilization energy ca. 1 kcal/mol greater than that of 2-cyanoprop-2-yl (Y') and ca. 2 kcal/mol greater than of the radical $^{\circ}CMe_2COOMe(X)$, all these three species being considerably more stable (10 kcal/mol or more) than the secondary radical ($^{\circ}CHMeCOOMe$). This justifies the necessity of a tertiary leaving group in CTAs suitable for MMA polymerization (Table 7).

Thus, the transfer constant of 2-cyano-4-methylpent-2-yl dithiobenzoate(2q) is expected to be higher than that of 2-cyanoprop-2-yl dithiobenzoate (2a), and indeed, the enthalpy barrier for the fragmentation of the S-Y bond is computed to be much smaller for the intermediate radical deriving from 2q than for that from 2a (Table 6). This is in agreement with the improved polydispersity in the early stages of the process reported in Table 2.

As far as the nature of the Z residue is concerned, strong electron-withdrawing groups, such as 4-cyanophenyl and 3,5-bis(trifluoromethyl)phenyl, considerably increase the enthalpy barrier for fragmentation of S-Xand S-Y bonds and decrease the enthalpy barrier for the addition of the X[•] and Y[•] radicals. Thus, they are predicted to considerably enhance the addition rate of both radicals to the dithiocarboxyl function and to decrease the fragmentation rate of S-X and S-Y bonds. This confirms the improved performance observed in the first 2 h of CTAs carrying electron-withdrawing Z groups (Table 2), which implies a faster depletion of the initial RAFT agent.

Conclusions

The effect of substituents on the phenyl group (Z) of dithiobenzoate RAFT agents in the polymerization of MMA has been examined. Electron-withdrawing Z groups, which confer a higher electrophilic character to the thiocarboxylic sulfur, enhance the radical addition to the C=S double bond leading to narrower polydispersities of the polymers from the early stages of the polymerization. The opposite is true for electron-donating Z group. Ortho substituents on phenyl diminish the effectiveness of the RAFT agent by reducing the degree of conjugation of phenyl with the C=S double bond. The beneficial steric effect of tertiary leaving groups was also confirmed. Solvent effects were relatively minor, although the lower propagation rate constant for the polymerization of MMA in benzene (versus acetonitrile or DMF) manifested in improved polydispersities at the expense of conversion. An increase in the polymerization temperature from 60 to 90 °C also proved beneficial, apparently because of an increase in the chain-transfer constant of the RAFT agents accompanied by the expected higher rate of polymerization. DFT calculations suggest that the experimental results reflect variations of the enthalpy barrier for the addition and fragmentation reactions involved in the process with different Z and R groups.

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