Macromolecules **2005,** *38,* 1591−1598

Block Copolymers of γ-Methacryloxypropyltrimethoxysilane and Methyl Methacrylate by RAFT Polymerization. A New Class of Polymeric Precursors for the Sol−Gel Process

Véronique Mellon, David Rinaldi, Elodie Bourgeat-Lami, and Franck D'Agosto*

Laboratoire de Chimie et Procédés de Polymérisation UMR 140 CNRS/ESCPE, Bât 308 F,
43 Boulevard du 11 Novembre 1918, BP 2077, 69616 Villeurbanne Cedex, France

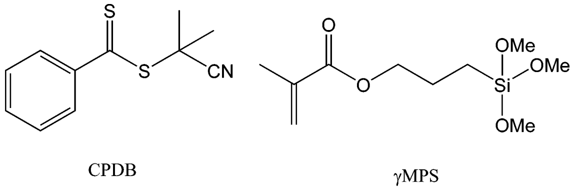
Received September 10, 2004; Revised Manuscript Received December 16, 2004

ABSTRACT: Reversible addition−fragmentation chain transfer (RAFT) polymerization of the reactive monomer γ-methacryloxypropyltrimethoxysilane (γMPS) mediated by 2-cyanoprop-2-yl dithiobenzoate (CPDB) has been studied in dioxane using 2,2′-azobis(isobutyronitrile) (AIBN) as initiator. Conditions were optimized for a polymerization temperature of 80 °C, and controlled PγMPS chains (up to M_n = 40 000 g mol^{-1}) exhibiting low polydispersity indexes (PDI < 1.3) were synthesized. Their characterization by matrix-assisted laser desorption ionization time-of-flight (MALDI-ToF) mass spectrometry showed that the expected structure was obtained although degradation of the dithiobenzoate chain end occurred. Syntheses of block copolymers based on γMPS and methyl methacrylate (MMA) were performed starting from either the PγMPS (M_n = 32 100 g mol^{-1}, PDI = 1.16, PMMA calibration) or the PMMA block (M_n = 21 000 g mol^{-1}, PDI = 1.14). The success of the block copolymerization was showed by the shift toward higher molar mass of the size exclusion chromatography (SEC) chromatograms recorded before and after block copolymerization. Proton NMR analyses of P(MMA-*b*-γMPS) allowed to calculate the molar mass of the PγMPS blocks (17 400 g mol^{-1}) which agreed with the targeted one (18 150 g mol^{-1}).

Introduction

Organic/inorganic hybrid materials have attracted considerable attention in the past decade as attested to by the explosion of research activity in this area.[1−11] The sol−gel technique, initially developed for the production of inorganic glasses by polymerization of silicon alkoxides, now applies to a variety of inorganic precursors. This synthetic technique mainly relies on base or acid-catalyzed hydrolysis and condensation reactions of metal alkoxides to form an oxide network. The low-temperature processing characteristic of the sol−gel technology offers unique opportunities and allows the elaboration of hybrid materials containing suitable organic functionalities with applications in optics, coatings, and catalysis. The organic functionality is usually incorporated using conveniently substituted organo(alkoxy)silanes. The latter carry alkoxide groups that can react with the oxide framework and link together the organic and inorganic components, the organic part being a small organic molecule, an oligomer, or a polymer. Among the huge variety of available organosilanes, those containing polymerizable organic substituents (epoxy, vinyl, or methacryloxy groups) such as γ-methacryloxypropyltrimethoxysilane (γMPS) (Scheme 1) have been widely studied.[12−22] γMPS has been used for instance as coupling agent in the chemical modification of inorganic solids such as clays and silica and enables the design construction of organic/inorganic nanocomposite colloids with a variety of shapes and morphologies.[15−19] Organic/inorganic hybrid networks can also be formed by different synthetic pathways using various precursors for the sol−gel reaction as reviewed by Wilkes.[10] Among the various methods, alkoxysilyl-functionalized polymers are co-condensed with tetraethoxysilane to afford transparent hybrid materials.[20−22] The alkoxysilyl functionality either is introduced at the end of the polymer chain or is distributed along the chain in statistical copolymers of γMPS with styrene produced by free radical polymerization.

Scheme 1. Chemical Structures of 2-Cyanoprop-2-yl Dithiobenzoate (CPDB) and γ-Methacryloxypropyltrimethoxysilane (γMPS)



Despite the great importance of γMPS in the design of hybrid organic−inorganic materials, there are only very few examples of sol−gel precursors with controlled architectures based on this reactive monomer. Block copolymers with one block carrying alkoxysilyl functionalities would be particularly well suited as reactive building blocks for nanotechnology applications. Amphiphilic block copolymers can self-assemble into a variety of supermolecular structures and can be used as colloid stabilizers, nanoreactors, or templates for making inorganic solids[23,24] and hollow nanospheres.[25] Such well-defined structures may now be achieved by controlled radical polymerizations. The only examples of controlled radical polymerization of γMPS have been performed by ATRP[26] (atom transfer radical polymerization).[27,28] Nevertheless, these teams only introduced few γMPS units in a multiblocks copolymer based on methyl methacrylate (MMA) and poly(ethylene glycol) methyl ether methacrylate. NMP (nitroxide-mediated polymerization)[29] and RAFT (reversible addition−fragmentation chain tranfer)[30−32] can also be applied to functional monomers bearing a potentially reactive side

---

* Corresponding author: e-mail franck.dagosto@lcpp.cpe.fr; Tel 33-472-431770; Fax 33-472-431768.

10.1021/ma048143j CCC: $30.25

groups although the three techniques do not show the same level of versatility.

Controlled radical polymerization using RAFT[33−35] is applicable to a wide range of monomers and can be performed in a wide variety of solvents under a broad range of conditions. In this process, a dithioester chain transfer agent (CTA), S=C(Z)−SR, reacts with either the primary radical derived from an initiator or a propagating polymer chain ($P^{\bullet}$), forming a new CTA and eliminating $R^{\bullet}$, which is able to reinitiate the polymerization. The polymerization is controlled by the transfer of the CTAs between dormant and active chains. Molar mass control can be adjusted by the relative amount of reagents involved in the polymerization; the end-functionality of the resulting chains is controlled by the nature of the substituents Z and R on the CTA. Since this technique is relatively insensitive to numerous functionalities, we used it to polymerize γMPS which had not been polymerized yet by RAFT polymerization. Indeed, as far as we know, the only example of a silane-based monomer polymerized by RAFT has been 3-[tris(trimethylsiloxy)silyl]propyl methacrylate (TRIS).[36]

As part of a program devoted to the synthesis of macromolecular architectures for further use in hybrid organic−inorganic material synthesis, this paper is the first step toward RAFT-controlled polymer architectures incorporating methoxysilyl functions using 2-cyanoprop-2-yl dithiobenzoate (CPDB) (Scheme 1) as CTA. The kinetics were first investigated at different temperatures and optimized conditions were then used for the synthesis of block copolymers of γMPS and MMA.

Experimental Section

Materials. γMPS (98%, Gelest) was purified by distillation under reduced pressure. MMA (98%, Acros) was passed through a column of activated basic alumina (Acros, 50−200 μm) in order to remove the inhibitor. 2,2′-Azobis(isobutyronitrile) (AIBN, 98%, Merck) used as initiator was purified by recrystallization in ethanol. Dioxane (99.8%, Aldrich) was distilled from $LiAlH_4$ under reduced pressure. 2-Cyanoprop-2-yl dithiobenzoate (CPDB) was synthesized according to a procedure described elsewhere.[37]

Polymerization Procedure and Kinetics. Polymerizations were performed in a round-bottom flask capped with a septum. A typical polymerization recipe is as follows. The reaction vessel was loaded with dioxane (5 mL), monomer (4.75 mL, 4.963 g, 2.0×10^{-2} mol), trioxane (0.308 g, 3.42×10^{-3} mol), i.e., molar ratio γMPS/trioxane = 6:1), CTA (0.022 g, 9.9×10^{-5} mol), and AIBN (0.005 g, 3.1×10^{-5} mol). As described previously,[38] trioxane was used as an internal reference for the determination of the conversion using proton NMR (^1H NMR) spectroscopy, by comparison with the vinyl protons of γMPS (6.1 and 5.5 ppm), since trioxane gives a clean peak at 5.1 ppm. For accuracy, the area of this peak should be about the same as that of a γMPS vinylic proton at the beginning of the polymerization. As there are six protons in trioxane, the molar ratio of γMPS/trioxane was chosen as 6:1. The mixture was deoxygenated by five freeze−pump−thaw cycles. The temperature was then raised using a thermostated oil bath. Polymerizations were carried out under an argon atmosphere. Samples were withdrawn from the polymerization mixture at different reaction times and placed in liquid nitrogen to stop polymerization and then stored at −20 °C. Monomer consumption was followed by ^1H NMR analysis of each sample. ^1H NMR analysis was performed without evaporation of the polymerization solvent by mixing 0.2 mL of each sample with deuterated choloroform ($CDCl_3$; 1:3 v/v).

Table 1. Theoretical Number-Average Molar Mass ($M_{n,theo}$) and Number-Average Molar Masses (M_n) and Polydispersity Indexes (PDI) Obtained by Size Exclusion Chromatography Using Polystyrene (PS) Standards or Poly(methyl methacrylate) (PMMA) Standards of Poly(γ-methacryloxypropyltrimethoxysilane) (PγMPS) Synthesized by 2-Cyanoprop-2-yl Dithiobenzoate (10^{-2} mol L^{-1})-Mediated RAFT Polymerization of γMPS (2 mol L^{-1}) in Dioxane at Different Reaction Temperatures and Conversions

	PS standards		PMMA standards		
conv (%)	M_n (g mol^{-1})	PDI	M_n (g mol^{-1})	PDI	$M_{n,theo}$ (g mol^{-1})
			T = 60 °C		
15	6 600	1.16	7 200	1.14	7 500
22	8 900	1.15	9 200	1.17	11 400
29	12 300	1.12	12 700	1.15	14 900
41	16 500	1.10	17 200	1.11	21 000
86	29 100	1.10	30 600	1.11	43 300
			T = 70 °C		
4	7 800	1.20	8 500	1.17	2 100
41	18 600	1.11	19 600	1.12	20 500
56	22 500	1.12	23 900	1.12	28 000
71	24 800	1.11	27 300	1.08	35 600
80	29 800	1.11	32 600	1.09	40 000
			T = 80 °C		
11	6 400	1.20	6 700	1.17	5 500
24	14 600	1.12	15 200	1.13	12 200
64	23 900	1.11	25 600	1.10	32 100
83	28 600	1.13	29 500	1.16	41 900
88	29 200	1.11	31 300	1.11	44 600
92	30 900	1.13	32 700	1.13	46 300

Block Copolymerization Procedure. Block copolymers were synthesized either (i) in one pot by adding MMA (0.88 g, 8.85×10^{-3} mol) to the γMPS polymerization media (experiment depicted in Table 1, 80 °C, conversion 92%, together with AIBN (molar ratio PγMPS/AIBN = 3) or (ii) in a two-step reaction by isolating a first block of PMMA (see Supporting Information) and using it (1.159 g, 5.5×10^{-5} mol) as macro-CTA for the polymerization of γMPS (1.3 mL, 5.5×10^{-3} mol) in the presence of AIBN (0.0014 g, 8.5×10^{-6} mol) and trioxane (0.078 g, mol) in 7.5 mL of dioxane. Degassing and heating steps were identical to the homopolymerization procedure.

Polymer Characterization. Molar masses and molar mass distributions were determined by size-exclusion chromatography (SEC) with THF as eluent (flow rate = 1 mL/min) at 40 °C using three columns (2 Polymer Laboratories Gel Mixted-C (5×10^4 Å) and 1 Polymer Laboratories Gel Mixed $5 \times 10^4 - 5 \times 10^2$ Å), a refractometric detector (Waters 410), and a photodiode array detector (UV detector, Waters 996) using polystyrene (PS) or poly(methyl methacrylate) (PMMA) standards for calibration. The theoretical number-average molar mass (M_n) was obtained using

$$M_n = M_{CTA} + M_{\gamma MPS}\frac{[\gamma MPS]x_{\gamma MPS}}{[CTA]}$$

where M_{CTA} and $M_{\gamma MPS}$ are the molar masses of RAFT agent and γMPS, respectively, and $x_{\gamma MPS}$ is the fraction conversion. The contribution of the molar mass of the chains initiated by AIBN was neglected.

^1H NMR measurements were carried out on a Bruker DRX 300 spectrometer with deuterated chloroform ($CDCl_3$) as solvent at room temperature. The chemical shift scale was calibrated relative to the TMS peak used as reference.

Monomer consumption was also determined by SEC by comparison of the peak intensity of the residual monomer to the peak intensity of the formed polymer. The conversion data obtained via this technique were then compared to the one obtained by ^1H NMR. As these techniques are independent, the excellent accordance between the two sets of conversion data constitutes an accurate double checking when required (see Supporting Information).

Matrix-assisted laser desorption ionization time-of-flight (MALDI-ToF) mass spectrometry analyses were performed using a Voyager-DE STR (Applied Biosystems, Framingham, MA) equipped with a nitrogen laser emitting at 337 nm with

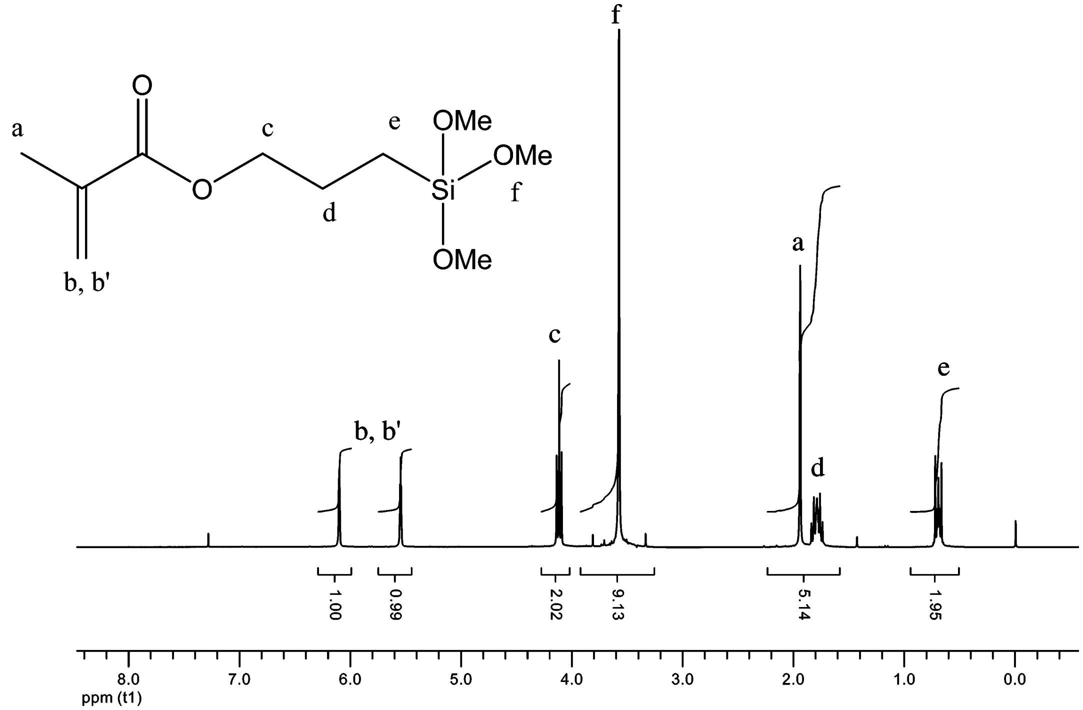


Figure 1. 300 MHz proton NMR spectrum of distilled γ-methacryloxypropyltrimethoxysilane (deuterated chloroform, number of scans = 16).

a 3 ns pulse duration. The instrument was operated in linear and reflectron mode. Ions were accelerated to a final potential of 20 kV. Spectra were the sum of 300 shots, and an external mass calibration was used (Sequazyme). Samples were prepared by dissolving the polymers in THF at a concentration of 10 mg mL^{-1}. The matrix used for all experiments was dithranol and was dissolved in THF (10 mg mL^{-1}). A volume of 45 μL of the matrix solution was then mixed with 5 μL of the polymer solution. An aliquot of 1 μL of the resulting mixture was spotted on the MALDI sample plate and air-dried. Samples were analyzed with NaI as cationizing agent.

Results and Discussion

Purification of the Monomer. As often mentioned in the literature,[39] because of the presence of the reactive trimethoxysilyl group, γMPS is sensitive to self-condensation and should be manipulated with care. However, to determine accurate RAFT kinetics, purification is necessary. For example, removing the inhibitor (monomethyl ether, MEHQ) present in the commercial monomer by filtration through an activated basic alumina column would lead to an instantaneous condensation of the liquid monomer onto the column together with an overheating. Therefore, the purification was performed by distillation (120 °C, 0.1 mmHg) under argon and reduced pressure. Since these harsh conditions could have degraded the monomer, the recovered product, stored at 4 °C in a Schlenk tube under argon, was analyzed by ^{1}H NMR spectroscopy (Figure 1). The calculated ratio of the methoxy protons (f at 3.6 ppm) and rest of the protons of the molecule is in agreement with a successful purification without any condensation of the trimethoxysilyl functions.

Preliminary Comments. Once the monomer was carefully purified, RAFT polymerization kinetics could be undertaken. 2-Cyanoprop-2-yl dithiobenzoate (CPDB) was chosen as chain transfer agent so as to assess its efficiency as a good controlling agent in the RAFT polymerization of γMPS.

Indeed, γMPS is a methacrylate derivative for which requirements for a CTA to be effective in the RAFT polymerization are that the rate of addition of the propagating radicals to the CTA must be fast relative to the rate of propagation. The leaving group must be capable of initiating new chains. As the radical polymerization of γMPS should involve rather sterically hindered propagating radicals, an efficient reinitiating R group, as the tertiary carbon centered R groups, is necessary. CPDB appears to be a good candidate since the 2-cyanoprop-2-yl dithiobenzoate group fulfills this requirement. In addition, the CPDB has recently been successfully used in the RAFT polymerization of 3-[tris(trimethylsiloxy)silyl]propyl methacrylate (TRIS),[36] a monomer whose structure is rather similar to γMPS. AIBN was used as azo initiator in all the experiments.

CPDB-Mediated RAFT Homopolymerizations of γMPS. *Kinetics.* RAFT homopolymerizations were performed in dioxane ([γMPS] = 2 mol L^{-1}) with CPDB. The molar ratio CPDB/AIBN was fixed to 3 since Saricilar et al.[36] reported the successful bulk CPBD-mediated homopolymerization of TRIS under similar conditions. The mixtures were degassed by five freeze−pump−thaw cycles before thermostating the polymerization media to three different temperatures of 60, 70, and 80 °C. The evolutions of conversion vs time together with the corresponding pseudo first-order kinetics plots are given in Figure 2 for the three temperatures. The experiment carried out at 60 °C was very slow, with a polymerization time exceeding 20 h to reach 80% conversion. Fifty-five percent conversion was reached in less than 5 h at 70 °C, whereas 90% conversion could be reached in the same time period when the polymerization was performed at 80 °C. Inhibition periods were also observed as shown by the pseudo-first-order plots (Figure 2b). At 60 °C, there was a strong inhibition period of around 3 h, which decreased to 2 h at 70 °C and less than half an hour at 80 °C. The inhibition can be caused by various factors discussed elsewhere.[40] As

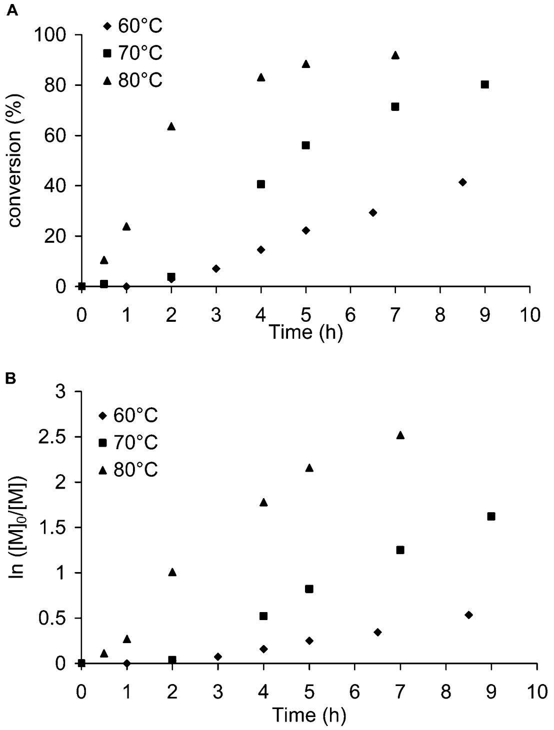


Figure 2. (a) Monomer conversion vs time curves and (b) pseudo-first-order plots for 2-cyanoprop-2-yl dithiobenzoate (CPDB, 10^{-2} mol L^{-1})-mediated RAFT polymerization of γ-methacryloxypropyltrimethoxysilane ($[M]_0 = 2$ mol L^{-1}) at 60, 70, and 80 °C in dioxane. Molar ratio CPDB/AIBN = 3.

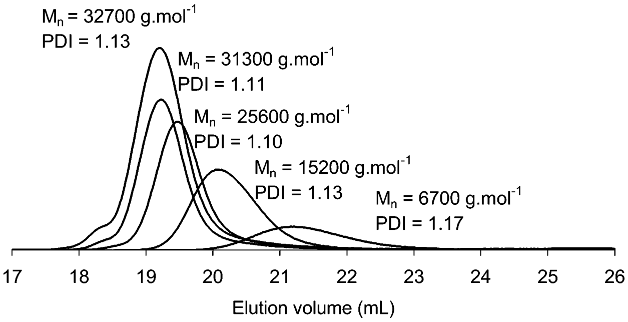


Figure 3. Evolution of number-average molar masses (M_n) and polydispersity indexes (PDI) obtained by size exclusion chromatography (using poly(methyl methacrylate) standards) for 2-cyanoprop-2-yl dithiobenzoate (CPDB, 10^{-2} mol L^{-1})-mediated RAFT polymerization of γ-methacryloxypropyltrimethoxysilane (2 mol L^{-1}) in dioxane at 80 °C for different conversions (see Table 1). Molar ratio CPDB/AIBN = 3.

the scope of the present paper is focused on the synthetic aspect of the process, these factors will not be argued here. It can easily be deduced from these evolutions that a decrease in the temperature from 80 to 60 °C seriously affects the conversion.

SEC Analyses. The evolutions of the molar masses vs conversion are given in Table 1 and in Figure 3. The general trend observed is that experimental molar masses increase linearly with conversion (see Supporting Information). The polydispersity indexes (PDI) are in all the cases very low; however, the obtained molar masses calculated on the basis of either a PS or a PMMA calibration do not agree with the theoretical values, showing the inadequacy of these calibrations for analyzing PγMPS chains.

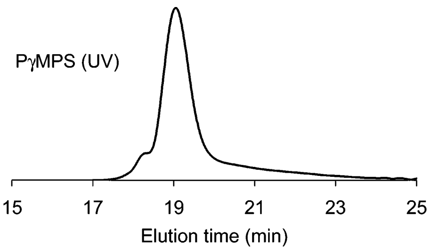
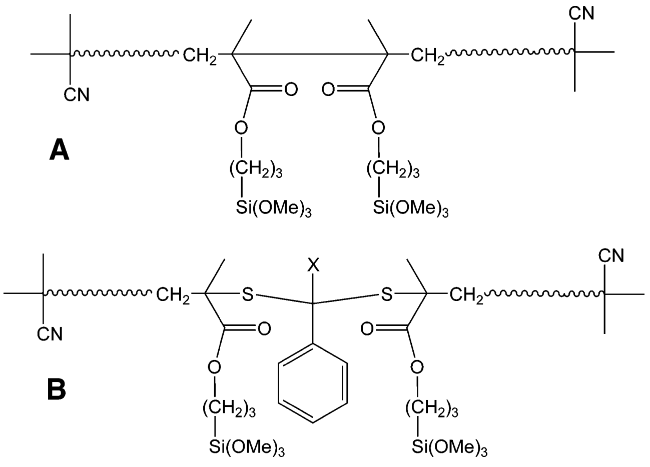


Figure 4. Size exclusion chromatography analysis of poly(γ-methacryloxypropyl trimethoxysilane) (PγMPS) synthesized by 2-cyanoprop-2-yl dithiobenzoate (CPDB, 10^{-2} mol L^{-1})-mediated RAFT polymerization ([γMPS] = 2 mol L^{-1}, in dioxane at 80 °C, molar ratio CPDB/AIBN = 3, 92% conversion). UV detection at 309 nm.

Scheme 2. Possible Structures for the Shoulder Observed during the Size Exclusion Chromatography Analyses of Poly(γ-methacryloxypropyltrimethoxysilane)



At high conversion, a second peak, relatively small with a molar mass peak twice that of the main peak, appeared (Figure 3). This population has already been observed in several cases for RAFT polymerization of methacrylate derivatives[36,41] and discussed for other monomers.[42] The authors often suggested that coupling reactions by combination of propagating radicals are occurring, although the preferred mode of termination for methacrylate-based radicals is disproportionation.[43] They also proposed that this shoulder may be due to termination of the intermediate macroradical, but they never investigated the true origin. In the case of coupling reactions by combination of propagating radicals, the structure of the resulting macromolecules (structure **A**, Scheme 2) would not incorporate any benzyl or dithiobenzoate group. It would structurally look like chains obtained by conventional free radical polymerization initiated by AIBN. In the case of termination of the intermediate macroradical, the resulting macromolecules (structure **B**, Scheme 2) would carry a "middle" phenyl group symmetrically bound to two sulfur atoms. To discriminate between the two structures, an investigation using online UV detection in a series of SEC measurements was carried out. A homo-PγMPS was first synthesized by conventional free radical polymerization using AIBN as initiator. The resulting long chain PγMPS did not give any signal by SEC using UV detection at 309 nm whereas CPDB strongly absorbed. Thus, neither the repetitive monomer unit nor the cyanoisopropyl residue seems to be detectable at 309 nm, and the UV detection of a population generated by coupling reactions (Scheme 2A) should not be possible. Considering our RAFT synthesized PγMPS,

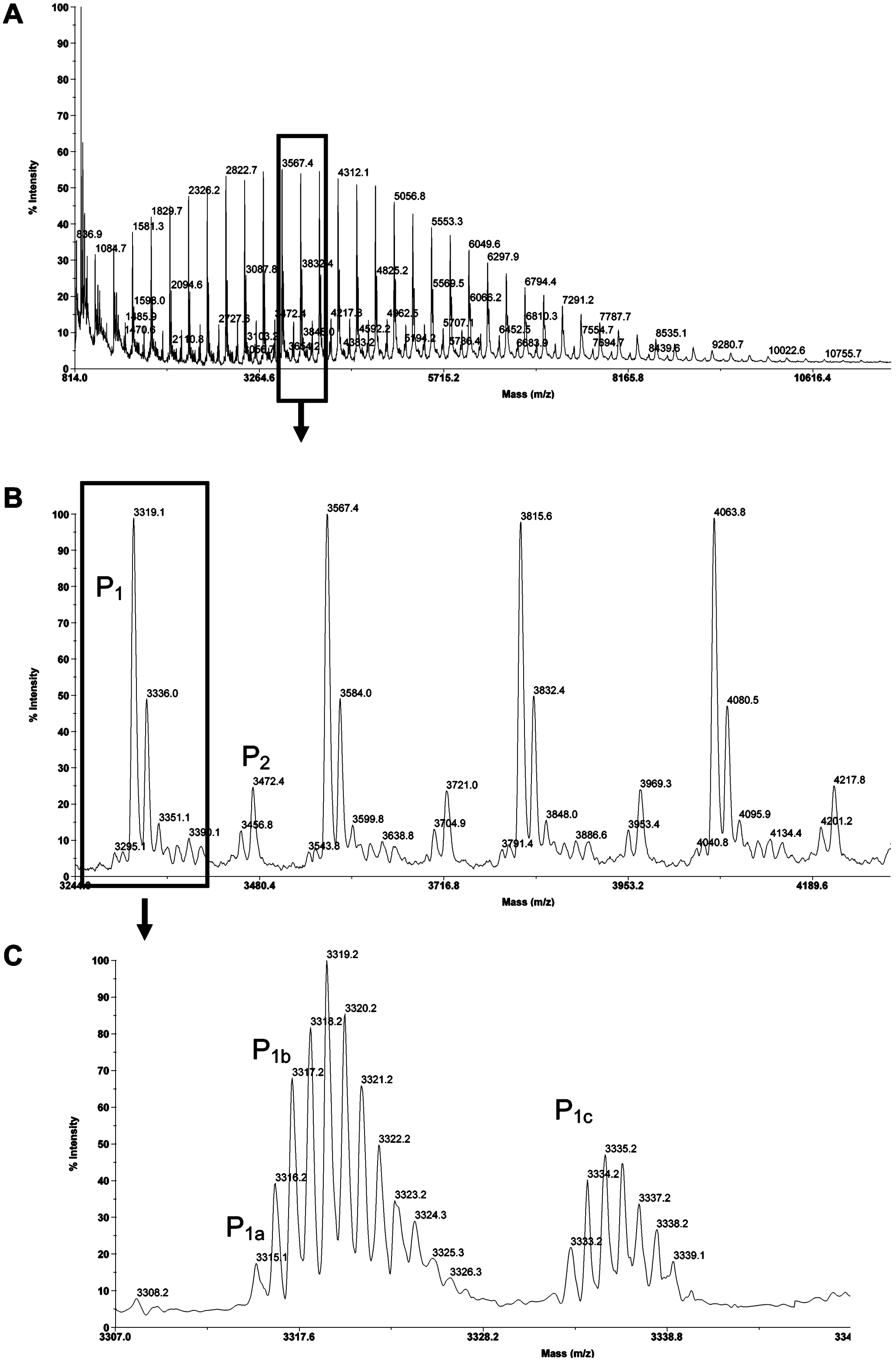
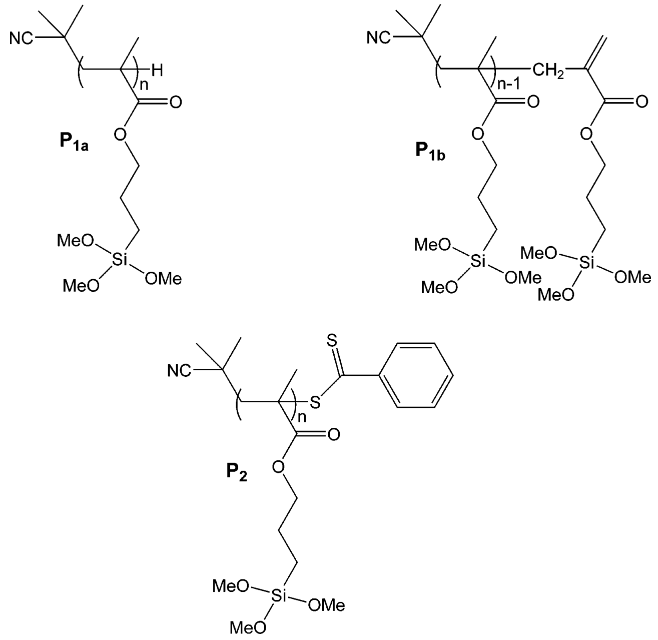


Figure 5. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry analyses of an oligomer of poly(γ-methacryloxypropyltrimethoxysilane) (dithranol as matrix, accelerating potential of 20 kV, laser: 337 nm nitrogen laser): (A) linear mode; (B) enlargement; and (C) corresponding area recorded in the reflectron mode.

the observed strong UV absorption of the main peak is generated by the presence of dithiobenzoate end groups onto the dormant chains. Surprisingly, the shoulder also gave a signal (Figure 4). Considering the corresponding molar mass (double than the dormant chain one), this shoulder may correspond to the presence of terminated intermediate radicals (i.e., bearing a phenyl group Scheme 2B). Because of the rather sterically hindered intermediate radical, the latter termination mode may be operating when the probability of adding monomer units onto propagating radical is low, i.e., at high conversion consistent with our observations. Without being able to discriminate, X in Scheme 2 could either be a proton (radical) or a small group which does not influence the molar mass of the structure. Figure 4 also shows a tail probably corresponding to the presence of

Scheme 3. Main Chemical Structures (P_{1a}, P_{1b}, P_2) Identified by Matrix-Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry Analyses of a Poly(γ-methacryloxypropyltrimethoxysilane) Oligomer



small chains carrying a living dithioester chain end which were not observable with a RI detector alone.[44]

MALDI-ToF Mass Spectrometry Analyses. As the expected trends were evidenced (linear increase of molar mass with conversion, low PDI) but no indication on the true molar mass values was obtained, a MALDI-ToF mass spectrometry study on a sample of PγMPS prepared by CPDB-mediated RAFT polymerization was undertaken. A PγMPS oligomer with a theoretical M_n of 4600 g mol^{-1} (corresponding to a low conversion sample) was analyzed by MALDI-ToF mass spectrometry (Figure 5). The molar mass of the γMPS unit (248.3 g mol^{-1}) is found between two consecutive main peaks of the distribution, which is in agreement with a nondegradation of the reactive repetitive unit. Furthermore, the obtained M_n (4390 g mol^{-1}) is also in good agreement with the theoretical M_n (4600 g mol^{-1}). However, the enlargement of an arbitrary area of the spectrum (Figure 5B) shows two main populations, P_1 and P_2. The molar mass of P_2 (3472.9 g mol^{-1}) is consistent with the expected structure depicted in Scheme 3, cationized by Na^+ and with a polymerization degree of 13. A close examination of P_1 area in the reflectron mode together with a simulation of the assumed structures reveals that two populations are indeed present: P_{1a} (molar mass of 3315.2 g mol^{-1}) and P_{1b} (molar mass of 3317.2 g mol^{-1}), which are consistent with the structures presented in Scheme 3. P_{1a} and P_{1b} could be the result of either fragmentation reactions operating under MALDI-ToF mass spectrometry analysis conditions[45] or chain termination reactions by transfer (P_{1a}) or disproportionation (P_{1b})[43] operating during the RAFT polymerization. P_{1c} may correspond to P_{1a} and P_{1b} cationized by K^+. It is worth mentioning that the relative intensities of the different populations observed is not quantitative. Besides, if the relative intensity of the populations observed was reflecting the real proportions of the chains present during the polymerization process, the obtainment of a controlled character over the temperature range as presented above would be amazing. Therefore, populations P_{1a} and P_{1b} were probably mainly formed under the ionization conditions (even considering the terminated chains due to AIBN initiation). The chains formed during the CPDB-mediated RAFT polymerization of γMPS may therefore be the expected ones, i.e., end-functionalized by the groups forming the initial CTA and exhibiting molar masses which agree with molar masses calculated on the basis of the obtained conversions.

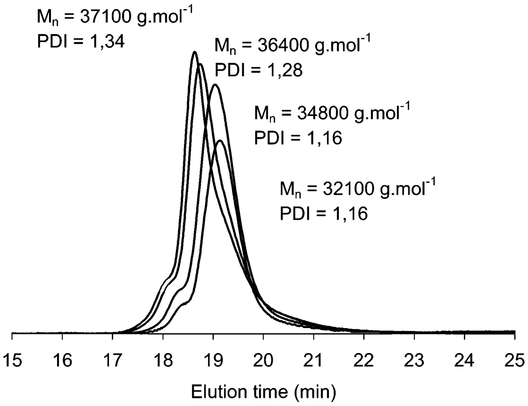


Figure 6. Evolution of number-average molar masses (M_n) and polydispersity indexes (PDI) obtained by size exclusion chromatography (using poly(methyl methacrylate) (PMMA) standards) for poly(γ-methacryloxypropyltrimethoxysilane) (PγMPS) macrochain transfer agent (macro-CTA)-mediated RAFT polymerization of MMA in dioxane at 80 °C. ($[MMA]_0 = 1.77$ mol L^{-1}, $[P\gamma MPS] = 9.56 \times 10^{-3}$ mol L^{-1}, molar ratio macro-CTA/AIBN = 3).

Block Copolymers of γMPS and MMA. *Preparation of P(γMPS-b-(MMA-co-γMPS)).* Block copolymers can be synthesized by controlled radical polymerization either (i) in a two-step reaction by isolating the first block after the polymerization of a monomer and using it as a controlling agent in the polymerization of a second monomer or (ii) in one pot by adding a second monomer at the end of the polymerization of a first monomer. The second strategy was investigated as the isolation of the PγMPS was quite tricky. Indeed, no selective solvent could be found to cleanly precipitate the polymer. Furthermore, a systematic gelation, probably due to the confinement of the reactive trimethoxysilyl functions which then underwent condensation reactions, was observed when trying to dry out the homopolymer under high vacuum. As a result, the polymerization of MMA using PγMPS as macro-CTA was carried out by adding MMA at the end of the polymerization of γMPS (90% conversion), together with AIBN (molar ratio PγMPS/AIBN = 3). The expected copolymer is then a block copolymer in which the second block is a statistical copolymer of MMA and γMPS: *P*(γMPS-*b*-(MMA-*co*-γMPS)). As shown by the evolution of the SEC chromatograms in Figure 6, the expected shift toward high molar masses as well as the rather low PDI obtained (<1.4) are in agreement with the formation of a block copolymer.

However, the shoulder observed in the homopolymerization of γMPS and that we assigned to chains coming from the termination of the intermediate macroradical is still present all over the block copolymerization and is still detectable under UV at 309 nm. Besides, this population seems to be shifting toward higher molar masses with increasing the conversion (Figure 6). Two assumptions could be made. (i) This

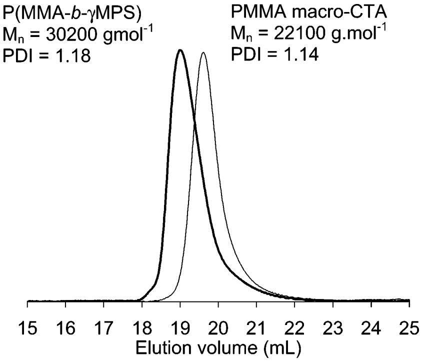


Figure 7. Evolution of number-average molar masses (M_n) and polydispersity indexes (PDI) obtained by size exclusion chromatography (using poly(methyl methacrylate) (PMMA) standards) for the PMMA macro-chain-transfer agent (macro-CTA) and the obtained block copolymer during PMMA macro-CTA-mediated RAFT polymerization of γ-methacryloxypropyltrimethoxysilane (γMPS) (0.6 mol L^{-1}) in dioxane at 80 °C after 79% conversion. Molar ratio macro-CTA/AIBN = 3.

population is acting as “living” chains. In that case, the assumption made in the case of homopolymerization consisting in considering this population as terminated intermediate radicals would then be wrong. We overruled the formation of “living” chains exhibiting double molar masses[46] at the present time as no consistent formation scheme could be put forward. (ii) This population does not correspond to “living” chains. The observed peak would then correspond to terminated intermediate radicals formed in each withdrawn sample. However, the discussion is open to scientific debate.

Preparation of P(MMA-b-γMPS). As the last strategy could not allow the synthesis of pure blocks of PγMPS, we decided to inverse the sequence and to perform the CPDB-mediated RAFT polymerization of MMA first (see Supporting Information). Precipitation of the final PMMA in methanol gave a clean polymer exhibiting all the characteristics required (theoretical M_n = 19 000 g mol^{-1}, calculated M_n = 21 000 g mol^{-1}, PDI = 1.14 obtained by SEC using a PMMA calibration) to be used as a macro-CTA in the polymerization of γMPS. The polymerization was performed with the molar ratio γMPS/macro-CTA chosen so that the theoretical molar mass of the PγMPS block was 23 000 g mol^{-1} after 100% conversion. After 8 h, the polymerization was stopped, 79% conversion was reached, and the final polymer was analyzed by SEC (Figure 7). The observed shift of the chromatogram is consistent with the formation of a block copolymer although the PDI increases slightly, probably due to the presence of remaining PMMA dead chains which have not been elongated. According to the known absolute molar mass of the PMMA block (21 000 g mol^{-1}) and the conversion of γMPS (79%), a PγMPS block of 18 150 g mol^{-1} should be obtained; i.e., the theoretical molar composition of the recovered block copolymer should be 25.8/74.2 (γMPS/MMA). Analysis of the obtained block copolymer by ^{1}H NMR spectroscopy (see Supporting Information) gives an experimental composition of 25.0/75.0, which would correspond to a molar mass of 17 400 g mol^{-1} for the PγMPS block, in good agreement with the theoretical values.

Conclusions

To our knowledge, this study reports the first example of 2-cyanoprop-2-yl dithiobenzoate (CPDB)-mediated reversible addition−fragmentation chain transfer (RAFT) polymerization of the reactive monomer γ-methacryloxypropyltrimethoxysilane (γMPS). RAFT polymerization of γMPS mediated by CPDB was studied in dioxane using AIBN as initiator. The conditions were chosen in order to isolate controlled PγMPS chains (up to M_n = 40 000 g mol^{-1}) exhibiting low polydispersity indexes (PDI < 1.3). PγMPS was characterized by MALDI-ToF mass spectrometry which showed that the expected structure was obtained although degradation of the dithiobenzoate chain end occurred. These chains were further used as macrochain transfer agent (macro-CTA) in the polymerization of MMA. However, as they could not be isolated, only P(γMPS-*b*-MMA-*co*-γMPS) could be synthesized. Syntheses of pure block copolymers based on γMPS and MMA were successfully achieved by the use of PMMA macro-CTA and open up the route to a wide range of macromolecular architectures based on γMPS. This new class of functional block copolymers contains reactive side groups along the PγMPS block that can be hydrolyzed and condensed into an organic/inorganic hybrid material by the sol−gel approach. Moreover, block copolymers may self-assemble into supramolecular structures and offer unique opportunities in the elaboration of well-defined organic/inorganic nanocomposites with tailored morphologies and textures (nanoparticles, porous films, hollow spheres, etc.) which are assessed in our laboratory.

Acknowledgment. The authors thank F. Delolme (Service Central d’Analyse du CNRS, Vernaison, France) for MALDI-ToF mass spectrometry analyses and C. Novat (LCPP, Villeurbanne, France) for SEC analyses. The authors also thank Drs. M. Lansalot (CNRS-bioMérieux, Lyon, France) and Z. Ma (LCPP, Villeurbanne, France) for creative discussions.

Supporting Information Available: Monomer conversion determinations, evolution of molar masses vs conversion for γMPS RAFT homopolymerizations, experimental details for the synthesis of PMMA by CPDB-mediated RAFT polymerization, and calculation of the composition of the block copolymers of γMPS and MMA. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Sanchez, C.; Ribot, F. *New J. Chem.* **1994**, *18*, 1007−1047.
(2) Judeinstein, P.; Sanchez, C. *J. Mater. Chem.* **1996**, *4*, 511−525.
(3) Sanchez, C.; Soler-Illia, G. J. D. A. A.; Ribot, F.; Lalot, T.; Mayer, C. R.; Cabuil, V. *Chem. Mater.* **2001**, *13*, 3061−3083.
(4) Pomogailo, D. *Russ. Chem. Rev.* **2000**, *69*, 53−79.
(5) Kickelbick, G. *Prog. Polym. Sci.* **2003**, *28*, 83−114.
(6) Bourgeat-Lami, E. In *Dendrimers, Assemblies and Nanocomposites*; Arshady, R. A. G. A., Ed.; Citus Books: London, 2002; p 149.
(7) Bourgeat-Lami, E. *J. Nanosci. Nanotechnol.* **2002**, *2*, 1−24.
(8) Bourgeat-Lami, E. In *Encyclopedia of Nanoscience and Nanotechnology*; H. S.; N.; Ed.; Scientific Publishers: Los Angeles, 2004; Vol. 8, pp 305−332.
(9) Schmidt, J. *Sol-Gel Sci. Technol.* **1994**, *1*, 217−231.
(10) Wen, J.; Wilkes, G. L. *Chem. Mater.* **1996**, *8*, 1667−1681.
(11) Schottner, G. *Chem. Mater.* **2001**, *13*, 3422−3435.
(12) Joseph, R.; Zhang, S.; Ford, W. T. *Macromolecules* **1996**, *29*, 1305−1312.
(13) Yu, Y.-Y.; Chen, W.-C. *Mater. Chem. Phys.* **2003**, *82*, 388.
(14) Mauger, M.; Dubault, A.; Halary, J. L. *Polym. Int.* **2004**, *53*, 378−385.
(15) Bourgeat-Lami, E.; Lang, J. *J. Colloid Interface Sci.* **1999**, *210*, 281−289.
(16) Negrete-Herrera, N.; Letoffe, J.-M.; Putaux, J.-L.; David, L.; Bourgeat-Lami, E. *Langmuir* **2004**, *20*, 1564−1571.
(17) Reculusa, S.; Mingotaud, C.; Bourgeat-Lami, E.; Duguet, E.; Ravaine, S. *Nano Lett.* **2004**, *4*, 1677−1682.

(18) Bartholome, C.; Beyou, E.; Bourgeat-Lami, E.; Chaumont, P.; Zydowicz, N. *Macromolecules* **2003**, *36*, 7946−7952.

(19) Tissot, I.; Reymond, J. P.; Lefebvre, F.; Bourgeat-Lami, E. *Chem. Mater.* **2002**, *14*, 1325−1331.

(20) Wei, Y.; Yang, D.; Tang, L.; Hutchins, M. K. *J. Mater. Res.* **1993**, *8*, 1143−1152.

(21) Coltrain, B. K.; Landry, C. J. T.; O'Reilly, J. M.; Chamberlain, A. M.; Rakes, G. A.; Sedita, J. S.; Kelts, L. W.; Landry, M. R.; Long, V. K. *Chem. Mater.* **1993**, *5*, 1445−1455.

(22) Chang, T. C.; Wang, Y. T.; Hong, Y. S.; Chiu, Y. S. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1972−1980.

(23) Underhill, R. S.; Liu, G. *Chem. Mater.* **2000**, *12*, 2082−2091.

(24) Zhao, H.; Douglas, E. P. *Chem. Mater.* **2002**, *14*, 1418−1423.

(25) Zhou, J.; Li, Z.; Liu, G. *Macromolecules* **2002**, *35*, 3690−3696.

(26) Matyjaszewki, K. *Controlled Radical Polymerization*; American Chemical Society: Washington, DC, 1998.

(27) Du, J.; Chen, Y. *Macromolecules* **2004**, *37*, 6322−6328.

(28) Koh, K.; Ohno, K.; Tsujii, Y.; Fukuda, T. *Angew. Chem., Int. Ed. Engl.* **2003**, *42*, 4194−4197.

(29) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661−3688.

(30) Donovan, M. S.; Sanford, T. A.; Lowe, A. B.; Sumerlin, B. S.; Mitsukami, Y.; McCormick, C. L. *Macromolecules* **2002**, *35*, 4570−4572.

(31) Donovan, M. S.; Lowe, A. B.; Sumerlin, B. S.; McCormick, C. L. *Macromolecules* **2002**, *35*, 4123−4132.

(32) Vosloo, J. J.; Tonge, M. P.; Fellows, C. M.; D'Agosto, F.; Sanderson, R. D.; Gilbert, R. G. *Macromolecules* **2004**, *37*, 2371−2382.

(33) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, G.; Moad, C. L.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559−5562.

(34) Chiefari, J.; Moad, G.; Rizzardo, E.; Gridnev, A. A. (E.I. Du Pont De Nemours and Company; Commonwealth Scientific and Industrial Research Organization). 9847927, 1998.

(35) Rizzardo, E.; Chiefari, J.; Mayadunne, R. T. A.; Moad, G.; Thang, S. H. *ACS Symp. Ser.* **2000**, *768*, 278−296.

(36) Saricilar, S.; Knott, R.; Barner-Kowollik, C.; Davis, T. P.; Heuts, J. P. A. *Polymer* **2003**, *44*, 5169−5176.

(37) Moad, G.; Chiefari, J.; Chong, Y. K.; Krstina, J.; Mayadunne, R. T. A.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym. Int.* **2000**, *49*, 993−1001.

(38) D'Agosto, F.; Charreyre, M.-T.; Veron, L.; Llauro, M.-F.; Pichot, C. *Macromol. Chem. Phys.* **2001**, *202*, 1689−1699.

(39) Brinker, C. J.; Scherer, G. W. In *The Physics and Chemistry of Sol−Gel Processing*; Press, A., Ed.: Elsevier Science: London, 1990; pp 108−216.

(40) Coote, M. L. *Macromolecules* **2004**, *37*, 5023−5031.

(41) Zhu, J.; Di, Z.; Zhu, X.; Chen, G. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 2558−2565.

(42) Chong, Y. K.; Kristina, J.; Le, T. P. T.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2003**, *36*, 2256−2272.

(43) Zammit, M. D.; Davis, T. P.; Haddleton, D. M. *Macromolecules* **1996**, *29*, 492−494.

(44) According to the comments of one of the reviewer of this paper, although no direct evidence could be put forward and due to the inadequacy of the calibration of the SEC, the possibility of intermolecular condensation of trimethoxy groups cannot be completely ruled out.

(45) D'Agosto, F.; Hughes, R.; Charreyre, M.-T.; Pichot, C.; Gilbert, R. G. *Macromolecules* **2003**, *36*, 621−629.

(46) Moad, G.; Mayadune, R. T.; Rizzardo, E.; Skidmore, M.; Thang, S. H. *ACS Symp. Ser.* **2003**, *854*, 520−535.

MA048143J