



Synthesis of novel random and block copolymers of *tert*-butyldimethylsilyl methacrylate and methyl methacrylate by RAFT polymerization

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ABSTRACT

Hydrophobic-hydrolysable copolymers consisting of methyl methacrylate (MMA) and *tert*-butyldimethylsilyl methacrylate (TBDMSMA) have been synthesized for the first time by Reversible Addition–Fragmentation chain Transfer (RAFT) polymerization technique using cumyl dithiobenzoate (CDB) and cyanoisopropyl dithiobenzoate (CPDB) as chain transfer agents (CTAs). The monomer reactivity ratios for TBDMSMA ($r_1 = 1.40 \pm 0.03$) and MMA ($r_2 = 1.08 \pm 0.03$) have been determined using a non-linear least-squares fitting method. Well-defined random copolymers PMMA-co-PTBDMSMA have been prepared. Then, the versatility of the RAFT process to synthesize silylated block copolymers with controlled molecular weights and low polydispersities has been demonstrated using two strategies: the synthesis of PMMA–SC(=S)Ph or PTBDMSMA–SC(=S)Ph as macro-chain transfer agent (macro-CTA) for use in a two step method or an one-pot method which consists in the successive addition of the two monomers. Diblock copolymers with narrow molecular weight distributions ($PDI < 1.2$) were obtained from the one-pot method with number-average molecular weight values within the range 10,000–22,000 g mol^{-1} .

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1. Introduction

The development of synthetic polymers containing hydrolytically labile bonds has been an ongoing activity for many years in pharmaceutical, biomedical, agrochemical and antifouling areas. In all concerns, the chemical structure of the polymer is designed to release drugs or biocides via a mechanism of polymer erosion [1–4]. Several types of erosion are reported in the literature, including water-soluble polymers that have been insolubilized by hydrolytically unstable cross-links, polymers that are initially water-insoluble and are solubilized by hydrolysis, ionization of pendant groups, and hydrophobic polymers that are converted to small water-soluble molecules by backbone cleavage [5]. The type of polymer erosion is then dictated by the specific application.

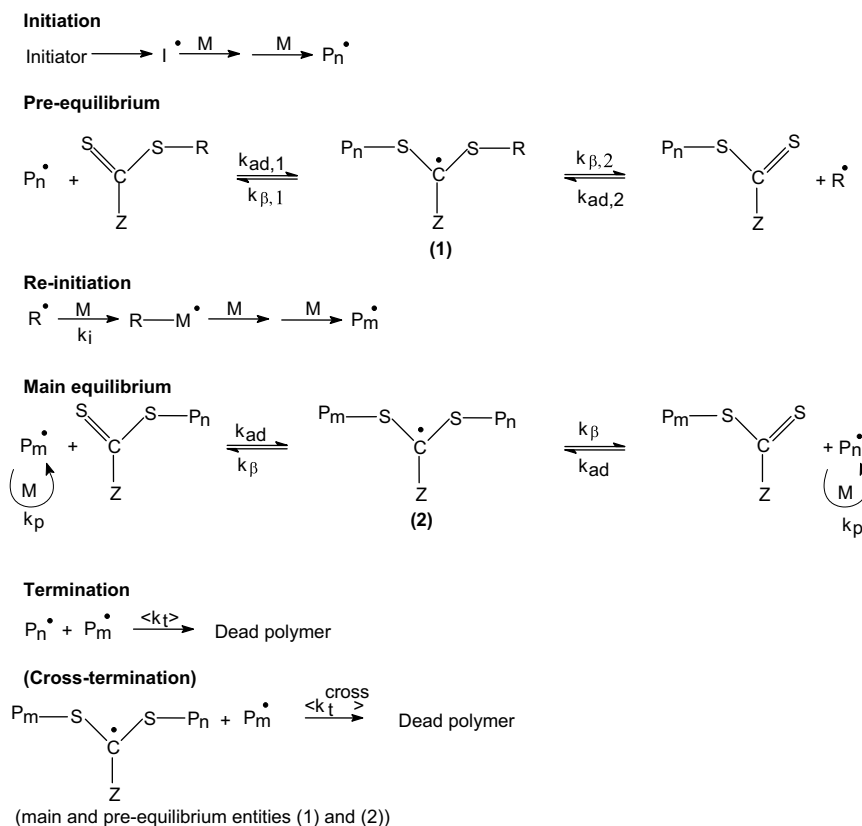
In our research group, systems based on the conversion of water-insoluble macromolecules to water-soluble ones by a reaction of a pendant groups with sea water have been developed for antifouling applications. Poly(meth)acrylic resins bearing hydrolysable pendant groups have been synthesized through chemical modifications [6] or polymerization methods [7–9].

With the development of several methods of controlled radical polymerization (CRP), including nitroxide-mediated polymerization

(NMP) [10], atom transfer radical polymerization (ATRP) [11,12], and reversible addition–fragmentation chain transfer (RAFT) polymerization [13–15], well-defined polymers with complex architectures including block, graft, and star structures could be prepared. Although their chemistry varies considerably, a common feature of these methods is the need to protect the majority of the growing polymer chains from the bimolecular termination reactions that normally occur in conventional free-radical polymerization. Among them, the RAFT polymerization is an interesting process to synthesize polymers with controlled molecular weights, low polydispersities and, which can be reactivated for the synthesis of block copolymers. The success of the RAFT process is the use of an efficient dithioester chain transfer agent (CTA) that allows, in the addition–fragmentation steps, to establish a dynamic equilibrium between the active propagating radicals and the dormant polymer chains [16]. The overall RAFT polymerization is generally divided into two sets of reactions, that is, so-called pre-equilibrium, which involves the initial RAFT agent and includes the initialization of the living process, and the main equilibrium between growing and dormant polymer chains (Scheme 1). To the basic reaction should be added the common reactions of a conventional radical polymerization including the initiation, the propagation and termination steps. The effectiveness of the RAFT agents in terms of their transfer ability and control of molecular weight and polydispersities strongly depends on the nature of the Z and R groups. Highly effective RAFT agents are thiocarbonylthio compounds, where R is a free-radical leaving group that

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Scheme 1. General scheme of the RAFT process using a dithioester as CTA.

is capable of reinitiating polymerization activity and Z is a group that modifies the reactivity of the carbon sulphur double bond on the one hand and the stability of the intermediate macro-CTA radical on the other hand. Nevertheless, a retardation effect as well as the presence of an induction period have been reported to occur in many dithiobenzoate-mediated RAFT polymerizations, including (meth)acrylate monomers [13,17–22]. These two kinetic effects are still undergoing debate in the scientific community and have been very recently reviewed by an IUPAC task group [23]. The RAFT process is well-known to exhibit a high degree of compatibility with a wide range of functional monomers while giving excellent access to complex architectures ranging from block to star polymers. Several studies of the RAFT copolymerization of (meth)acrylic monomers from monofunctional chain transfer agent have been published [13,14,24–36]. In addition to propagation and termination reactions from conventional copolymerizations, Feldermann et al. [36] reported that the macroradicals may react with the RAFT agent in the pre-equilibrium and main equilibrium steps of Scheme 1. Depending on the reactivity and stability of these macroradicals and the intermediate species (1) and (2), respectively, the rate coefficients k_{ad} and k_{β} may be influenced by the type of monomer at the terminal position. Therefore, a difference in these rate coefficients may alter the ratio of the two macroradicals compared to conventional free-radical polymerizations.

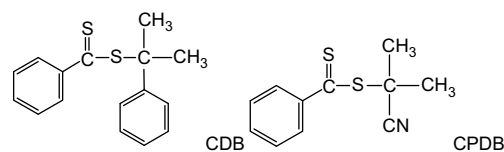
The current paper is focused on the synthesis of well-defined random and diblock copolymers bearing silylated ester groups as hydrolysable pendant groups with the use of cumyl dithiobenzoate (CDB) and cyanopropyl dithiobenzoate (CPDB) as CTA (Scheme 2). Scientific data on the controlled/living radical polymerization of hydrolysable trialkylsilyl (meth)acrylates are scarcely reported into the academic literature. Together with the synthesis of random copolymers, the reactivity ratios were assessed with and without the use of a chain transfer agent. Several methods have been reported to determine the monomer

reactivity ratios including non-linear curve fitting and non-linear least-square (NLLS) methods [37–39]. In this study, the non-linear least-squares fitting method through the Van Herk's program has been used to determine the reactivity ratios [39]. In addition, the Penultimate Unit Model (PUM) has been considered as recommended into the literature [40–43]. Beside the determination of the reactivity ratios of the monomers, several block copolymers PMMA-block-PTBDMSMA were prepared. To obtain a well-defined block copolymer, the synthetic order for the block formation (AB or BA block copolymerization) is often important [34]. Then, the versatility of the RAFT process to synthesize silylated copolymers with controlled molecular weights and low polydispersities has been demonstrated using two strategies: the synthesis of PMMA-SC(=S)Ph or PTBDMSMA-SC(=S)Ph as macro-chain transfer agent (macro-CTA) for use in a two step method or the one-pot method which consists in the successive addition of the two monomers.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA) and toluene were purchased from Acros, and distilled under reduced pressure before use.



Scheme 2. Chemical structures of the RAFT agents cumyl dithiobenzoate (CDB) and cyanopropyl dithiobenzoate (CPDB) used in the present study.

2,2'-Azobisisobutyronitrile (AIBN) was purchased from Aldrich and purified by recrystallization from methanol. 2-Phenylprop-2-yl dithiobenzoate (cumyl dithiobenzoate: CDB) and 2-cyanoprop-2-yl dithiobenzoate (CPDB) were synthesized with procedures described in the literature [14,44]. *Tert*-butyldimethylsilyl methacrylate (TBDMSMA) was prepared according to the literature [9].

2.2. Reactivity ratios determination

Toluene solutions of MMA (1.5 M), TBDMSMA (1.5 M), CDB (0.45 M) and AIBN (0.09 M) were first prepared and added to the reaction mixtures to obtain concentrations of total monomer, CDB and AIBN equal to 1.5 M, 2.25×10^{-3} M and 4.5×10^{-4} M, respectively. The molar ratio of TBDMSMA was increased from 0.2 to 0.8. The solutions were put in cylindrical tubes and degassed by three freeze–thaw–pump cycles. After degassing, the tubes were filled with argon, sealed, and heated at 70 °C in a constant-temperature oil bath for 4 h. Then, the experiments were also done without CDB for 2 h. The polymerization was stopped by rapid cooling in liquid nitrogen and by opening the polymerization tubes to air. The reaction mixtures were evaporated under vacuum until constant mass to remove the solvent and residual monomers. In all cases, the monomer conversions do not exceed 10%. The composition of copolymers and their molecular weights are given in Tables 1 and 2. The Van Herk's program was used to evaluate the monomer reactivity ratios with 95% of confidence.

2.3. Random copolymer synthesis

MMA (5.63 g, 5.63×10^{-2} mol), TBDMSMA (3.75 g, 1.87×10^{-2} mol), AIBN (31.7 mg, 1.93×10^{-4} mol) and CTA (262.6 mg, 9.65×10^{-4} mol of CDB or 213.2 mg, 9.65×10^{-4} mol of CPDB) were added to a 50 ml volumetric flask, and filled with distilled toluene. Then, the reaction mixture was transferred into a 100 ml round-bottomed flask equipped with a magnetic stir bar. The degassing and polymerization procedures were the same as described above. In this case, the polymerization was conducted until no evolution of monomer conversion (about 90 h). Then, the polymer was precipitated into a mixture of pentane/diethylether (97/3 v/v), filtered, and dried under vacuum for 24 h at room temperature.

2.4. Macro-CTA synthesis

PMMA–SC(=S)Ph (called macro-CTA1). MMA (29.40 g, 0.294 mol), AIBN (141.2 mg, 8.6×10^{-4} mol), CPDB (0.955 g, 4.3×10^{-3} mol), and toluene (160.0 ml) were added to a 500 ml round-bottomed flask equipped with a magnetic stir bar. The degassing and polymerization procedures were the same as described above. In this case, the polymerization was stopped after 5 h of reaction to limit the monomer conversion to 70%. Then, the polymer was precipitated into pentane, filtered, and dried under vacuum for 24 h at room temperature. The macro-CTA1 was obtained with a final yield of 74% (22.0 g) and a number-average molecular weight $M_n = 6300$; PDI = 1.14 (SEC, PMMA calibration).

PTBDMSMA–SC(=S)Ph (called macro-CTA2). To a 500 ml round-bottomed flask equipped with a magnetic stir bar were added TBDMSMA (40.0 g, 0.20 mol), AIBN (135.0 mg, 8.2×10^{-4} mol), CPDB (0.91 g, 4.1×10^{-3} mol), and toluene (100.0 ml). The degassing and polymerization procedures were the same with above. In this case, the polymerization was stopped after 4 h of reaction and the polymer was precipitated into methanol. The macro-CTA2 was obtained with a final yield of 67.5% (27.0 g) and $M_n = 12,300$; PDI = 1.10 (SEC, universal calibration).

2.5. Synthesis of diblock copolymers using macro-CTA

Diblock copolymers PMMA–block–PTBDMSMA (or PTBDMSMA–block–PMMA) were prepared following a typical procedure. To a 100 ml round-bottomed flask equipped with a magnetic stir bar were added the macro-CTA1 (or macro-CTA2), AIBN as initiator with a macro-CTA to AIBN ratio close to 5, and toluene as solvent. The degassing and polymerization procedures were the same as earlier described and the polymerization time is 24 h. Block copolymers were precipitated into methanol in the case of PMMA–block–PTBDMSMA copolymer or a mixture methanol/pentane (80/20; v/v) to separate the homopolymer PTBDMSMA from PTBDMSMA–block–PMMA copolymers, filtered, and dried under vacuum for 24 h.

2.6. Block copolymers synthesis by the one-pot method

For the first block PTBDMSMA, the polymerization procedure was the same to that of PTBDMSMA–CTA synthesis shown above but the reaction was keeping until a total monomer conversion (>98%). When the polymerization was achieved, a solution of MMA monomer and AIBN in toluene previously degassed was added in the reaction mixture (Table 4). The polymerizations were conducted until no evolution of the monomer conversion. The polymers were then precipitated into a mixture methanol/pentane (80/20; v/v), filtered, and dried under vacuum for 24 h.

2.7. Kinetics of the copolymerization

TBDMSMA (6.0 g; 0.03 mol), CDB (225 mg; 8.3×10^{-4} mol), AIBN (27.3 mg; 1.66×10^{-4} mol) and toluene (11.2 g) were added to a 100 ml round-bottomed flask equipped with a magnetic stir bar. The TBDMSMA polymerization procedure was the same as shown above. When the polymerization was achieved (24 h, 97% of conversion), a pre-degassed solution composed of MMA (6.0 g; 0.06 mol), AIBN (27.3 mg; 1.66×10^{-4} mol) and toluene (11.2 g) was added. The copolymerization was monitored by withdrawing samples through a degassed syringe at different timed intervals for ^1H NMR and SEC with PMMA standards analysis.

2.8. Characterization techniques

The average molecular weights (M_n and M_w) and the polydispersity index (M_w/M_n or PDI) of polymers were determined by

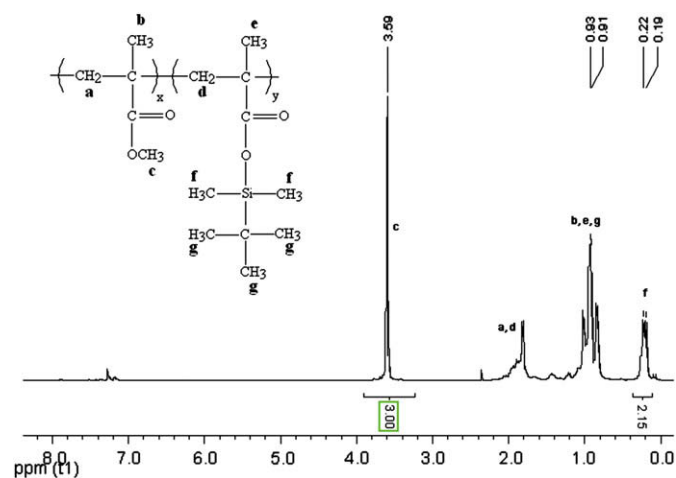


Fig. 1. ^1H NMR spectrum of MMA–TBDMSMA copolymers synthesized via the RAFT process (400 MHz, CDCl_3).

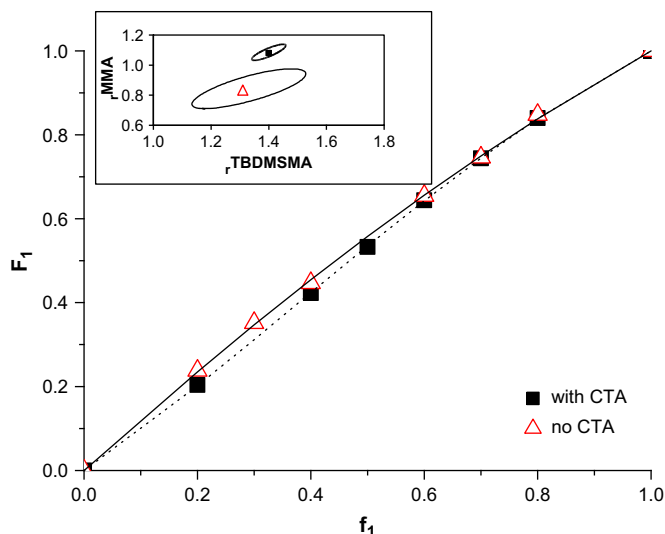


Fig. 2. Mayo–Lewis plots showing the correlation between the copolymer and feed composition for the methyl methacrylate and tert-butyl dimethylsilyl methacrylate system [45]. The straight and dashed lines refer to the best fit. The upper part shows the r -values and the errors of these parameters obtained using the Van Herk's program with 95% of confidence.

Size Exclusion Chromatography (SEC) using a Waters 501 pump equipped with a refractive-index detector (DRI 410), a Kontron 432 HPLC UV detector and five Waters Styragel HR columns (2 HR0.5, HR1, HR3, HR4; 7.8×300 mm). Tetrahydrofuran was used as an eluent at 30°C and at a flow rate of 1.0 mL min^{-1} . The molecular weight and polydispersity index data were compared against narrow standards of PMMA, $M_p = 620\text{--}3.64 \times 10^5\text{ g mol}^{-1}$, obtained from Polymer Laboratories. The M_n , M_w and PDI values of copolymers were measured by a triple detector instrument (TD-SEC; Viscotek TDA 302 Model) consisting of size exclusion chromatography (SEC, in THF with a flow rate of 1.0 mL min^{-1}) with three linear columns (Polymer Laboratories, two Mixed-C, $5\ \mu\text{m}$ columns and one linear column, $100\ \text{\AA}$, $5\ \mu\text{m}$), a refractive index (RI) detector, a light scattering (LS) detector ($\lambda = 670\text{ nm}$, 3 mW , 90° scattering angle), and a viscometer (VISC).

The monitoring of polymerizations and the characterization of copolymers were carried out by ^1H NMR spectroscopy using a Bruker Avance 400 spectrometer. CDCl_3 and DMSO-d_6 were used as deuterated solvents. For the quantitative NMR measurements, the data acquisition parameters were as follows: delay time = 3 s , pulse width = $2.9\ \mu\text{s}$, number of scans = 128.

3. Results and discussion

3.1. Random copolymerization

The copolymer systems methyl methacrylate (MMA)–tert-butyl dimethylsilyl methacrylate (TBDMMSMA) have been studied at

Table 1

Feed and instantaneous copolymer molar composition of TBDMMSMA (1) for RAFT copolymerization with MMA in toluene at 70°C in presence of CDB as CTA.

f_1	F_1	M_n of copolymer (g mol^{-1})	PDI
0.20	0.204	20,800	1.3
0.40	0.423	17,300	1.3
0.50	0.533	18,600	1.27
0.60	0.644	16,200	1.31
0.70	0.744	14,700	1.54
0.80	0.840	14,700	1.41

Table 2

Feed and instantaneous copolymer molar composition of TBDMMSMA(1) for a conventional radical copolymerization with MMA in toluene at 70°C .

f_1	F_1	M_n of copolymer (g mol^{-1})	PDI
0.20	0.238	59,700	1.84
0.30	0.352	62,400	1.64
0.40	0.447	67,600	1.61
0.60	0.655	62,700	2.04
0.70	0.746	58,500	1.83
0.80	0.848	58,400	1.75

Table 3

Reactivity ratios for the copolymerization of TBDMMSMA(1) and MMA(2) with and without CDB as RAFT agent (toluene, 70°C). Data obtained from the Van Herk's program.

Experiments	r_1	r_2
With CTA	1.40 ± 0.03	1.08 ± 0.03
Without CTA	1.31 ± 0.09	0.83 ± 0.06

70°C in toluene using a RAFT and non-RAFT control. The molar composition of the copolymers was assessed via ^1H NMR spectroscopy from the integrations of the three protons of the $-\text{OCH}_3$ group in MMA ($\sim 3.6\text{ ppm}$) and the six protons of the $-\text{Si}(\text{CH}_3)_2$ group in the TBDMMSMA ($\sim 0.22\text{ ppm}$) monomer units (Fig. 1).

Fig. 2 shows the Mayo–Lewis plots evaluated from the NMR data (Tables 1 and 2) combined with the best fit (line) using the r -values assessed with the program CONTOUR based on a non-linear method of error assessment (Table 3) [46–48]. The 95% confidence intervals for the reactivity ratios are depicted in the upper part of Fig. 2. Data from Fig. 2 suggest a small influence of the RAFT agent on the copolymer composition. Nevertheless, the 95% confidence interval for the non-RAFT-control system is offset from the data obtained by RAFT copolymerization.

Table 3 shows small differences of the reactivity ratios for the two experiment sets. The difference between the reactivity ratios seems to be more pronounced for the r_2 value which increases slightly with the RAFT agent. As discussed by Feldermann et al. [36], these results are mainly due to compositional changes in the copolymer, which may be caused by changes in the individual radical populations coming from differently stable RAFT adduct radicals and different initiation and pre-equilibrium rates. The composition of the copolymers with initially low contents of the silylated monomer (or high contents of MMA) seems to be more affected by the RAFT agent. The CDB-mediated copolymerization leads to a slight increase of the amount of MMA units in the copolymer compared to the conventional radical copolymerization. Consequently, the incorporation of MMA is enhanced and the composition drift is reduced.

As reported by Deb [49,50] and Fukuda et al. [43], most systems are seen to follow the penultimate model better than the terminal

Table 4

Effect of the penultimate monomer unit on the reactivity ratios for the copolymerization of TBDMMSMA(1) and MMA(2) with and without CDB as RAFT agent (toluene, 70°C).

Experiments	Parameter	Current value	Parameter	Current value	Standard deviation
With CTA	r_{11}	1.44	r_{22}	1.03	0.000926
	r_{21}	1.06	r_{12}	0.92	
Without CTA	r_{11}	1.97	r_{22}	0.75	0.00354
	r_{21}	2.06	r_{12}	4.61	

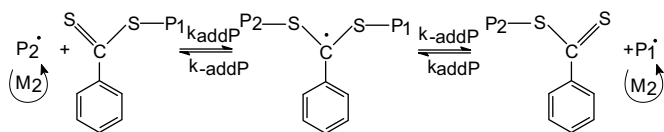
Table 5

RAFT copolymerizations of MMA and TBDMSMA in toluene solution at 70 °C in presence of CDB or CPDB as CTA. Monomer concentration = 1.5 M, [MMA]/[TBDMSMA] = 75/25.

CTA	MMA conversion (%) ^a	TBDMSMA conversion (%) ^a	M_n (g mol ⁻¹) ^b	PDI	[MMA]/[TBDMSMA] molar composition in copolymer ^a
CDB	79.4	85.7	10,200	1.16	74/26
CPDB	88.6	92.6	11,000	1.16	73/27

^a Determined by ¹H NMR spectroscopy.

^b Measured by TD-SEC (universal calibration).



Scheme 3. Main equilibrium of the RAFT copolymerization using dithioester as CTA.

model. In addition, the penultimate unit effect (PUE) has been already reported to appear on chain transfer reactions [36,51,52]. This model requires eight propagation reactions and four reactivity ratios [41]. The Excel Solver was used to evaluate the penultimate unit effect (see [Supplementary data](#)). As described by Switala-zeliakow [38], several solutions for r -values could be obtained

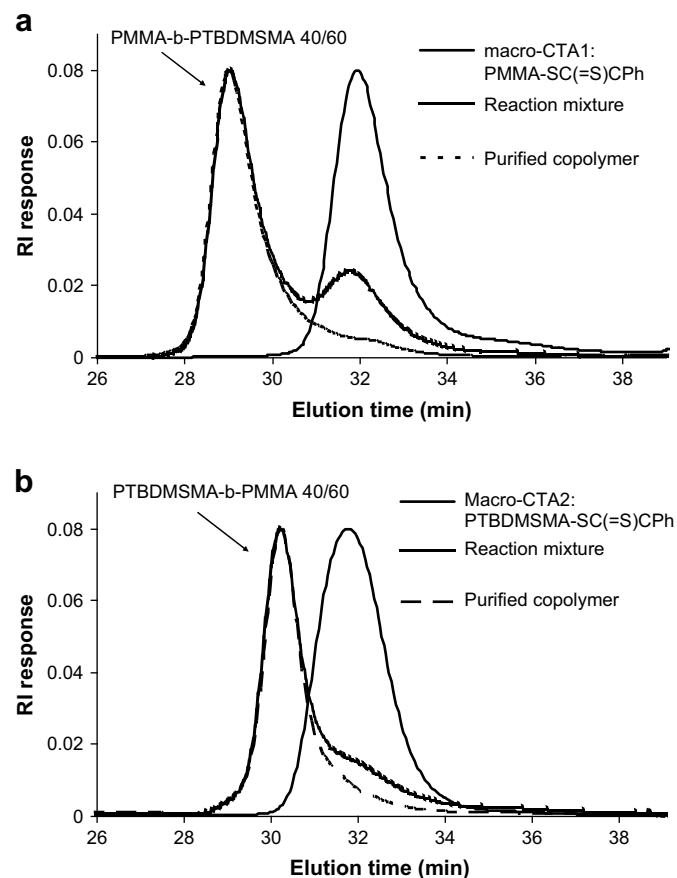


Fig. 3. SEC chromatograms of RAFT copolymerizations at 70 °C (a) of PTBDMSMA in the presence of PMMA-SC(=S)Ph as macro-CTA and (b) of MMA in the presence of PTBDMSMA-SC(=S)Ph as macro-CTA. For both copolymerizations: [MMA and TBDMSMA] = 1.5 M, [macro-CTA] = 9.5×10^{-3} M, [AIBN] = 2×10^{-3} M, polymerization time = 24 h.

depending on the initial r -values, and the confidence and precision variables. A current solution with the lower standard deviation was obtained by varying the initial values of r_{11} , r_{21} , r_{22} and r_{12} from 0 to 10 with a fixed value of the precision and the convergence equal to 1×10^{-7} (Table 4). The differences in the reactivity ratios are only minor for (r_{11} , r_{21}) and (r_{22} , r_{12}) values in the CDB-mediated copolymerization, which could indicate a slight penultimate effect. In a non-RAFT control system, the reactivity of the MMA-terminated macroradicals is shown to be strongly dependent on the penultimate monomer unit, decreasing its tendency to alternate with a TBDMSMA penultimate monomer unit.

Another RAFT agent, CPDB, was used in the RAFT mediated copolymerizations of MMA and TBDMSMA (Table 5). The ¹H NMR analysis of the purified copolymers confirmed the incorporation of both MMA and TBDMSMA units. Unimodal SEC chromatograms (not presented here) revealed a good control of the CDB- and CPDB-mediated polymerizations with narrow molecular weight distributions (PDI = 1.16). In addition, the molecular weights of these random copolymers were in close agreement with the theoretical values. In the two data sets, the monomer conversion is similar for the same polymerization time, indicating that the rate of polymerization is not so different for these two CTAs. However, the TBDMSMA conversion is slightly higher than the MMA one. This result is in agreement with the reactivity ratios determined above. Therefore, when the monomer conversions were not 100%, we obtain slight TBDMSMA-rich random copolymers compared to the initial monomer ratios.

3.2. Diblock copolymerization

The ability to prepare controlled architectures, such as block copolymers, is one of the features that distinguish controlled free radical from conventional free-radical polymerization. In the RAFT polymerization, the S=C(Z)S- moiety is transferred between growing and dormant chains ensuring the living character of the polymerization. When the second monomer is added, the polymerization can be continued giving a block copolymer. The main equilibrium of RAFT copolymerization is shown in Scheme 3, in which the order of addition of monomers is crucial for forming a narrow polydispersity block copolymer. In general, the first-formed polymeric thiocarbonylthio compound P1 (called macro-chain transfer agent or macro-CTA) should have a high transfer constant in the subsequent polymerization step to give the P2 block. In the other word, the leaving group ability of propagating radicals P1 should be comparable or higher than that of the propagating radicals P2. For example, to obtain a well controlled block copolymer of MMA and styrene, the polymerization needs to start with MMA following by addition of styrene [26,34].

As the monomers used in this work are both methacrylates, we attempt to check the leaving character of propagating radicals PMMA and PTBDMSMA in using them as macro-CTA for the polymerization of TBDMSMA and MMA, respectively. Block copolymers can be synthesized either by the one-pot method by adding a second monomer at the end of the polymerization of a first monomer or by a two-step reaction by isolating the first block and using it as a macro-CTA to continue the polymerization of the second monomer.

3.2.1. Block copolymers synthesis using macro-CTAs

The two-step method concerns firstly the synthesis of homopolymers that will be used as macro-CTAs in a second step. The isolation of the macro-CTA before addition of the second monomer allows obtaining pure block copolymer without contamination of the first monomer in the second block. Two macro-CTAs (PMMA-SC(=S)Ph called macro-CTA1) and (PTBDMSMA-SC(=S)Ph called

Table 6

RAFT block copolymerizations of TBDMSMA with PMMA-SC(=S)Ph ($M_n = 6300$; PDI = 1.14, entry 1) and MMA with PTBDMSMA-SC(=S)Ph ($M_n = 12,300$; PDI = 1.17, entry 2) as macro-CTAs at 70 °C for 24 h: [MMA and TBDMSMA] = 1.5 M, [macro-CTA] = 9.5×10^{-3} M, [AIBN] = 2×10^{-3} M.

Entry	$M_{n, \text{copo}}^{\text{th}}$ (g mol ⁻¹) ^a	$M_{n, \text{copo}}^{\text{exp}}$ (g mol ⁻¹) ^b	PDI	Monomer conv. (%) ^c	$f_{\text{macro-CTA}}$ (%) ^d	[MMA]/[TBDMSMA] molar ratios		
						Initial mixture	Mixture after reaction ^e	Final diblock copolymer ^c
1	PMMA-SC(=S)Ph as macro-CTA 23,000	30,200	1.24	88	50	40/60	43/57	27/73
2	PTBDMSMA-SC(=S)Ph as macro-CTA 20,800	17,900	1.13	90	90	60/40	57.5/42.5	60/40

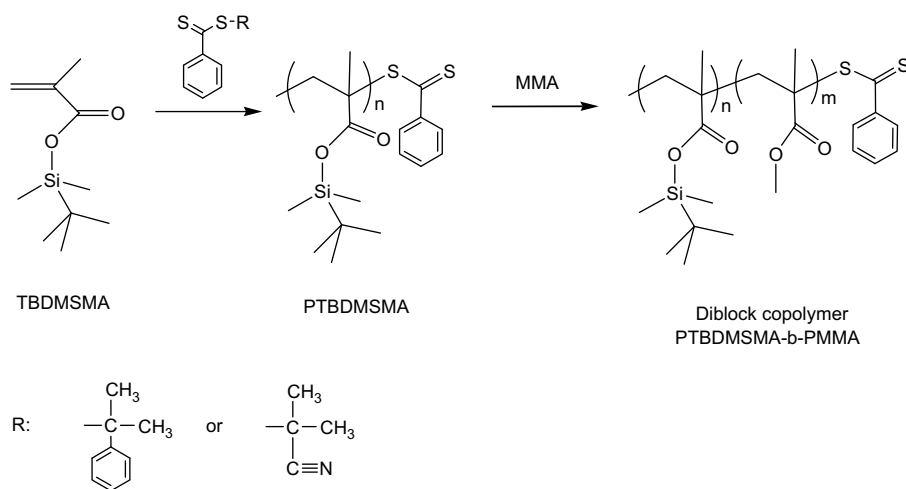
^a Using Eq. (1) with $MW_{\text{MMA}} = 100 \text{ g mol}^{-1}$ and $MW_{\text{TBDMSMA}} = 200 \text{ g mol}^{-1}$.

^b Measured by TD-SEC (universal calibration).

^c Determined by ¹H NMR spectroscopy.

^d Calculated using Eq. (2).

^e After elimination of free monomer.

**Scheme 4.** Block copolymerization of TBDMSMA and MMA by the RAFT process.

macro-CTA2) were synthesized in toluene solution at 70 °C using CPDB as CTA. The polymerizations were stopped at a monomer conversion of about 70%. In these conditions, a good control of molecular weights and their distributions were obtained for both polymers (macro-CTA1: $M_n = 6300$; PDI = 1.14, and macro-CTA2: $M_n = 12,300$; PDI = 1.17). As MMA and TBDMSMA are both methacrylic monomers that can copolymerize, we will check the ability of each macro-CTA to control the subsequent polymerization. For each copolymerization, a molar ratio of 40% of macro-CTA was used.

Fig. 3 shows the overlay of SEC chromatograms of purified macro-CTA and block copolymers before and after purification.

Chain extensions attributed to the formation of the diblock copolymers are confirmed by a shift of SEC curves towards shorter elution times. However, the SEC chromatograms of reaction mixtures before purification reveal a bimodal distribution for both entries, and more specifically for the polymerization of TBDMSMA in the presence of macro-CTA1. The residual peak at 32 min of retention time corresponds to the macro-CTA which is not active or prematurely terminated. In addition, it is necessary to note that PTBDMSMA has a hydrodynamic volume smaller than PMMA as described in a previous study [9] which explain why in the SEC analysis a PMMA of 6300 (g mol⁻¹) elutes with the same elution

Table 7

Copolymerization of TBDMSMA and MMA by the one-pot method.

Entry	First block PTBDMSMA Conditions: [TBDMSMA] = 1.5 M [CDB]/[AIBN] = 5; $V_{\text{total}} = 20 \text{ mL}$; 70 °C				Diblock copolymers PTBDMSMA-block-PMMA [TBDMSMA]/[MMA] from 20/80 to 80/20 [macro-CTA]/[AIBN] = 5; $V_{\text{total}} = 40 \text{ mL}$; 70 °C					
	M_n^{th} ^a	M_n^{exp} ^b	PDI	Conv. (%) ^c	$M_{n, \text{copo}}^{\text{th}}$ ^d	$M_{n, \text{copo}}^{\text{exp}}$ ^b	PDI	MMA conv. (%) ^c	[TBDMSMA]/[MMA] molar ratio	
										Initial
3	3580	6300	1.13	>99	18,500	14,000	1.07	98	20/80	21/79
4	6670	9200	1.14	97	21,480	18,500	1.10	89	25/75	27/73
5	6040	8700	1.14	98	14,770	14,900	1.07	92	40/60	42/58
6	7640	9900	1.15	98	12,870	15,800	1.08	88	60/40	63/37
7	8430	11,000	1.16	>99	13,030	15,200	1.10	87	70/30	73/27
8	9080	11,200	1.16	>99	12,300	15,200	1.10	82	80/20	85/15

^a Calculated using the following equation: $M_n^{\text{th}} = ([\text{Monomer}]/[\text{CTA}]) \times \text{Conv.} \times MW_{\text{Monomer}}$.

^b Determined by SEC with the universal calibration.

^c Determined by ¹H NMR.

^d Calculated using Eq. (1).

time (~ 32 min) than a PTBDMSMA of 12,300 (g mol^{-1}). Moreover, the efficiency of the purification steps depends on the difference of solubility of both the PMMA and PTBDMSMA blocks in methanol and pentane. Low-molecular weight PMMA chains are more soluble in methanol than the corresponding PTBDMSMA chains. A high molar content of silylated units within the diblock copolymer chains enhances the efficiency of the purification step by using methanol as a non-solvent of the diblock copolymer. Pentane is mainly used as a good solvent of PTBDMSMA chains and a non-solvent of PMMA chains.

Results from Table 6 show that the monomer conversion is relatively high and comparable ($\sim 90\%$) for both copolymerizations. The theoretical molecular weight ($M_{n,\text{copo}}^{\text{th}}$) of the resulting copolymer is calculated according to the following Eq. (1):

$$M_{n,\text{copo}}^{\text{th}} = M_{n(\text{macro-CTA})} + \frac{[\text{Monomer}]}{[\text{macro-CTA}]} \times \text{Conv.} \times \text{MW}_{\text{Monomer}} \quad (1)$$

With the macro-CTA1, the purified PMMA-block-PTBDMSMA copolymer has a molecular weight value higher than the theoretical molecular weight. In the case of PTBDMSMA-block-PMMA copolymer, the molecular weight is close to the theoretical one. In addition, the use of macro-CTA2 seems to give a better control of the polymerization with a lower PDI value.

To compare the ability of these two macro-CTAs in subsequent polymerizations, we have estimated their efficiency ($f_{\text{macro-CTA}}$), which is defined as follows:

$$f_{\text{macro-CTA}} = \frac{R^f \times (100 - R^i)}{R^i \times (100 - R^f)} \times 100 \quad (2)$$

where R^i and R^f are the molar proportions of the first monomer within the initial macro-CTA chains and within the final diblock copolymer chains, respectively. As shown in Table 6, $R^i = 43\%$ and $R^f = 27\%$ for macro-CTA1, and $R^i = 42.5\%$ and $R^f = 40\%$ for macro-CTA2.

One example from the literature reported that only 54% of PMMA-SC(=S)Ph macro-CTA ($M_n = 22,300 \text{ g mol}^{-1}$ and PDI = 1.17) previously synthesized with the use of a fluorinated-CTA was transformed into a diblock copolymer PMMA-block-PS ($M_n = 147,000 \text{ g mol}^{-1}$ and PDI = 1.20) [33]. In our case, an $f_{\text{macro-CTA1}}$ value was assessed to be close to 50% while $f_{\text{macro-CTA2}}$ value is close to 90%. The block copolymerization of TBDMSMA from a PMMA-SC(=S)Ph is not so satisfactory. This result could be explained by a faster fragmentation of the intermediate radical PTBDMSMA-S-C(Ph)-S-PMMA from the PTBDMSMA side. The high leaving ability of PTBDMSMA segment compared to PMMA one could be due to a steric effect of *tert*-butyldimethylsilyl group which is more bulky than the methyl group of PMMA.

3.2.2. PTBDMSMA-block-PMMA by one-pot method

As shown above, the copolymerization should be started with TBDMSMA to give a better-controlled character. In addition, the first monomer should be totally consumed to avoid the formation of a random copolymer in the second block. The homopolymerization of TBDMSMA leads to a higher value of monomer conversion ($>98\%$) and the resulting PTBDMSMA is very well controlled as shown above. For these reasons, TBDMSMA is chosen to prepare the first block as a quick and efficient transformation of the dormant PTBDMSMA chains into block copolymer has been observed (Scheme 4).

The synthesis of the first block PTBDMSMA has been carried out by varying the theoretical molecular weight (M_n values from 3500 to 9000 g mol^{-1} ; Table 7). Results from SEC analysis of reaction

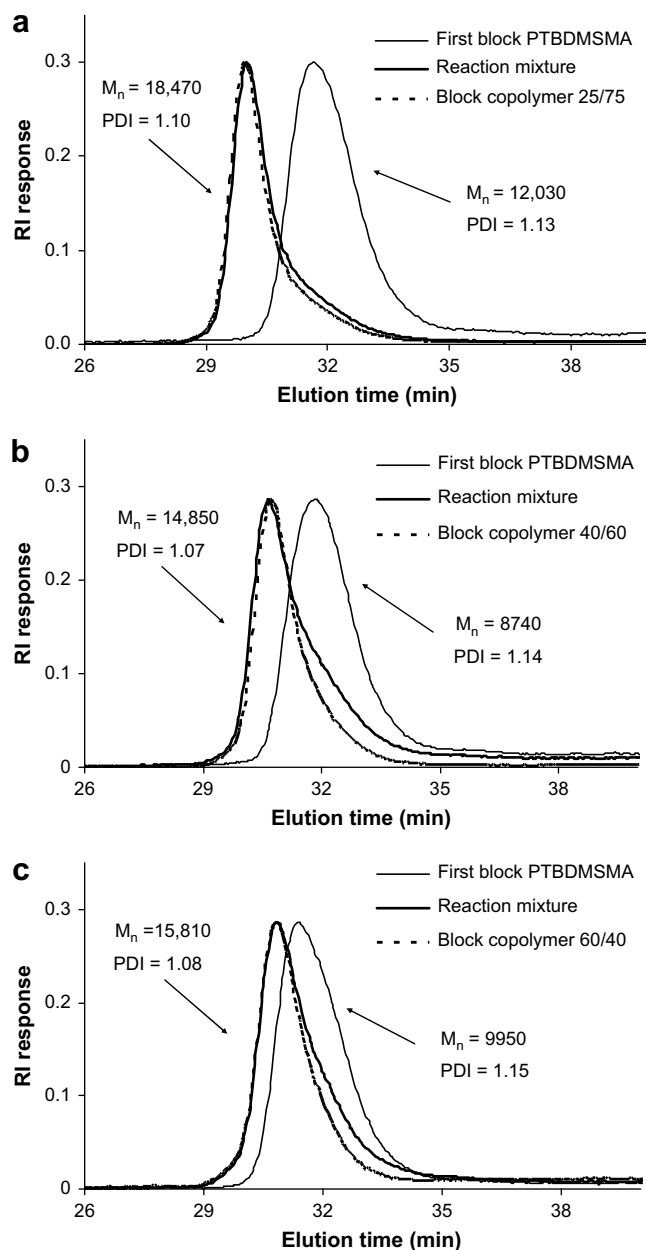


Fig. 4. SEC chromatograms of diblock copolymers prepared by the one-pot method: (a) [TBDMSMA]/[MMA] = 25/75; (b) [TBDMSMA]/[MMA] = 40/60; and (c) [TBDMSMA]/[MMA] = 60/40.

mixtures show a good control of the polymerization resulting in a narrow macro-CTA (PDI < 1.16). However, the molecular weight values obtained are slightly higher than the theoretical ones for all cases. This deviation is explained by the low chain transfer constant of CDB which is inducing a low initialization of the living process, leading to substantial molecular weights before the pre-equilibrium has passed [9]. The second block was obtained by the MMA chain extension, yielding to copolymers with TBDMSMA/MMA molar ratios varying from 20/80 to 80/20. In all cases, the MMA conversion was found to be within the range 82–98%. These uncompleted consumptions of MMA lead to a decrease of the MMA proportion in the final copolymers.

Fig. 4 illustrates that the extension of the chain is successful for all setups. The dormant chain is a good transfer agent, resulting in

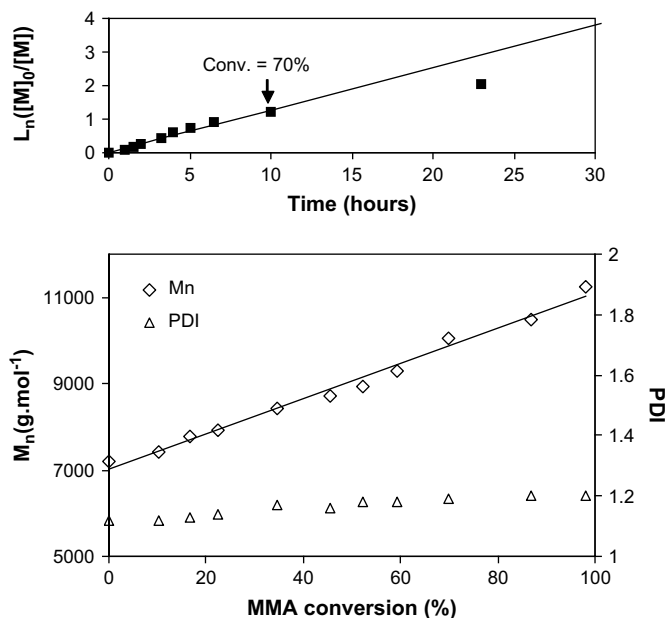


Fig. 5. RAFT copolymerization of MMA in toluene solution at 70 °C mediated by PTBDMSMA-SC(=S)Ph via the one-pot method. Pseudo first-order rate plot and evolution of M_n versus MMA conversion: [MMA] = 1.5 M, [PTBDMSMA-SC(=S)Ph] = 2.0×10^{-2} M, [AIBN] = 4.0×10^{-3} M.

a narrow block copolymer product (PDI ~ 1.10), with PTBDMSMA chains distributed evenly within the product decreasing therefore its experimental value of MMA monomer unit content.

The comparison of SEC chromatograms of PTBDMSMA-block-PMMA 40/60 copolymers obtained by the one-pot and the two-step methods from PTBDMSMA-SC(=S)Ph as macro-CTA reveals similar results and shows that the one-pot method is advantageous because no purification is needed for the macro-CTA and is not time consuming (Figs. 3b and 4b).

3.2.3. Kinetics of the diblock copolymerization

The homopolymerization of TBDMSMA was conducted until a high monomer conversion (98%). To the first PTBDMSMA block ($M_n = 7200 \text{ g mol}^{-1}$, PDI = 1.15) solution was added MMA with a MMA/TBDMSMA molar ratio of 67/33. Fig. 5 shows the copolymerization kinetic of MMA by the one-pot method using PTBDMSMA-SC(=S)Ph as macro-CTA. A conversion of MMA close to 98% is obtained for 50 h of reaction. However, the first-order kinetic of MMA copolymerization was conducted until about 70%. In addition, no inhibition period was observed. When performing RAFT polymerization using a polymeric RAFT agent, that is, effectively skipping the pre-equilibrium, no induction period can be observed [23,53].

A linear evolution of M_n versus monomer conversion is obtained together with a narrow molecular weight distribution of the block copolymer all along the polymerization (PDI are between 1.15 and 1.20). This result confirms the good controlled character of the copolymerization of MMA using PTBDMSMA-SC(=S)Ph as macro-CTA.

4. Conclusion

In this paper, the copolymerization of a trialkylsilyl methacrylate monomer (TBDMSMA) with MMA has been investigated for the first time by the RAFT process. The reactivity ratios assessed from the non-linear least-squares fitting method were found to be

$r_1 = 1.40 \pm 0.03$ and $r_2 = 1.08 \pm 0.03$ for TBDMSMA and MMA in a RAFT-control system, respectively. A slight penultimate effect has been shown for the RAFT mediated radical polymerizations.

It has been demonstrated that the ability to synthesize well-defined diblock and random copolymers based on MMA and TBDMSMA via the RAFT process. This result is very important as anionic polymerization such as Group Transfer Polymerization has failed. We have demonstrated that the diblock copolymers can be prepared from PMMA-SC(=S)Ph or PTBDMSMA-SC(=S)Ph macro-CTAs using the one-pot and the two-step strategies. The PTBDMSMA-SC(=S)Ph macro-CTA has demonstrated a higher efficiency to subsequent polymerization with MMA.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2009.04.075.

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