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RAFT polymerization of hydrophobic acrylamide derivatives

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Abstract

Several hydrophobic acrylamide derivatives: the *N*-*tert*-butylacrylamide (TBAm), the *N*-octadecylacrylamide (ODAm) and the *N*-diphenylmethylacrylamide (DPMAm) have been polymerized by reversible addition–fragmentation chain transfer (RAFT) process in the presence of azobis(isobutyronitrile) (AIBN) and *tert*-butyl dithiobenzoate (*t*BDB) as initiator and reversible chain transfer agent (CTA), respectively. Homopolymerizations were compared as regards to kinetics and molecular weight (MW) control, and the results were discussed according to the monomer structure and to the influence of several experimental parameters, such as the [CTA]/[AIBN] ratio and the [Monomer]/[CTA] ratio. TBAm and ODAm monomers exhibited a well controlled polymerization (polydispersity index (PDI) below 1.3 for number average molecular weight (M_n) until 30,000 g mol^{-1}) over a wide range of conversion (until 70%), whereas DPMAm conversion remained below 20% partly due to steric hindrance. The molecular weights of several poly(TBAm) samples determined by four independent analytical techniques, size exclusion chromatography/on-line light scattering detector (SEC/LSD), ^{1}H NMR, ^{13}C NMR and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS), were in agreement, close to the theoretical ones. Moreover, the MALDI-TOF MS analyses suggested the presence of parasite chains resulting from irreversible termination onto RAFT intermediate radicals.

Keywords: Reversible addition–fragmentation chain transfer; Hydrophobic acrylamide derivatives; MALDI-TOF mass spectrometry

1. Introduction

In the last decade, much work has been dedicated to the elaboration of hydrophobically modified polyacrylamides due to their wide and increasing interest for both academic studies and practical applications. These materials can indeed serve as suitable model systems for investigating structure–properties relationship (viscosity for instance), as a function of internal (length and number of hydrophobic grafts, molar masses, etc.) or external (shear rate, pH, temperature, etc.) parameters. Due to their associating properties, they can be found in various fields such as water treatment, oil recovery, coatings [1–3], paper making, as well as in drug delivery systems [4–7].

These polymers can be produced according to various routes: (i) by covalent grafting of hydrophobic arms onto preformed reactive acrylate-based (co)polymers [8]; (ii) by free-radical copolymerization of acrylamide with a hydrophobic acrylamide derivative (which can be an alkyl acrylamide or a polymerizable surfactant) using a solution or micellar polymerization process [9]; (iii) a third and more recent way deals with the synthesis of hydrophobic polyacrylamide exhibiting a block copolymer structure, able to self-organize into polymeric micelles [10,11] or to selectively adsorb onto a hydrophobic substrate. Such a synthesis requires an efficient polymerization technique to get well-defined structures.

The recent development of various controlled radical polymerization (CRP) techniques has opened the way to the synthesis of polymer chains of controlled molecular weight from a wider variety of monomers than in the case of ionic polymerizations. Then, it should be possible to prepare controlled polymer chains from acrylamide derivatives. However, among the three main CRP techniques, NMP (nitroxide mediated polymerization) [12], ATRP (atom transfer radical polymerization) [13,14] and RAFT

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(reversible addition–fragmentation chain transfer) [15–17], the last one seems the best suited for polymerizing acrylamide derivatives.

In fact, very few nitroxide compounds were used to polymerize acrylamide derivatives [18,19]. Concerning ATRP process, it encountered some problems related to the inactivation of the catalyst system (presence of a nitrogen atom in the monomer), leading to limited conversion and/or molecular weights [20–22], although recent articles about dimethylacrylamide (DMAm) [23a] and *N*-isopropylacrylamide (NIPAm) [23b] showed some improved results.

Now, concerning the RAFT process, it indeed allows the polymerization of acrylamide derivatives in a controlled way. Several water-soluble acrylamide derivatives have already been polymerized by RAFT, non-ionic ones such as DMAm [16,24–26], NIPAm [27,28], dimethylaminoethyl methyl acrylamide (DMAEMAm) [29] and *N*-acryloylmorpholine (NAM) [30,31], as well as ionic ones such as sodium 2-acrylamido-2-methylpropane sulfonate (AMBS) [32], sodium 3-acrylamido-3-methyl butanoate (AMBA) [32] and a sulfobetaine [33]. These various examples confirm the versatility of the RAFT process to synthesize well controlled water-soluble poly(acrylamide) based polymers. Concerning hydrophobic (non water-soluble) acrylamide derivatives, none has been polymerized by RAFT so far.

With the aim to prepare amphiphilic block copolymers from various hydrophilic/hydrophobic acrylamide derivatives, we decided to first investigate the RAFT homopolymerization of several hydrophobic acrylamide monomers, *N*-*tert*-butyl acrylamide (TBAm), *N*-octadecyl acrylamide (ODAm) and *N*-(diphenylmethyl) acrylamide (DPMAm) (Fig. 1). They are all mono-substituted acrylamide derivatives, bearing either a short (TBAm) or a long (ODAm) alkyl side-chain, or an aromatic side-chain (DPMAm).

N-*tert*-butyl acrylamide has long been homopolymerized [34] or copolymerized [4–7,35–39] by conventional free radical polymerization. It has also been polymerized by ATRP [22,40]. However, according to the used ligand, these assays led to either high conversion (94%) but poor control (PDI = 2.9) [40], or good control (PDI = 1.15) but limited M_n and conversion ($M_n = 4100$ g mol^{-1}, 38% conversion after 19 h) [22]. It has not been polymerized by RAFT so far. Concerning *N*-octadecyl acrylamide, it has been homopolymerized and copolymerized by conventional free radical polymerization [41–45] but not by any controlled radical polymerization technique.

In this work, the RAFT polymerization of the chosen three acrylamide derivatives was carried out in the presence of AIBN as initiator and *tert*-butyl dithiobenzoate (*t*BDB, Fig. 1) as chain transfer agent (CTA). This dithioester proved to be very efficient to polymerize hydrophilic acrylamide derivatives, like *N*-acryloylmorpholine [30] and dimethylacrylamide [46]. The results were compared in terms of kinetics, molecular weights (MW) and molecular weight distributions (MWD).

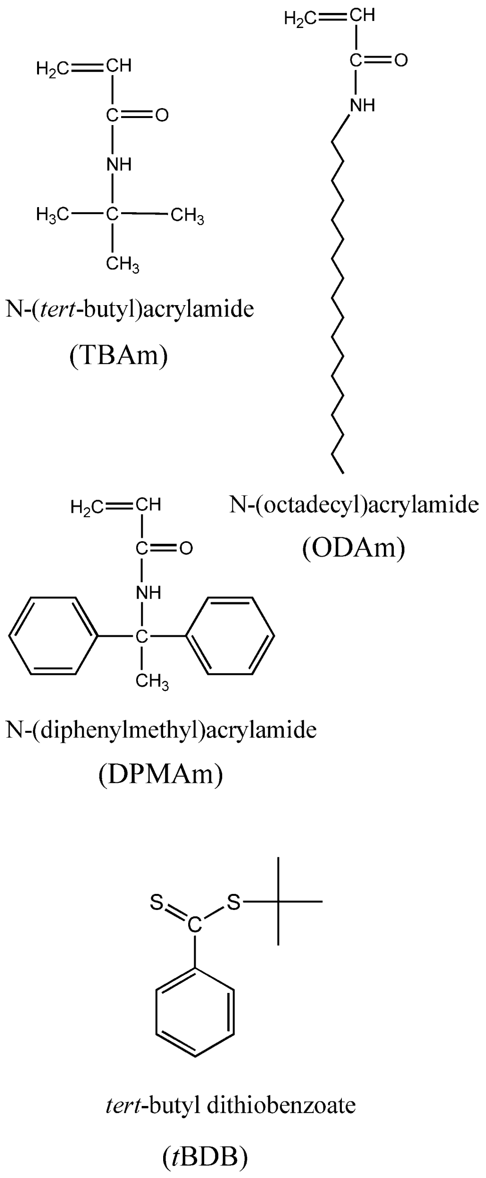


Fig. 1. Monomer and dithioester structures.

We then decided to study more deeply the RAFT polymerization of TBAm with *t*BDB, especially to demonstrate the influence of several experimental parameters, such as the dithioester to initiator molar ratio, [CTA]/[AIBN], and the monomer to dithioester molar ratio, [*M*]/[CTA], on the kinetics and the control of molecular weights. On a general point of view, few systematic studies [25,28,47–51] have been carried out with the RAFT technique to compare the influence of such experimental parameters on the polymerization of a given monomer, in terms of polymerization duration, limit of conversion, adequacy between experimental and calculated M_n values and polydispersity index.

Finally, we determined the real MW of several poly (TBAm) samples using four independent analytical techniques, SEC/LSD (on-line light scattering detector), ^{1}H NMR, ^{13}C NMR and MALDI-TOF MS. In addition, MALDI-TOF MS analyses allowed us to elucidate the nature of parasite chain populations.

2. Experimental section

2.1. Materials

N-tert-butylacrylamide (TBAm) (Aldrich, 97%), *N*-octadecylacrylamide (ODAm) (Polysciences, Inc.) and *N*-diphenylmethylacrylamide (DPMAm) (Polysciences, Inc.) were used without further purification. 2,2′-Azobis(isobutyronitrile) (AIBN) (Fluka, 98%) was purified by recrystallization from ethanol. 1,4-Dioxane (Acros, 99%) was distilled over $LiAlH_4$ (110 °C). Trioxane (Acros, 99%) and DMF (Aldrich, 99,8%) were used as received. *tert*-butyl dithiobenzoate (*t*BDB) synthesis has been described recently [30].

2.2. RAFT polymerizations

Monomer, dithioester, AIBN, dioxane and trioxane (internal reference for ^{1}H NMR determination of monomer consumption) were introduced into a Schlenk tube equipped with a magnetic stirrer (Table 1). The mixture was degazed by four freeze–evacuate–thaw cycles and then heated under nitrogen in a thermostated oil bath.

For all experiments, the temperature was set at 90 °C and the initial monomer concentration was kept equal to 1 mol L^{-1}.

Periodically, samples were withdrawn from polymerization media for analyses. For kinetic study, conversions were determined by ^{1}H NMR using a Bruker Avance 200 MHz spectrometer [52]. Typically, 500 μL of deuterated chloroform, $CDCl_3$, was added to 150 μL of each sample.

2.3. Characterization of the polymer samples

Prior to characterization, the polymer samples were precipitated into an appropriate solvent. As shown by Karlsson et al. [53], poly(TBAm) is soluble in a large variety of solvents except hexane and pentane. However, TBAm monomer is also insoluble in these two solvents. Fortunately, DMSO appeared as a good candidate: it solubilized TBAm monomer while it precipitated poly (TBAm). Polymer was recovered by filtration, washed with the same solvent and finally dried under vacuum during a few days. The complete elimination of residual monomer and DMSO was confirmed by ^{1}H NMR analysis.

Concerning poly(ODAm) and poly(DPMAm), precipitations were carried out in a large volume of diethyl ether. The polymer was recovered by filtration, washed several times with the same solvent and finally dried under vacuum up to constant weight.

The molecular weights of the various homopolymers were determined either by:

- Size exclusion chromatography (SEC) in THF (SDS, 99%), using a Waters column (Styragel HR4E). The flow rate was maintained at 1 mL min^{-1} using a Waters 1515 isocratic HPLC pump. Detection was performed using a Waters 2410 refractive index detector. The molecular weight and polydispersity data were determined using the Waters Breeze software package. Analyses were performed by injection of 20 μL of polymer solution (5 mg mL^{-1}) in THF.
- Size exclusion chromatography (SEC) coupled to a light scattering detection (LSD) using two Waters Styragel columns (HR4 and HR1). The mobile phase consisted of THF (from SDS) with a flow rate of 1 mL min^{-1} using a Spectra-Physics Isochrom LC pump. On-line double detection was provided by a 18-angles DAWN light scattering photometer ($\lambda = 632$ nm, Wyatt Technologies) associated with a differential refractometer (DRI Waters 410). The specific refractive index increment (dn/dc) for poly(TBAm) in THF (0.097) has been determined with a NFT ScanRef monocolor interferometer operating at

Table 1
RAFT polymerization of TBAm, ODAm and DPMAm (initial concentrations) in the presence of AIBN (initiator) and *t*BDB (RAFT agent)

Run	Monomer (M)	Solvent	Temperature (°C)	$[M]_0$ (mol L^{-1})	$[tBDB]_0/[AIBN]_0$	Calculated M_n^{a} for 100% conversion (g mol^{-1})
1	TBAm	Dioxane	90	1	3.3	50,000
2	ODAm	Dioxane	90	1	3.3	50,000
3	DPMAm	DMF	90	1	3.3	50,000
4	TBAm	DMF	90	1	3.3	50,000
5	TBAm	Dioxane	90	1	3.3	50,000
6	TBAm	Dioxane	90	1	10	50,000
7	TBAm	Dioxane	90	1	3.3	100,000
8	TBAm	Dioxane	90	1	10	100,000
9	TBAm	Dioxane	90	1	10	30,000
10	TBAm	Dioxane	90	1	10	6350

[a] Calculated $M_n = ([M]_0/[tBDB]_0) \times M_{monomer} \times \text{conversion} + M_{tBDB}$.

633 nm. The molecular weight and polydispersity index were determined using the Wyatt ASTRA SEC/LS software package.

- Matrix assisted laser desorption/ionisation-time of flight mass spectrometry (MALDI-TOF MS) spectra were recorded on an Applied Biosystems Voyager-DE STR equipment using a nitrogen laser (337 nm) and an accelerating potential of 25 kV. Samples were prepared by mixing a solution of poly(TBAm) in THF (10 g L^{-1}) and a solution of 3-β-indole acrylic acid (IAA) matrix in THF (10 g L^{-1}). Then, 1 μL of the resulting mixture was deposited onto the sample slide and the solvent was evaporated at room temperature. Spectra were recorded in the reflector mode with external calibration (Sequazyme).
- ^{1}H and ^{13}C NMR spectroscopy, using a Bruker Avance 400 spectrometer operating at 400 MHz (^{1}H) and 100 MHz (^{13}C), respectively.

3. Results and discussion

RAFT controlled radical polymerization is based on an equilibrium between active and dormant species generated by a reversible addition–fragmentation process [15] (Scheme 1). The chain transfer agent (CTA) is typically a dithioester which efficiency depends on the nature of the substituents R and Z as well as on the type of monomer [54,55]. Here, *tert*-butyl dithiobenzoate was used as one of the best chain transfer agents for acrylamide derivatives, and the RAFT polymerization of the three selected hydrophobic acrylamide derivatives (*N*-*tert*-butylacrylamide (TBAm), *N*-octadecylacrylamide (ODAm), and *N*-diphenylmethyl acrylamide (DPMAm)) were compared.

3.1. Comparative study of the RAFT polymerization of three hydrophobic acrylamide derivatives

RAFT polymerization of *N*-*tert*-butylacrylamide (TBAm) and *N*-octadecylacrylamide (ODAm) were carried out in dioxane using AIBN as the initiator and *tert*-butyl dithiobenzoate (*t*BDB) as the chain transfer agent (CTA). Concerning *N*-diphenylmethyl acrylamide (DPMAm), polymerization was performed in the same conditions except the solvent (DMF) since it was not soluble in dioxane (runs 1–3 in Table 1). Monomer concentration had to be decreased to 1 mol L^{-1} to provide solubilization of the monomers. The CTA/initiator ratio was initially set at 3.3 to get a sufficiently high polymerization rate taking into account the low concentration of the medium [51]. The amount of CTA was calculated so that the theoretical molecular weight at 100% conversion was 50,000 g mol^{-1} in the three cases. The polymerizations were performed at 90 °C to limit the retardation phenomenon observed with acrylamides when using dithiobenzoates as CTA [30,51].

The comparison of the kinetics (Fig. 2) shows that TBAm and ODAm polymerized in a very similar way in dioxane, with 70% conversion reached within 2 h. In the same time, DPMAm conversion reached only 10%. Such a low polymerization rate for DPMAm may be explained by steric hindrance due to the close presence of the two phenyl moieties and/or by the use of DMF as solvent.

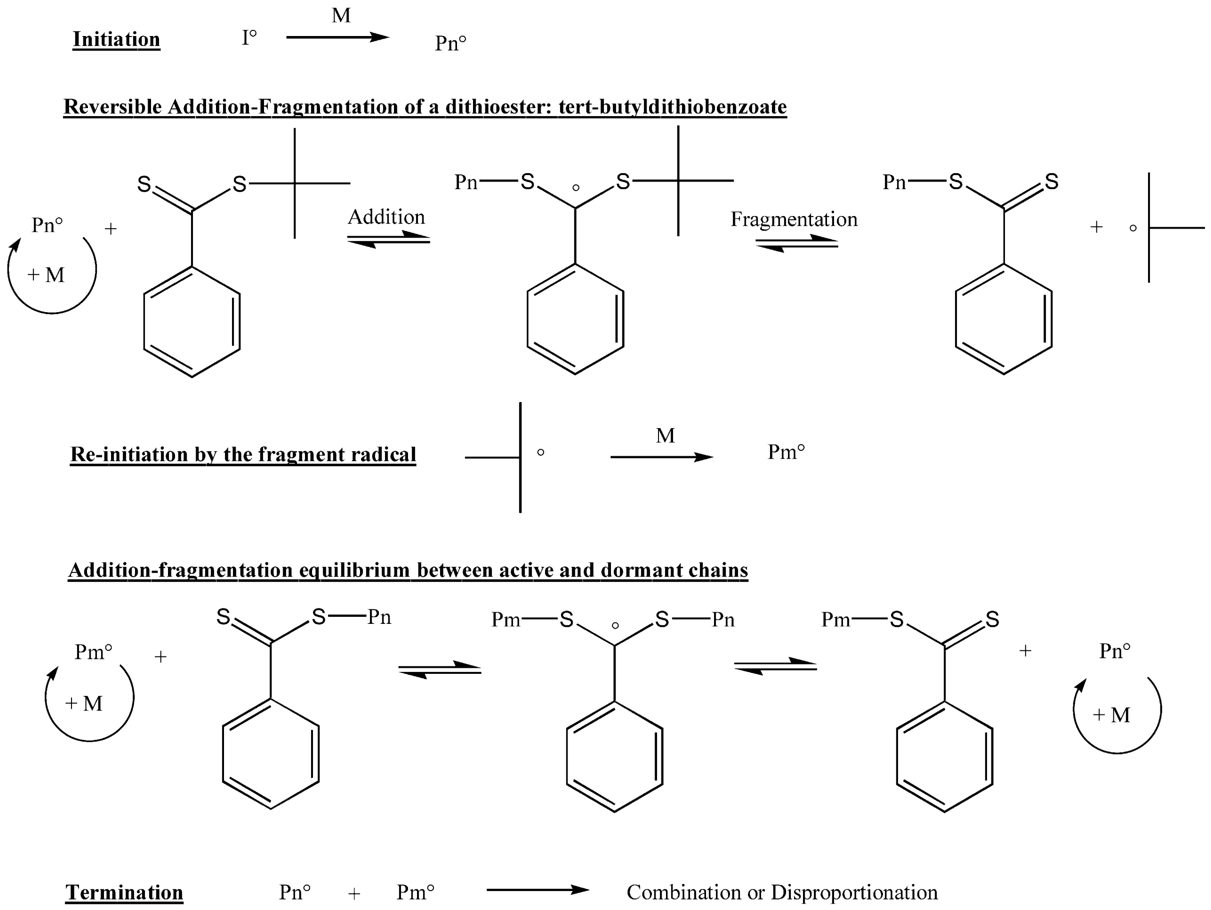
To evidence a possible influence of DMF on the RAFT polymerization of DPMAm, polymerization of TBAm was carried out again under the same conditions as in run 1 but using DMF as solvent (run 4). The comparison of the kinetics (runs 1 and 4) indicated a strong solvent effect: only 25% conversion could be reached within 2 h in DMF instead of 70% in dioxane. Moreover, comparison between DPMAm and TBAm polymerizations in DMF (runs 3 and 4) confirmed the steric effect originated from DPMAm monomer structure (conversion “plateau” at 15% instead of 35% for TBAm). It is known that monomers having a long side chain polymerize faster than those with a short side chain, due to a reduced k_t value [56]. However, in the case of very bulky monomers, k_p also decreases such that $k_p/k_t^{1/2}$ ratio decreases [57,58].

In all cases, a conversion “plateau” was observed after 2 h, related to AIBN decomposition. In fact, at 90 °C, 99% AIBN is decomposed within 2 h; then, the polymerization strongly slows down and the corresponding conversion determines the value of the conversion ‘plateau’. Final conversion reached nearly 80% for TBAm and ODAm and about 15% for DPMAm.

For TBAm and ODAm monomers, M_n values increased linearly with conversion (Fig. 3(a)), confirming the control of these RAFT polymerizations, at least until 60% conversion. However, experimental M_n values were not in agreement with the calculated ones, probably due to the use of polystyrene standards, not very adequate to reflect the hydrodynamic volume of these polyacrylamide derivatives in the column. This hypothesis was confirmed later by light scattering analyses (see the last part of this article). The polydispersity index (PDI) slightly increased with conversion without exceeding 1.4 (Fig. 3(b)).

Concerning the comparison of TBAm polymerization in dioxane and in DMF, evolution of the molecular weights was very different (Fig. 4). For polymerization in DMF, a stagnation of M_n values with conversion was observed contrary to the linear increase in the case of dioxane. In addition, PDI values were significantly higher (1.5–1.6 instead of 1.2–1.3).

Both observations indicated that RAFT polymerization of TBAm in DMF was no longer a living system but was dominated by irreversible transfer reactions to the solvent. In fact, DMF is known (considering conventional free radical polymerization) as a non-degrading transfer agent. For instance, during conventional polymerization of NAM in DMF, MW were affected (M_n values of 79,000 instead of 107,000 g mol^{-1} in dioxane) while kinetics remained unchanged [59]. Here however, in the presence of a



Scheme 1. RAFT general mechanism in the presence of *tert*-butyldithiobenzoate.

RAFT agent (and of dormant chains), the radical resulting from transfer to DMF, [HC(O)N(CH$_3$)CH$_2$°], can add to the RAFT agent (or to a dormant chain) leading to a new kind of intermediate radicals (in comparison with those corresponding to growing chains of poly(TBAm), Scheme 1). As these new intermediate radicals have a longer lifetime than the usual ones, we believe that they would undergo more termination reactions which would explain the slowing down of the polymerization performed in DMF and thus the lower conversion ‘plateau’.

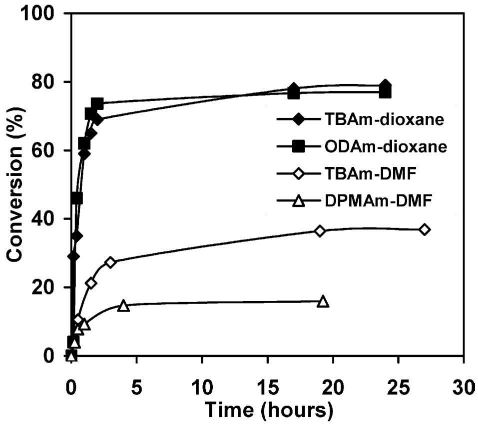


Fig. 2. Monomer conversion vs. time plots for TBAm, ODAm and DPMAm polymerization at 90 °C in the presence of *t*BDB; $[M]_0 = 1$ mol L^{-1}; $[t\text{BDB}]_0/[\text{AIBN}]_0 = 3.3$; solvent, dioxane or DMF (runs 1–4).

Finally, it seems preferable to use another solvent than DMF for RAFT polymerization of these hydrophobic acrylamide derivatives, especially at this low monomer concentration. It might be possible to find another solvent to improve DPMAm conversion, however, with such a bulky monomer, it would be difficult to get a high polymerization rate. Consequently, DPMAm polymerization was no further studied. Concerning ODAm monomer, it was no longer considered for experimental reasons (too high viscosity of the medium which made difficult to follow the kinetics). Then, TBAm was selected and its RAFT polymerization in dioxane was investigated more deeply.

3.2. Influence of [tBDB]/[AIBN] ratio on RAFT polymerization of TBAm

According to the RAFT mechanism, an improvement of the control of the polymerization is expected when decreasing [AIBN] [17] since termination reactions will be disfavored in comparison with reactions involving only one radical species (propagation or addition–fragmentation reactions). Indeed, we recently found that increasing the

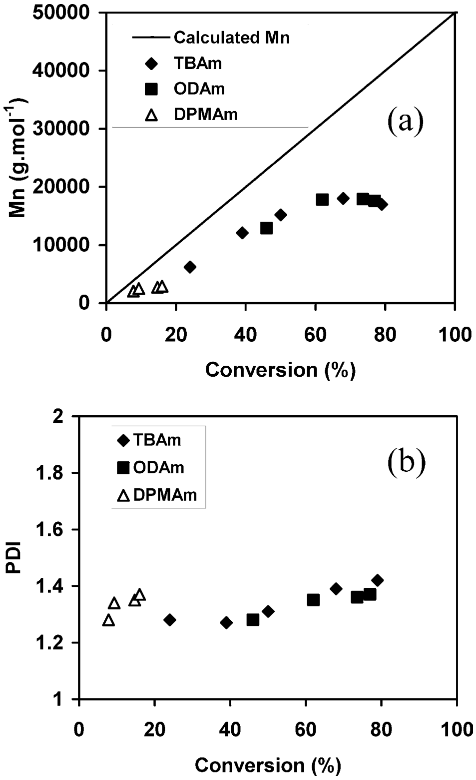


Fig. 3. Number-average molecular weight M_n (a) and polydispersity index PDI (b) vs. monomer conversion plots for TBAm, ODAm and DPMAm polymerization at 90 °C in the presence of *t*BDB; $[M]_0 = 1\ \mathrm{mol\ L^{-1}}$; $[t\mathrm{BDB}]_0/[\mathrm{AIBN}]_0 = 3.3$ (runs 1–3).

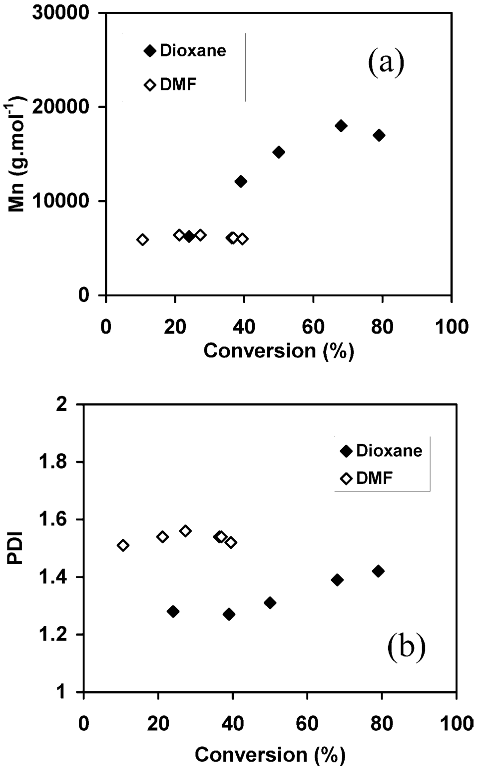


Fig. 4. Number-average molecular weight M_n (a) and polydispersity index PDI (b) vs. monomer conversion plots for TBAm polymerization in dioxane and in DMF at 90 °C in the presence of *t*BDB (runs 1 and 4, respectively); $[M]_0 = 1\ \mathrm{mol\ L^{-1}}$; $[M]_0/[t\mathrm{BDB}]_0 = 400$; $[t\mathrm{BDB}]_0/[\mathrm{AIBN}]_0 = 3.3$.

[*t*BDB]/[AIBN] ratio from 3.3 to 10 (at a constant [*t*BDB]) led to lower PDI values for the polymerization of an hydrophilic acrylamide derivative, *N*-acryloylmorpholine [51]. Then, it was of interest to investigate the influence of this parameter in the case of TBAm monomer. Several RAFT polymerizations of TBAm were carried out in the same conditions but with a [*t*BDB]/[AIBN] ratio increasing from 3.3 to 10, at a constant *t*BDB concentration corresponding to a calculated molecular weight at 100% conversion of either 50,000 g mol^{-1} (runs 5 and 6, respectively) or 100,000 g mol^{-1} (runs 7 and 8, respectively).

Concerning the kinetics, (Fig. 5), the polymerization rate was slower for a ratio of 10 than for a ratio of 3.3 (due to a lower number of propagating chains), inducing a lower conversion 'plateau' (45% instead of about 70%). The Ln($[M]_0/[M]$) vs. time plots were linear during the first hour of polymerization at 90 °C, confirming that the concentration of radical species remained constant. Afterwards, the observed curving indicated that generation of primary radicals did no longer balance the loss of propagating radicals via irreversible termination reactions.

Concerning the molecular weights, a good control of the polymerization was obtained (linear increase of M_n with conversion) for a targeted M_n of 50,000 g mol^{-1} (runs 5 and 6, Fig. 6). Likewise, the MWD were significantly narrow (<1.2) except above 60% conversion. No improvement was obtained at the ratio of 10.

On the contrary, for higher targeted M_n (100,000 g mol^{-1}, Fig. 7(a)), molecular weights were only controlled until 35–45% conversion. Then, M_n values levelled off. In the same time, PDI strongly increased with values of 1.6–1.7 instead of 1.1–1.3 below 40% conversion (Fig. 7(b)). This new

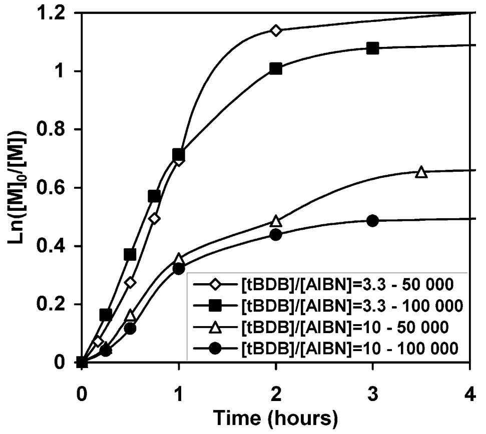


Fig. 5. Ln($[M]_0/[M]$) vs. time plots for TBAm polymerization at 90 °C in dioxane in the presence of *t*BDB with $[t\mathrm{BDB}]_0/[\mathrm{AIBN}]_0 = 3.3$ or 10 for targeted M_n of 50,000 or 100,000 g mol^{-1} at 100% conversion (runs 5–8); $[M]_0 = 1\ \mathrm{mol\ L^{-1}}$.

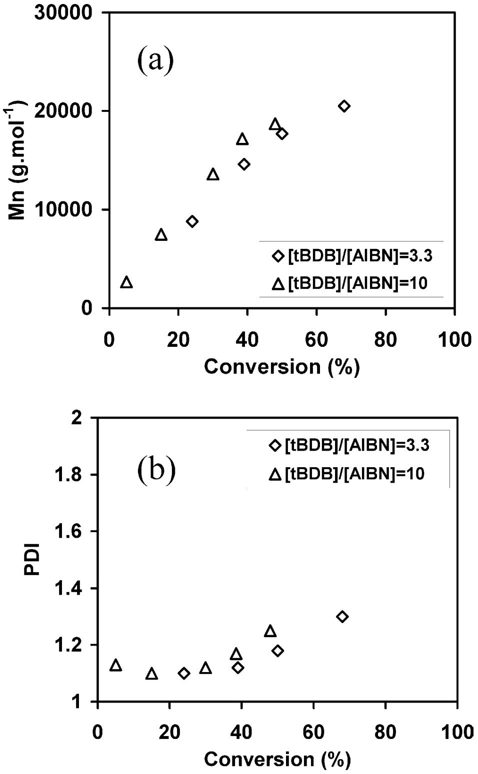


Fig. 6. Number-average molecular weight M_n (a) and polydispersity index PDI (b) vs. monomer conversion plots for TBAm polymerization at 90 °C in dioxane in the presence of *t*BDB with $[tBDB]_0/[AIBN]_0=3.3$ or 10 for targeted M_n of 50,000 g mol^{-1} at 100% conversion (runs 5, 6); $[M]_0=1$ mol L^{-1}, $[M]_0/[tBDB]_0=400$.

phenomenon, observed when targeting long chains, has been studied below for four different chain lengths.

Finally, increasing the [*t*BDB]/[AIBN] ratio from 3.3 to 10 did not result in lower PDI values for RAFT polymerization of TBAm contrary to what was observed for NAM [51]. This different behavior between TBAm and NAM monomers remains unclear. However, in order to get less dead chains, it will be better to choose a [*t*BDB]/[AIBN] ratio of 10 especially when aiming at synthesizing block copolymers from the poly(TBAm) blocks.

3.3. Influence of [TBAm]/[tBDB] ratio on RAFT polymerization of TBAm

When one wants to change the targeted molecular weight, the [Monomer]/[CTA] ratio must be modified. Four runs were compared in the same experimental conditions ([TBAm] = 1 mol L^{-1} in dioxane at 90 °C, [*t*BDB]/[AIBN] = 10) with increasing the targeted M_n at 100% conversion from 6000 to 30,000, 50,000 and finally 100,000 g mol^{-1} (runs 10, 9, 6 and 8 in Table 1, respectively).

For all these experiments, polymerization kinetics was similar (conversion vs. time curves almost coincide, results not shown). This surprising finding means that, in these conditions, the polymerization rate is independent of initiator concentration. In fact, as [DT]/[AIBN] ratio is maintained constant, [DT] is decreasing in the same time as [AIBN]. Then, it is possible that the decrease in polymerization rate due to the decrease in [AIBN] is balanced by the reduced retardation due to the decrease in [DT]. Such observation confirms the results previously obtained with NAM, i.e. kinetics remains similar when the targeted M_n is increased (at a constant monomer concentration) provided that the *tert*-butyl dithiobenzoate/AIBN ratio is maintained constant [51]. This conclusion is probably relative to the considered CTA/monomer system.

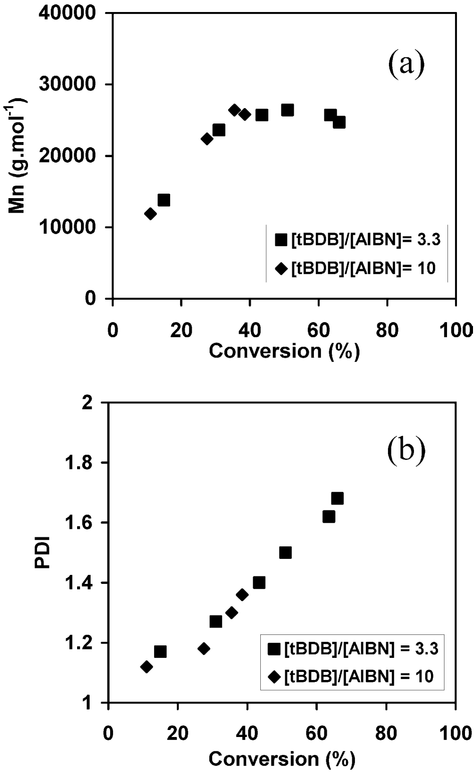


Fig. 7. Number-average molecular weight M_n (a) and polydispersity index PDI (b) vs. monomer conversion plots for TBAm polymerization at 90 °C in dioxane in the presence of *t*BDB with $[tBDB]_0/[AIBN]_0=3.3$ or 10 for targeted M_n of 100,000 g mol^{-1} at 100% conversion (runs 7, 8); $[M]_0=1$ mol L^{-1}; $[M]_0/[tBDB]_0=800$.

Concerning the molecular weights, evolution of M_n with conversion was linear until 35–45% conversion (Fig. 8). Afterwards, the phenomenon of M_n stagnation (and even decrease) was observed for high targeted molecular weights, especially for 100,000 g mol^{-1} (run 8). Moreover, PDI values were low before 35% conversion (1.1–1.2) but became much higher after (between 1.3 and 1.7). The lowest values of PDI were obtained in the case of the targeted MW of 6000 g mol^{-1} (PDI < 1.1).

A similar comparison was made with the two runs performed at a [*t*BDB]/[AIBN] ratio of 3.3 (runs 5 and 7). The results (evolution of M_n and PDI with conversion, not

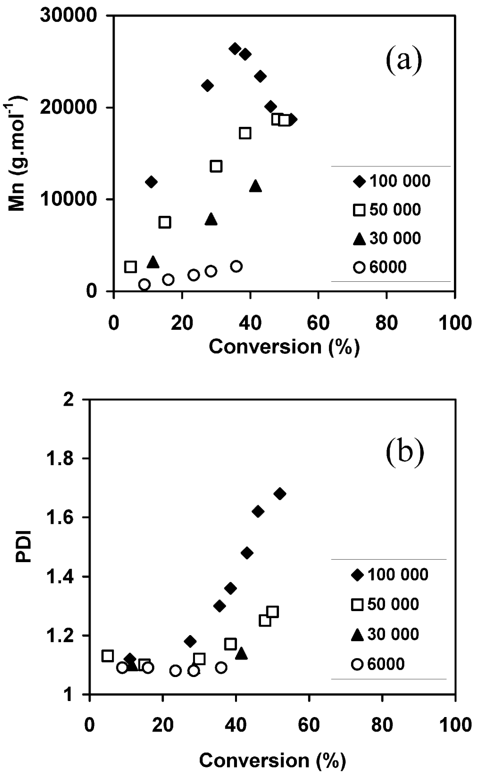


Fig. 8. Number-average molecular weight M_n (a) and polydispersity index PDI (b) vs. monomer conversion plots for TBAm polymerization at 90 °C in dioxane in the presence of *t*BDB for different targeted M_n at 100% conversion (Runs 6, 8–10); $[TBAm]_0 = 1$ mol L^{-1}; $[tBDB]_0/[AIBN]_0 = 10$.

shown) indicated the same tendency (levelling off then decrease of M_n), again more pronounced and earlier for 100,000 than for 50,000 g mol^{-1}. However, this phenomenon appeared at higher conversions (M_n decreased after 60–70% conversion for the ratio of 3.3 instead of 35–45% for the ratio of 10) and thus was less visible. Taking into account that polymerization rate is faster at the ratio of 3.3, both conversion ranges correspond to the same time.

To explain this stagnation (or even decrease) of M_n values with conversion, irreversible transfer reactions like transfer to the solvent or to the polymer have been considered (since irreversible termination reactions never result in a decrease of M_n). Concerning transfer to the solvent, dioxane is not known as transfer agent towards acrylamide derivatives [59]. Moreover, if it was acting so, it could hardly explain such a strong decrease of M_n at so low conversions. Concerning transfer to the polymer, it generally does not induce the appearance of new chains but of branched chains; then, it would not explain the decrease of M_n.

It was interesting to plot in parallel M_n and M_{peak} values vs. conversion for run 8 (Fig. 9). Whereas M_n values begin to level off (at 35% conversion) and then to decrease, M_{peak} values continue to increase until 50% conversion. Such differences indicate the appearance of new short chains while the main chains continue to grow. However, after 50% conversion, the main chains stop growing (M_{peak} remains constant) while conversion still increases. It is the growing of the short chains and the continuous appearance of new short chains (since M_n is still decreasing) which contribute to the monomer consumption.

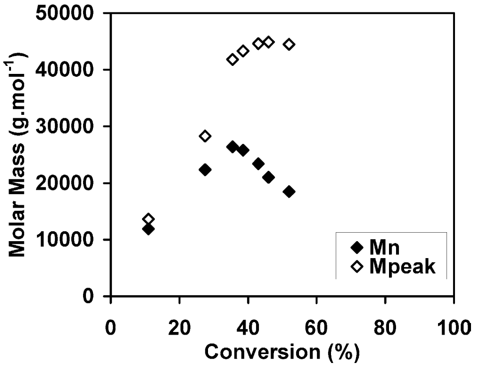


Fig. 9. Molecular weight M_n and M_{peak} vs. monomer conversion for TBAm polymerization in dioxane at 90 °C in the presence of *t*BDB (run 8); $[TBAm]_0 = 1$ mol L^{-1}; $[tBDB]_0/[AIBN]_0 = 10$.

The observation of the SEC chromatograms (Fig. 10) brings some more information. In the case of a high targeted MW (100,000 g mol^{-1}, run 8, Fig. 10(b)), the evolution of the SEC chromatograms with conversion is very different from that corresponding to a low targeted MW (30,000 g mol^{-1}, run 9, Fig. 10(a)). Although M_{peak} first increases regularly, a tail appears at the low molecular weight side of the peak confirming the presence of short chains, which is not the case in Fig. 10(a). This tail, which becomes more and more important with conversion, explains the significant increase in PDI. Further SEC analyses using a UV detector revealed that these short chains are not dead chains but dormant chains (terminated by a dithiobenzoate function absorbing at $\lambda = 309$ nm). This is an additional evidence that these short chains do not result from irreversible termination reactions.

In fact, this phenomenon becomes detectable after 1 h of polymerization. Knowing that 92% of the whole AIBN is decomposed within 1 h at 90 °C ($k_d = 7 \times 10^{-4}$ s^{-1}), the new chains cannot correspond only to chains lately initiated by AIBN. Another radical source may be present in the polymerization medium. A detailed study is on-going on this specific aspect of the polymerization.

3.4. Chain length and end-functionality control

Some poly(TBAm) samples were analyzed by four independent analytical techniques, MALDI-TOF MS, ^1H NMR, ^{13}C NMR and SEC/LSD for chain length and end-group characterization.

First, a MALDI-TOF MS analysis of poly(TBAm) was performed on a sample from run 10 (sample 10T6 at 36% conversion). The spectrum, recorded in the reflector mode, is well resolved (Fig. 11(a)). The difference between two main peaks of the distribution (127.1 mass units)

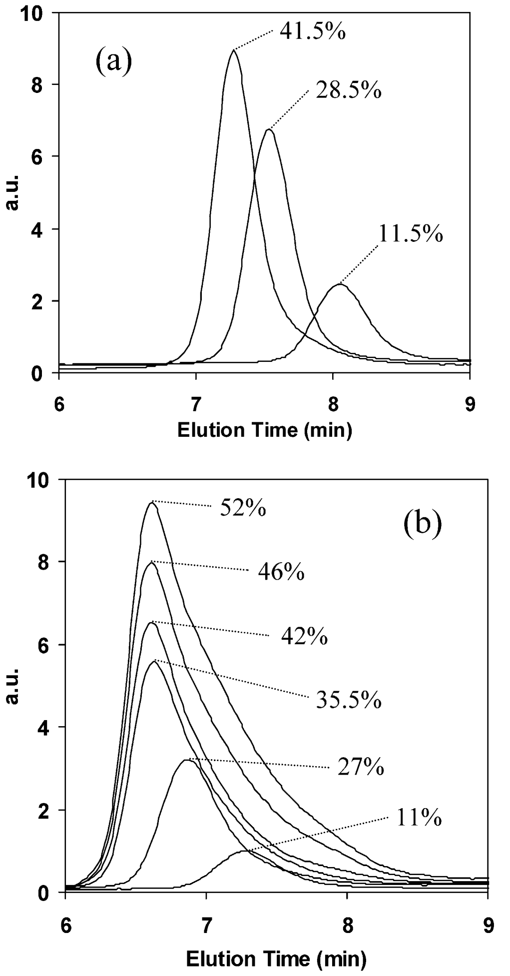


Fig. 10. Evolution of the SEC chromatograms (THF) of poly(TBAm) samples with conversion during RAFT polymerization in the presence of *t*BDB: run 9 (a) and run 8 (b); $[\text{TBAm}]_0 = 1$ mol L^{-1}; $[t\text{BDB}]_0/[\text{AIBN}]_0 = 10$.

corresponds to the TBAm molecular weight (127.18 g mol^{-1}). An enlargement between 2477 and 2872 mass units, shows the presence of four peaks in each repetitive sequence corresponding to several kinds of chains (Fig. 11(b)).

The main peak, P3 (2647.7 mass units), corresponds to chains of polymerization degree, $X = 19$, initiated by a *tert*-butyl radical and terminated by a dithiobenzoate function (Na^+ cationization, Table 2). These chains are the expected ones according to the RAFT mechanism.

Among the three small peaks, peak P1 (2620.8 mass units) may correspond to chains of polymerization degree, $X = 20$, initiated by a *tert*-butyl radical and terminated by a double-bond (Na^+ cationization). These chains would result from termination reactions via disproportionation. The corresponding proton-ended chains (at +2 mass units) are also present considering the shape of the isotopic distribution of peak P1 which indicates the overlap of several kinds of chains (in comparison with the isotopic distribution of peak P3) (Fig. 11(c)). The chains corresponding to termination reactions via combination (expected at 2678.96 mass units) were not observed.

In a previous MALDI-TOF MS study [60] concerning poly(NAM) chains synthesized with the same RAFT agent, some proton-ended chains were also observed but not the double-bond ended chains. It was demonstrated (by studying the chains before and after aminolysis) that these proton-ended chains were mostly resulting from fragmentation of some dithioester end-groups inside the spectrometer. Schilli et al. [28] arrived to the same conclusion for poly(*N*-isopropylacrylamide) chains by performing some post-source decay (PSD) experiments. Here, it may be possible that part of the proton-ended chains also resulted from fragmentation.

Concerning peak P2, its isotopic distribution is also indicating the overlap of several chain populations. The population at the monoisotopic mass (2631.7 mass units) corresponds to some dormant chains which would have undergone an oxidation reaction leading to thioester-ended chains (Na^+ cationization) [61]. The intermediate sulfine-ended chains (expected at 2664 mass units) were not observed. Such thioester-ended chains have already been observed by Vana et al. [62] for poly(methylacrylate) (after an oxidation reaction of the dithioester-ended chains with *tert*-butyl hydroperoxide) and by our group [60] for poly(NAM) (resulting from oxidation by air during storage). The polymerization solvent, dioxane, was peroxide-free since distilled before use.

Another population, at +2.3 or +3.0 mass units, could correspond either to: (i) dead chains initiated by AIBN (Na^+ cationization). However, it would be surprising to observe these chains, whereas the dormant chains initiated by AIBN (expected at 2658.9 mass units) are in the background noise. It is worthy to note that chains initiated by AIBN (whether dormant or proton-terminated) were not often observed in previous studies. Only Destarac et al. [63], Schilli et al. [28] and Ah Toy et al. [64] reported such kind of chains, although with a very low intensity. Taking into account that they were using a DT/AIBN ratio of 5, 3 and 3.6, respectively, it is not surprising that, at the used ratio of 10, these chains are hardly observable. (ii) 3-arm star polymer structure resulting from a termination reaction (via combination) onto an intermediate radical of the main RAFT equilibrium (Na^+ cationization). These structures although suspected [65–68] have never been observed until now, even if a recent article from Kwak et al. [68] describes the occurrence of 3-arm star species of low molecular weight which could model the 3-arm star polymer structures possibly produced during RAFT polymerization.

Finally, peak P4 (2703.6 mass units) was tentatively attributed although its intensity and resolution were low. It could correspond to a proton-ended intermediate radical (2706.0 i.e. at −2.4 mass units) resulting from a termination reaction via disproportionation [54] (the corresponding double-bond ended chain appearing under peak P1) or from a transfer reaction, both reactions occurring either during

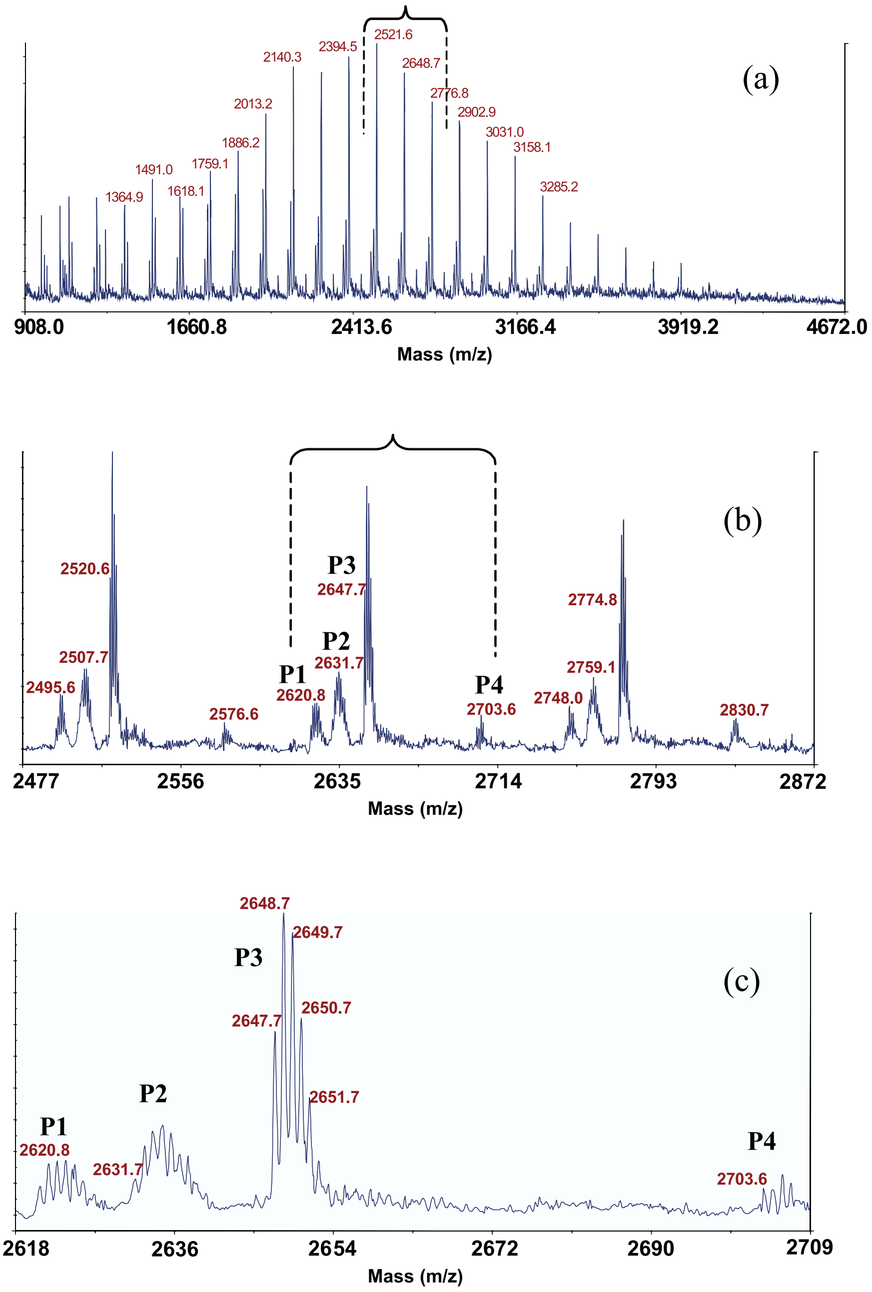


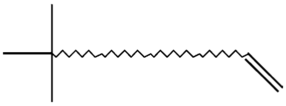
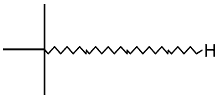
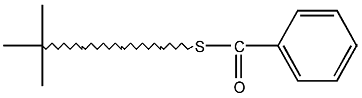
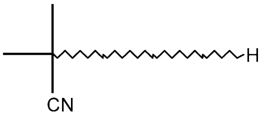
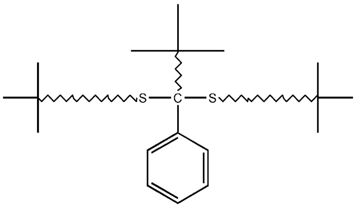
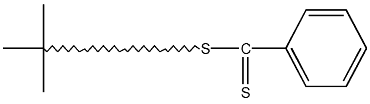
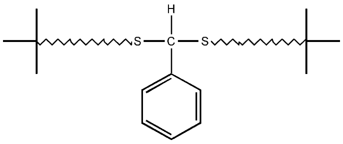
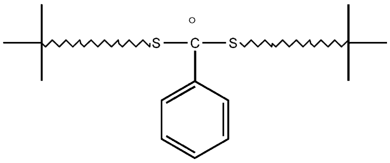
Fig. 11. MALDI-TOF MS spectrum of poly(TBAm) sample 10T6 (a) and enlargements of this spectrum (b, c) (reflector mode).

polymerization or when the sample was quenched in liquid nitrogen. Peak P4 could also correspond to an intermediate radical itself (2705.0 i.e. at −1.4 mass units) which would have been like ‘frozen’ at quenching. Such observations would imply that the intermediate radical be quite stabilized or possibly persistent at ambient temperature. In our previous study on poly(NAM), there was also a badly resolved peak at −2.3 mass units from the proton-ended intermediate radical structure [60]. Moreover, in a recent study of poly(methylacrylate) by electrospray ionization mass spectrometry coupled to size exclusion chromatography (SEC-ESI-MS) [64], the presence of these two species was also suspected (at −1.7 and −0.7 mass units, respectively). In fact, the study of side-reactions onto intermediate radicals is an on-going subject in several groups, whether they refer to reversible [64,69–71] or irreversible [65–68] termination reactions.

Concerning the ^{1}H NMR study, a spectrum was recorded for a purified poly(TBAm) sample from run 10 (sample 10T6 at 36% conversion) and brought some more information about the chain-end characterization (Fig. 12).

The protons of the poly(TBAm) backbone appear as large peaks, *a–d*, respectively corresponding to the –CH$_2$–, –CH–, –NH– and to the *tert*-butyl protons of the main chain.

Table 2
Poly(TBAm) chain structures corresponding to the various peaks in Fig. 11

Peak	Monoisotopic mass experimental	Monoisotopic mass theoretical	Structure	*X*	Cationization
P1	2620.8	2621.0		20	Na^+
		2623.0		20	Na^+
P2	2631.7	2631.9		19	Na^+
		2634.0		20	Na^+
		2634.7		18	Na^+
P3	2647.7	2647.9		19	Na^+
P4	2703.6	2706.0		19	Na^+
		2705.0		19	Na^+

X, polymerization degree of the considered chain.

Peaks between 7.3 and 8.1 ppm (*f*) have been attributed to the five protons of the dithiobenzoate end-group, and peak at 0.85 ppm (*d′*) to the nine protons of the *tert*-butyl end-group. The six protons of the cyanoisopropyl end-groups derived from AIBN (expected at 1.4 ppm) were not visible due to the high *d* peak. Finally, the peak at 4.6 ppm (*e*) has been assigned to the α–CH– proton of the dithiobenzoate function.

From the comparison of the integrals of the repetitive units and of the *tert*-butyl end-group $[(a+b+d)/12/(d'/9)]$, the average polymerization degree could be determined, $X_n=22$ (i.e. M_n of 2800 g mol^{-1}). In the case of a sample from run 9 (9T4, at 41% conversion), a value of $X_n=108$ was obtained (i.e. M_n of 13,700 g mol^{-1}).

Then, the ^{13}C NMR spectrum of a purified poly(TBAm) sample was also recorded (Fig. 13). The carbons of poly(TBAm) backbone, $-CH_2-$ and –CH–, appeared as large peaks, *a* and *b*, respectively. Peaks *c*–*e* were attributed to carbons of the grafted part, C=O, $-CH_3$ and quaternary carbon, respectively. The chain-ends were identified as low intensity peaks, at 127–129 ppm for the dithiobenzoate end-group (peak *f*) and at 32 ppm for the *tert*-butyl end-group (peak *d′*), close to the *tert*-butyl groups of the backbone (peak *d* at 29 ppm). The comparison of the integrals of these

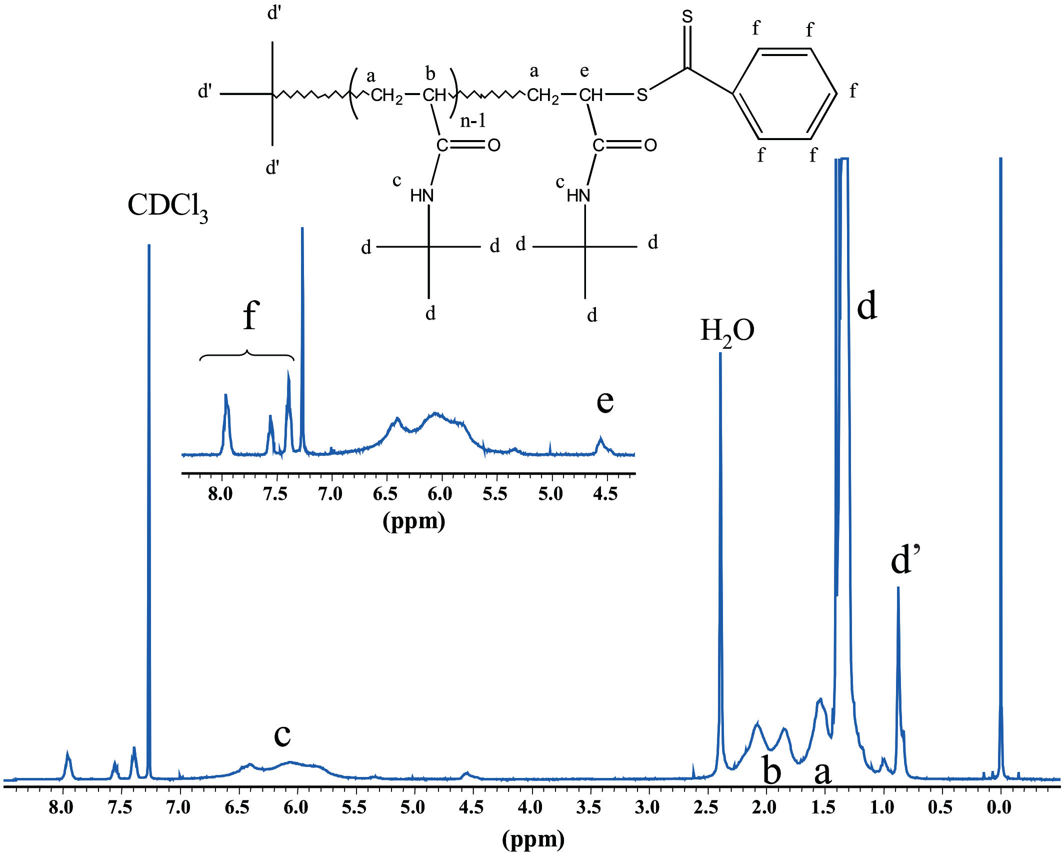


Fig. 12. ^{1}H NMR spectrum of poly(TBAm) sample 10T6.

peaks (*d*/*d*′) is possible since the corresponding carbons are of the same nature, which again allows the determination of the average polymerization degree. In the case of sample 9T4, a X_n value of 110 was obtained (i.e. M_n of 14,200 g mol^{-1}) in good correlation with the value arising from the ^{1}H NMR spectrum.

Finally, the same poly(TBAm) sample was analyzed by size exclusion chromatography coupled to on-line light scattering detection (SEC/LSD), which provided the absolute M_n value (14,000 g mol^{-1}, PDI = 1.05). The relative value obtained from the PS calibration curve (11,500 g mol^{-1}) indicates that the PS-based calibration under-estimates the MW of the poly(TBAm) samples.

The M_n values obtained from the four different analytical techniques could be compared with the calculated value for two samples: 9T4 and 10T6 (Table 3). The experimental values are in good correlation with each other, except the SEC/LSD value for sample 10T6 since this technique is not appropriate to characterize very low molecular weight samples ($<$5000 g mol^{-1}). In addition, these experimental values are close to the theoretical one, confirming the controlled behaviour of the RAFT polymerization of TBAm monomer in the presence of *tert*-butyl dithiobenzoate.

4. Conclusions

This article reports the first study on the RAFT polymerization of three hydrophobic acrylamide derivatives: the *N*-*tert*-butylacrylamide (TBAm), the *N*-octadecylacrylamide (ODAm) and the *N*-diphenylmethylacrylamide (DPMAm). They have been polymerized in dioxane or DMF, in the presence of AIBN and *tert*-butyl dithiobenzoate (*t*BDB) as initiator and reversible chain transfer agent,

Table 3
Comparison of M_n values obtained by different techniques for samples 9T4 and 10T6

Sample	Calculated M_n (g mol^{-1})	M_n SEC/LSD (g mol^{-1})	M_n ^{1}H NMR (g mol^{-1})	M_n ^{13}C NMR (g mol^{-1})	M_n MALDI-TOF MS (g mol^{-1})
9T4	12,500	14,000	13,700	14,200	13,500
10T6	2300	3900	2800	–	2650

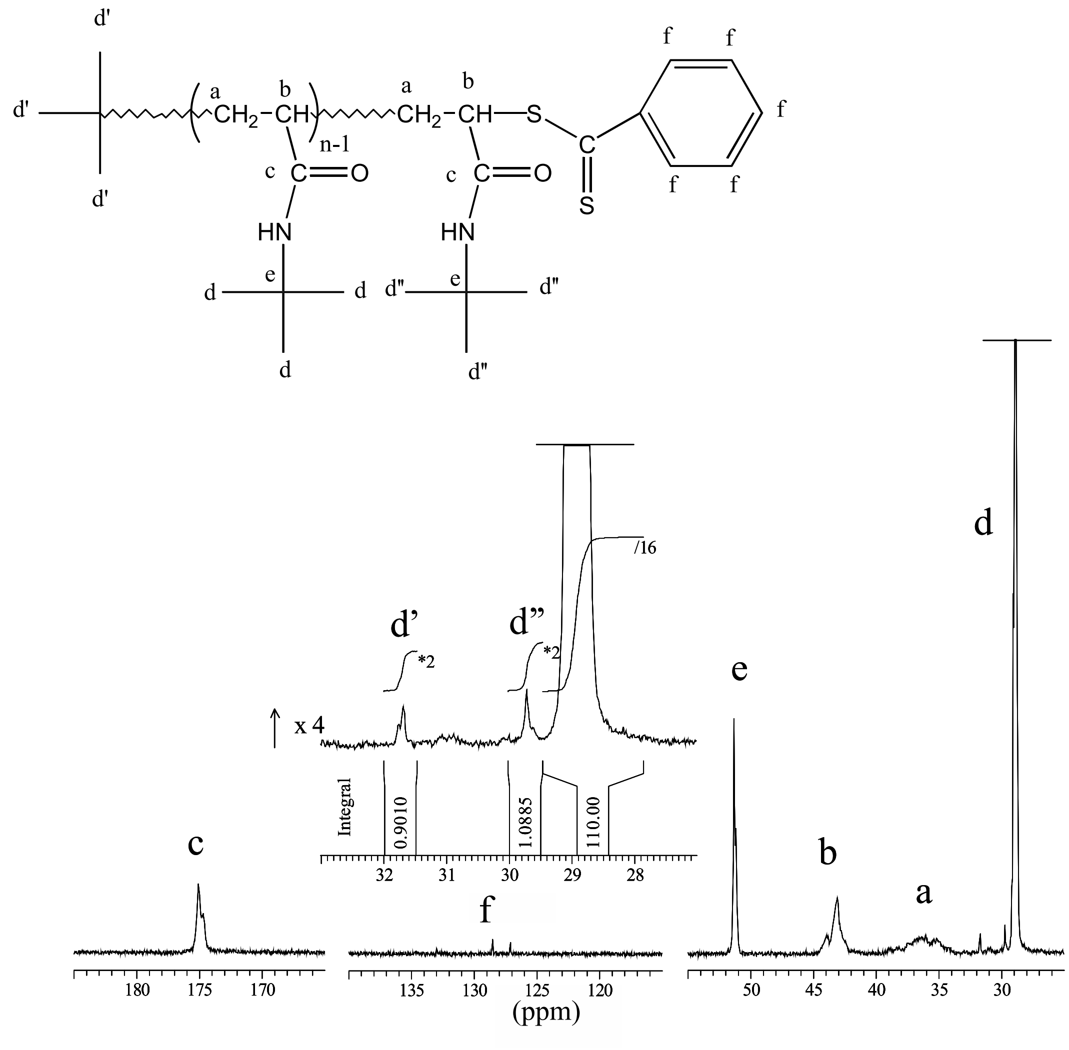


Fig. 13. ^{13}C NMR spectrum of poly(TBAm) sample 9T4.

respectively. The comparison of the polymerizations in terms of kinetics, molecular weights and molecular weight distributions of the obtained polymers, indicated a linear increase of M_n with conversion (until 60%) with polydispersity indices between 1.1 and 1.4, although the conversion remained very limited in the case of DPMAm probably due to steric hindrance.

In the case of TBAm polymerization, the study of the influence of the [*t*BDB]/[AIBN] ratio (using a ratio of 10 instead of 3.3) did not result in an additional improvement of the control, as was previously obtained in the case of an hydrophilic disubstituted acrylamide derivative, *N*-acryloylmorpholine [51]. Anyway, in order to get a minimum amount of dead chains, it will be better to choose a ratio of 10 especially when aiming at synthesizing block copolymers from the poly(TBAm) blocks.

A surprising phenomenon was observed during the synthesis of long chains (above 50,000 g mol^{-1}) with a stagnation (or even a decrease) of M_n and a simultaneous increase of PDI values above 40% conversion. The SEC chromatograms indicated the appearance of new short chains (dormant and not dead) and the stop of the growing of the main chains above 50% conversion. This phenomenon is currently studied in details and will be the subject of a future article.

Finally, several poly(TBAm) samples were characterized by four independent analytical techniques which confirmed the good control of the molecular weights and the end-functionalization of the chains, this last parameter being essential with the aim of synthesizing block copolymers. Amphiphilic block copolymers have been recently synthesized from several poly(TBAm) blocks as reported in an outcoming article [72].

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