

RAFT Polymerization Kinetics of α -Methylbenzyl Methacrylate by Dilatometry

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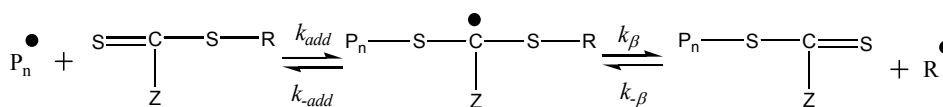
Abstract

This work presents a comparative study of the reversible addition–fragmentation chain transfer (RAFT) and free radical polymerizations of α -methylbenzyl methacrylate (α -MBM) in solution at 70 °C using 1-phenylethylthiobenzoate (1-PEDB) as RAFT agent and AIBN as thermal initiator. Reactions were monitored by dilatometry, which is a robust and economical technique to follow kinetic polymerization. Free radical polymerizations were carried out at initial monomer concentration $[\alpha\text{-MBM}]_0$ of 0.2, 0.5, 0.7 and 1.0 M at fixed $[\text{AIBN}]_0 = 1 \times 10^{-3}$ M and initial initiator concentration of 2, 5, 8 and 10×10^{-3} M at fixed $[\alpha\text{-MBM}]_0 = 0.5$ M. For the RAFT polymerizations the $[1\text{-PEDB}]_0$ was 4×10^{-3} M using the same reaction conditions as that in the free radical polymerizations. In RAFT polymerizations it was found that conversion profiles were lower than in free radical polymerization. Plots of conversion vs time indicated that the polymerizations followed first order kinetics in the range of $[\alpha\text{-MBM}]_0$ evaluated. However, only at low $[\text{AIBN}]_0$, i.e. 2 and 5×10^{-3} M, kinetics fitted adequately in the reaction time tested. ¹H NMR, IR, and UV-Vis spectrophotometric studies confirmed the presence of thiocarbonylthio moieties (-SCS-) in the polymer chains. Molecular weight data for the set of experiments carried out by free radical polymerization decreased when the monomer or the initiator concentration increased. The molecular weight distributions (MWDs) corresponding to the polymers obtained in the RAFT polymerizations were moderately narrow with polydispersities (\mathcal{D}) between 1.12 and 1.59

Keywords: RAFT polymerization, free radical polymerization kinetics, dilatometry, methacryloyl monomers, multi-angle light scattering

1. Introduction

The main advantages of free-radical chemistry are the undemanding conditions required for polymerization and the large number of monomers that can be polymerized. The disadvantage of this method lies in the uncontrollable polymer structure. However, the application of living free-radical polymerization has opened the possibility of generating controllable macromolecular architectures with mild reaction conditions (Otsu et al., 1982; Kato et al., 1995; Wang & Matyjaszewski, 1995a; Percec et al., 1995; Chiefari et al., 1998). Several living free radical polymerization techniques have been developed, including stable free radical polymerization (Georges et al., 1993), atom transfer radical polymerization (ATRP) (Kato et al., 1995; Wang & Matyjaszewski, 1995b; Percec et al., 1995), and reversible addition–fragmentation chain transfer (RAFT) (Chiefari et al., 1998; Le et al., 1998). The RAFT technique is probably the most versatile of those mentioned because it exhibits a high degree of compatibility with a wide range of functional monomers and is tolerant of water and oxygen in the system (Barner-Kowollik et al., 2003). The RAFT process is a polymerization in the presence of a dithio derivative that reacts by a series of reversible addition–fragmentation steps (Scheme 1).



Scheme 1. Fundamental reaction step in the RAFT mechanism proposed

Most publications in this field are devoted with styrene and acrylic acid derivatives (Moad et al., 2000; Perrier et al., 2002; Mayadunne et al., 1999). One of the main problems encountered in the RAFT polymerization of methacrylates is the selection of RAFT agents suitable for the efficient controlled synthesis of polymers or appropriate reaction conditions (Chiefari et al., 2003; Barner-Kowollik et al., 2001; Zhu et al., 2004a). Some examples of successful RAFT polymerization of functional methacrylates are poly(glycidyl methacrylate) (Zhu et al., 2004b), poly(6-[4-(4'-methoxyphenyl)phenoxy] hexyl methacrylate) (Hao et al., 2003), poly(3-[tris(trimethylsiloxy)silyl] propyl methacrylate) (Saricilar et al., 2003) and poly(dimethylaminoethyl methacrylate) (Sahnoum et al., 2005), which have been prepared with well-controlled molecular weights and narrow polydispersities.

On the other hand, our group is focused on the synthesis of functional vinyl monomers, their kinetics polymerization and physicochemical characterization (Percino et al., 2004a; Yáñez-Martínez et al., 2010; Zayas et al., 2000; Percino et al., 2007; Gutiérrez-Pérez et al., 1999; Percino et al., 2004b). Recently, we extended our researches at the CRP kinetics studies of such functional monomers (Yáñez-Martínez et al., 2011), in this sense it was found that the nature of the type of monomer in the ATRP system determined if the polymerization proceed; i.e. it was found that ethylbromopropionate (EBIB) could not initiate the polymerization of *N*-(S)- α -methylbenzyl methacryloylamine. But, well defined poly(α -methylbenzyl methacrylate) macroinitiators were prepared when EBIB and methylchloropropionate (MCP) were used as initiators, such ATRP initiators contain an ester or an amide group (Percino et al., 2011). Also, recently it was reported the RAFT polymerization of *N*-(S)-(-)- α -MBMA using typical RAFT agents (Soriano-Moro et al., 2011). Now, in this paper we study the RAFT polymerization kinetics of the racemic α -methylbenzyl methacrylate (α -MBM), under different reaction conditions using 1-phenylethyl dithiobenzoate (1-PEDB), which is an extensively used RAFT agent (Chong et al., 2003).

2. Experimental

2.1 Materials and Instruments

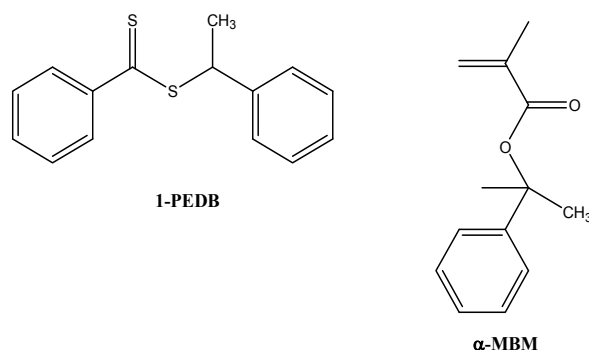
α -Methylbenzyl alcohol, methacryloyl chloride, magnesium powder, magnesium sulfate anhydrous, tetrahydrofuran (THF) and 1-phenylethyl bromobenzene were purchased from Aldrich. The initiator 2,2'-azobisisobutyronitrile (AIBN, Alfa Aesar) was purified by recrystallization in methanol. The remaining reagents and solvents were used directly as received from suppliers.

¹H-NMR spectra were obtained on a Varian Mercury VX300-MHz NMR spectrometer. IR spectra of the products were recorded on a Vertex 70 model Bruker FT-IR spectrophotometer by ATR. UV-vis spectra were obtained in chloroform at 25 °C using a quartz cell of 1 cm with an Ocean Optics SD2000 spectrometer and a UV-vis light source DT 1000CE from analytical instruments systems was used as an excitation source. Molecular weight data (M_w) were determined on a multi-angle light scattering detector (DAWN Heleos of 8 angles, Wyatt Technology Corp at 658 nm wavelength) using a refractive index detector (Optilab rEX, Wyatt Technology Corp at 690 nm) to determinate the specific refractive index increment (dn/dc) and molecular weight distributions were measured by size exclusion chromatography (SEC) on a Hewlett Packard modular system, comprising an auto injector, Polymer Laboratories 5.0 μ m bead-size guard column, followed by mixed PL Gel columns (1 K–4 M) using a differential refractive index detector (HP 147 A). The eluent was THF (HPLC grade) at flow rate of 1 mL/min at 40 °C. The system was calibrated using narrow polystyrene standards (ranging from 162 to 6.8×10^6 g/mol). Data acquisition was performed using Polymer Laboratories GPC software.

2.2 Synthesis

α -Methylbenzyl methacrylate (α -MBM, Scheme 2) were synthesized according to the following procedure: methylbenzyl alcohol (0.206 mmol) without solvent was reacted with freshly distilled methacryloyl chloride (0.309 mmol) and 33.4 mL of a 37% NaOH solution. After 6 h, the mixture was filtered to separate the two liquid phases from the salt formed. The liquid phases were separated and the oily phase was treated several times with a 10% Na₂CO₃ solution to obtain an uncolored liquid with a yield of 68%. IR (KBr), $\nu(\text{cm}^{-1})$: 1717 (s, ester, $\nu\text{C}=\text{O}$), 1156 (s, ester, $\nu\text{C}-\text{O}$), 1635 (s, vinyl, $\nu\text{C}=\text{C}$), 942 (s, δCH , $\text{CH}_2=$). ¹H NMR (CD₃Cl, 300 MHz) δ : 1.6 (d, 3H, CH₃), 2.0 (s, 3H, CH₃), 6.0 (t, 1H, CH), 6.2 (s, 1H, CH₂=), 5.6 (s, 1H, CH₂=), 7.4-7.2 (m, 5H, Ar).

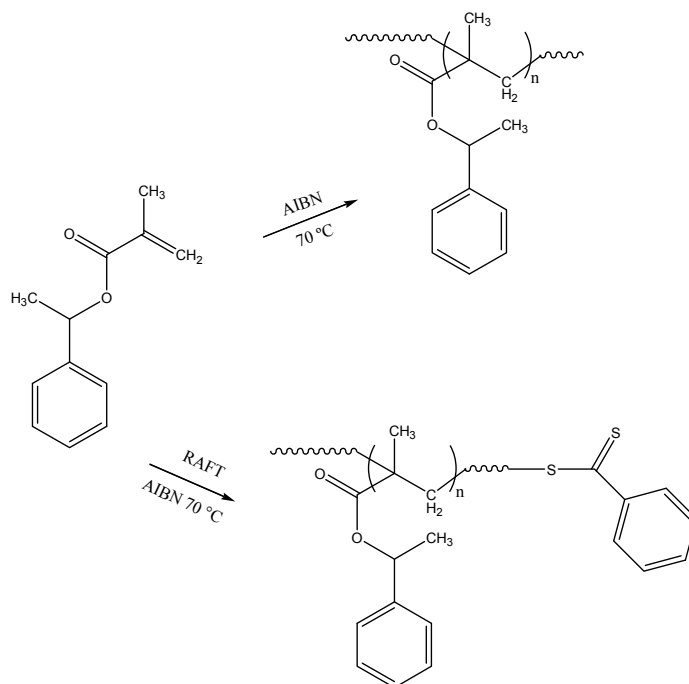
1-Phenylethyl dithiobenzoate (1-PEDB) was synthesized as reported in the literature (Le et al., 1998). ¹H NMR, δ (ppm): 1.8 (d, 3H, CH₃CH), 5.3 (q, 1H, SCHCH₃), 7.2-8.0 (m, 10H, ArH). ¹³C NMR, δ (ppm): 20 (CH₃), 50 (SCH), 126-146 (ArC), 227 (C=S).



Scheme 2. Structures of the RAFT agent and monomer used for the present work

2.3 Dilatometry

The polymerization reactions were monitored through a well-established dilatometric method, which is a robust and economical technique to follow kinetic polymerization in comparison with others systems (Saricilar et al., 2003; Percino et al., 2004a; Percino et al., 2011; Kurenkov et al., 2007; Bonilla-Cruz et al., 2007; Mota-Morales et al., 2010). A typical glass dilatometer is composed of a 5 mL bulb and a capillary tube of 2 mm internal diameter and 10 cm length. For a representative polymerization, a solution of monomer in solution, AIBN (in the case of conventional polymerization) and the RAFT agent (for the controlled polymerization), see Scheme 3, was placed in a 5 mL flask. Solutions were bubbled with ultrahigh-purity argon for 20 min and afterward were sealed with a rubber septum. Dilatometers were placed in a water bath at 70 °C (± 0.02). Reaction was stopped by cooling the dilatometer in an ice-water bath. The polymer was precipitated in methanol and dried in a vacuum. The monomer conversion was traced using a contraction factor k , according to $x = \Delta V/Vk$. Here ΔV is the change in volume present in the capillary; V is the initial solution volume. ΔV is determined by $\pi r^2 \Delta h$; where r is the inner capillary radius and Δh is the change in height of the solution contained in the capillary (both expressed in cm), k was experimentally calculated from $(\rho_p - \rho_m)/\rho_p$ ratio, where ρ_p and ρ_m are the densities of the polymer (1.021 g/mL for free radical polymerization and 1.1 g/mL for RAFT polymers) and monomer (0.912 g/mL), respectively. The density values were measured by a pycnometric method.



Scheme 3. Synthesis of poly(α -MBM) via free radical and RAFT polymerization

3. Results and Discussion

RAFT polymerization of α -MBM was evaluated, using 1-PEBD, an extensively used RAFT agent (Chong et al., 2003), which has a secondary expeller radical. As shown in Figure 1, the conversion decrease significantly, around of 84 %, when the 1-PEDB is added (Figure 1b) in comparison with the experiment set carried out without RAFT agent; such retardation is typical in the polymerization carried out with dithiobenzoates (Monteiro et al., 2001; Vana et al., 2002; Kwak et al., 2004; Bathfield et al., 2007), which is due to the formation and stability of intermediate radicals during the polymerization. Figure 1c shows that the kinetics adequately fit a first-order reaction (like show the R-square values), which indicated that the propagating radical concentration remained nearly constant throughout the reaction as is expected for the living systems. Furthermore, it is important to draw attention to the use of dilatometry as appropriate method to determinate the monomer consumption; especially, at early stage of the reaction, where the conversion could be very low and slight changes in the amount of polymer isolated by gravimetric method could give an erroneous kinetic behavior. Also the effect of the initiator concentration in the monomer conversion was evaluated. In this case, the conversion again decreases when RAFT agents was added into the reaction (see Figure 2a and 2b). The linearity in the kinetics fit adequately for experiments carried out at low $[I]_0$ (2 and 5×10^{-3} M), but at higher $[I]_0$, as in the experiments at 8×10^{-3} and 1×10^{-4} M, deviation in the linearity occur after of 125 min, which indicate that a high concentration radicals reduces the living and controlled behavior in the polymerization. As such the better initiator concentration was 2×10^{-3} M.

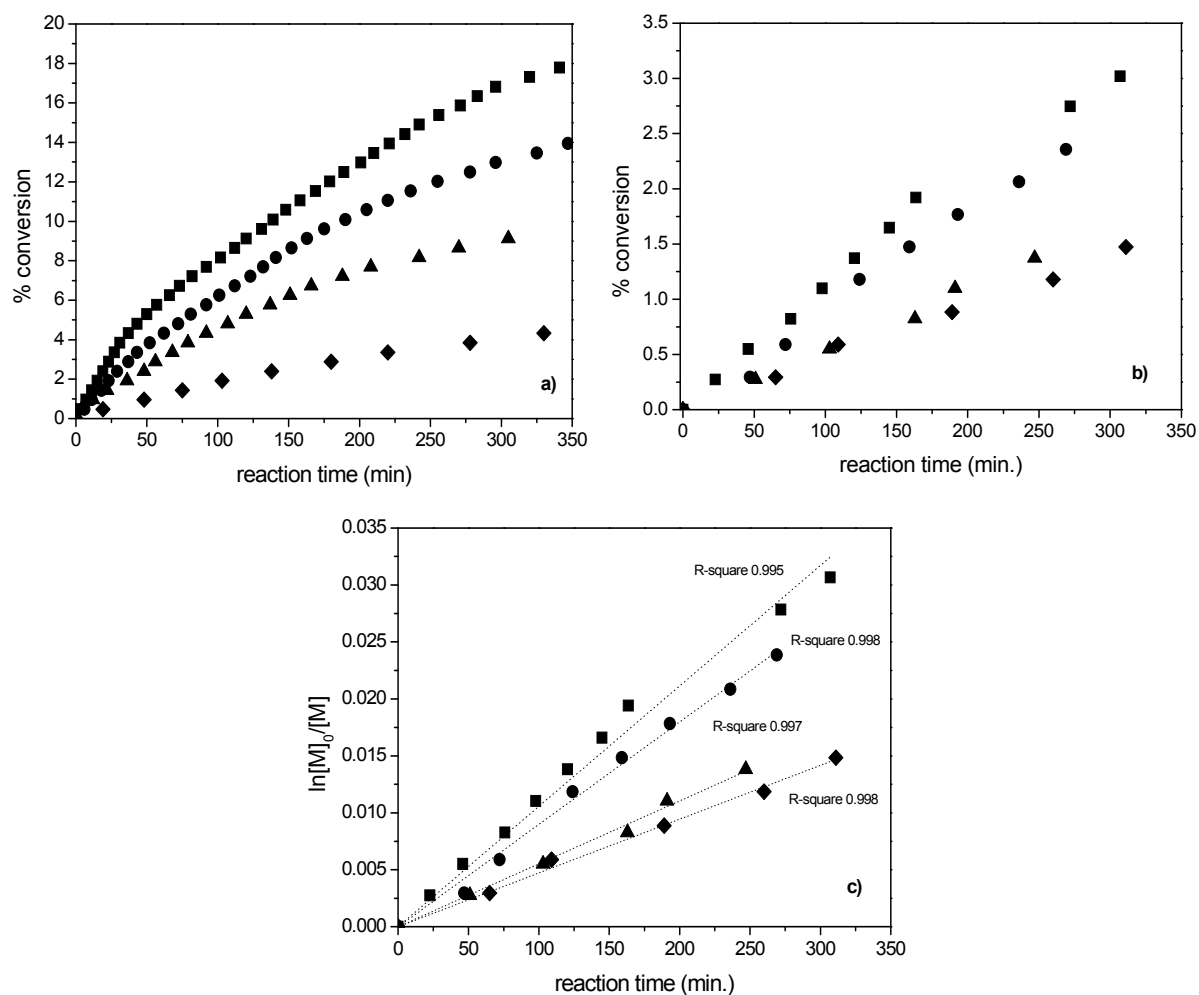


Figure 1. Polymerization of α -MBM at $[M]_0 = 0.2$ (\diamond), 0.5 (\blacktriangle), 0.7 (\bullet) and 1.0 M (\blacksquare). $[I] = 2 \times 10^{-3}$ M at 70°C , in toluene **a)** free radical polymerization, RAFT polymerization **b)** conversion profile and **c)** $\ln[M]/[M]_0$ trend using $[1\text{-PEDB}]_0 = 1 \times 10^{-3}$ M

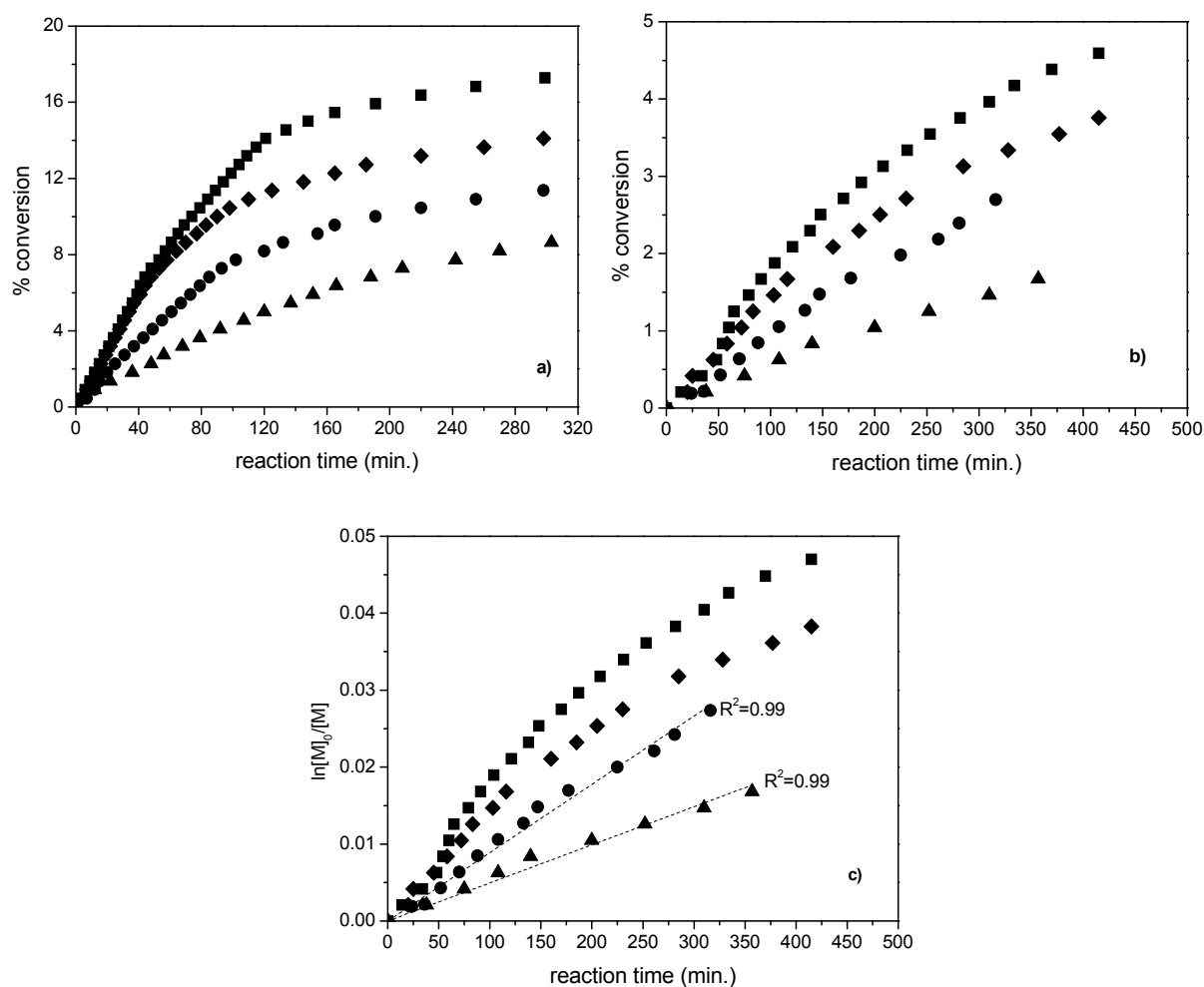


Figure 2. Polymerization of α -MBM at $[I]_0 = 2$ (▲), 5 (●), 8 (◆) and 10 (■) $\times 10^{-3}$ M at $[M]_0 = 0.5$ M at 70 °C, in toluene **a**) free polymerization, RAFT polymerization **b**) conversion profile and **c**) $\ln[M]/[M]_0$ trend at $[1\text{-PEDB}]_0 = 1 \times 10^{-3}$ M

Regarding to the polymers synthesized in presence of 1-PEDB, the ^1H NMR spectrum displayed a weak signal at around of 7.5 ppm (see inset in Figure 3), which is assignable to aromatic protons from of the RAFT fragment (Zhu et al., 2004c; Mori et al., 2005; Li et al., 2005; Yin et al., 2006). In addition, Figure 4 compares the infrared spectra of 1-PEDB, poly(α -MBM) synthesized with and without RAFT agent. The IR spectrum of polymer synthesized by RAFT exhibit absorption bands at ~ 1420 , 1225 and 760 cm^{-1} corresponding to S-CH, C=S and C-S stretching vibration, respectively (Bellamy et al., 1960; Coates, 2000; Zhang et al., 2005). To confirm the presence of the -SC(S)- groups incorporated into polymers, the UV-vis spectra of polymers with RAFT agent were recorded. Figure 5 shows the comparative analysis between UV spectra of the 1-PEDB (solid line), polymers obtained via RAFT at different RAFT agent concentration (dash line, **b** and **c**) and the corresponding polymer via free radical polymerization (dot line), the absorption λ_{max} around of 305 nm (π - π^* transition) is directly attributable to the presence of the thiocarbonylthio moiety at the end of the polymer chains (Soriano-Moro et al., 2011).

The molecular weight (Mw) data corresponding to the experiments carried out under free radical polymerization are summarized in Table 1 and 2, such values were estimated using the specific refractive index increment values, additionally, the second virial coefficient (A_2) values for these polymers were closed to zero, meaning that the strength of the interaction between the macromolecules and the solvent is equivalent to the macromolecule-macromolecule interaction strength (solvent theta).

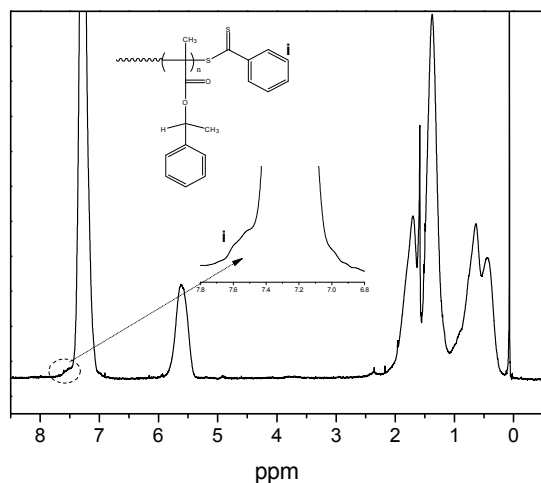


Figure 3. ^1H NMR spectrum in CDCl_3 of poly(α -MBM) synthesized in presence of 1-PEDB

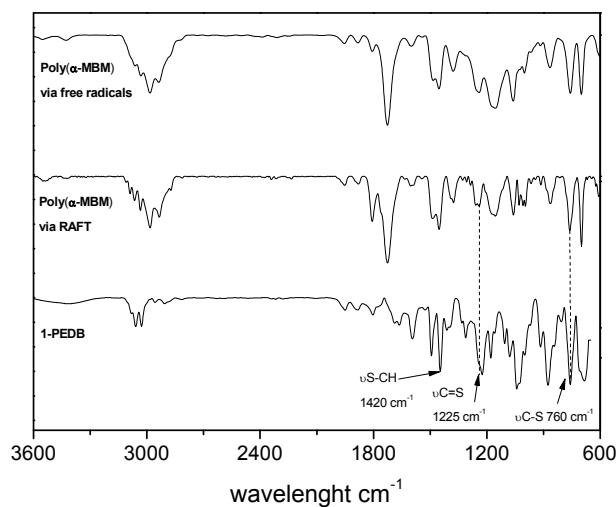


Figure 4. Infrared comparative analysis of 1-PEDB alone (bottom), poly(α -MBM) synthesized with (middle) and without (top) 1-PEDB

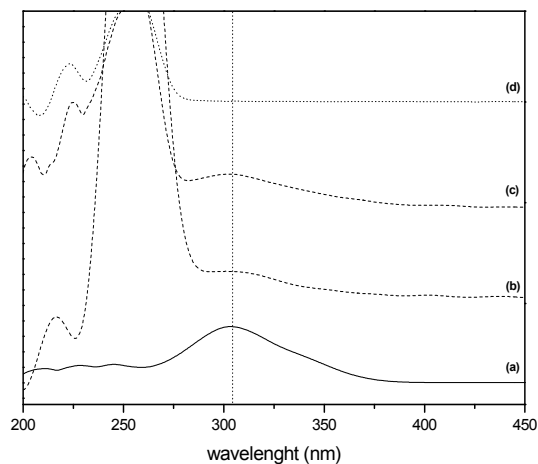


Figure 5. UV-vis spectra comparison of 1-PEDB (solid line, **a**) with poly(α -MBM) synthesized with (dash line, **b** and **c**) and without RAFT agent (dot line, **d**)

Table 1. Molecular weight data by MALS recorded in toluene

$[M]_0^a$ M	% conversion	Mw (g/mol)	dn/dc (mL/g)	$A_2 \times 10^4$ (molmL/g ²)
0.2	3.85	39 310	0.0667	7.077
0.5	8.65	103 300	0.0648	1.989
0.7	12.5	252 600	0.0569	3.570
1.0	15.86	714 900	0.0604	0.799

^a at fixed $[I]_0 = 2 \times 10^{-3}$ M

Table 2. Molecular weight data by MALS recorded in toluene

$[I]_0 \times 10^3^b$ M	% conversion	Mw (g/mol)	dn/dc (mL/g)	$A_2 \times 10^4$ (molmL/g ²)
2	3.85	103 300	0.0648	1.989
5	8.65	74 090	0.0614	2.096
8	12.5	41 090	0.0542	5.882
10	15.86	32 720	0.0673	3.569

^b at Fixed $[M]_0 = 0.5$ M

On the other hand, Figure 6 shows the size exclusion chromatography (SEC) traces for the polymers synthesized by RAFT polymerization; the values (between 5821 and 8091 g/mol) are substantially lesser than the corresponding polymers synthesized by free radical polymerization (Table 1). As it can be seen, that control in the molecular weight distribution was easily achieved at $[M]_0 = 0.5$ and $[I]_0 = 2 \times 10^{-3}$ M. Thus, in comparison with the system *N*-(S)-(-)- α -methylbenzylmethacryloyl amine/benzyl dithiobenzoate recently reported (Soriano-Moro et al., 2011) (with \mathcal{D} between 1.59 to 1.3) the system of α -MBM/1-PEDB possess a better living/controlled behavior, which put forward that the adequately choice of monomer/RAFT agent system plays a very important role (Favier et al., 2006). Currently, the synthesis of specific RAFT agents to improve the control for novel functional monomers is investigated.

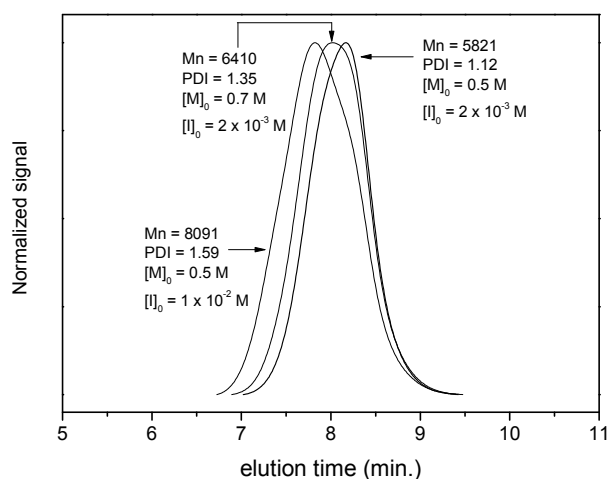


Figure 6. SEC traces for polymers synthesized via RAFT

4. Conclusions

Kinetics of the free radical and RAFT polymerizations of α -MBM was successfully monitored by dilatometry, which had demonstrated to be a robust and economical technique to follow kinetic polymerization in comparison with others systems. The plots of conversion vs time indicated that the polymerizations followed first-order kinetics for all monomer concentration evaluated, but such tendency is modified when high initiator

concentration was used. ^1H NMR, IR, and UV-Vis spectrophotometric studies confirmed the presence of thiocarbonylthio moieties (-SCS-) in the polymer chains. Polydispersity indexes (between 1.12 and 1.59) indicate that the control of the reaction is satisfactory using 1-PEDB, an extensively used RAFT agent. Finally, the control in the RAFT polymerization of α -MBM is better with respect to *N*-(S)-(-)- α -MBMA/BDB system, previously reported.

Acknowledgements

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