Polymer 50 (2009) 5024–5030

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Effect of stabilizer concentration and controller structure and composition on polymerization rate and molecular weight development in RAFT polymerization of styrene in supercritical carbon dioxide

Gabriel Jaramillo-Soto [a], Pedro R. García-Morán [a], Francisco J. Enríquez-Medrano [b], Hortensia Maldonado-Textle [b], Martha E. Albores-Velasco [c], Ramiro Guerrero-Santos [b], Eduardo Vivaldo-Lima [a,*]

[a] *Facultad de Química, Departamento de Ingeniería Química, Universidad Nacional Autónoma de Mexico, 04510 Mexico D.F., Mexico*
[b] *Centro de Investigación en Química Aplicada, Blvd. Enrique Reyna No. 140, Saltillo, Coahuila 25140, Mexico*
[c] *Facultad de Química, Departamento de Química Orgánica, Universidad Nacional Autónoma de Mexico, 04510 Mexico D.F., Mexico*

ARTICLE INFO

Article history:
Received 11 February 2009
Received in revised form
4 July 2009
Accepted 15 August 2009
Available online 29 August 2009

Keywords:
Supercritical carbon dioxide
RAFT polymerization
Dispersion polymerization

ABSTRACT

An experimental study on the reversible addition-fragmentation chain transfer (RAFT) polymerization of styrene in supercritical carbon dioxide is presented. A 38 mL, high-pressure view cell with two frontal and two lateral sapphire windows was used as reactor. Poly(styrene-block-dimethylsiloxane) was used as stabilizer. The performance as RAFT controllers of S-thiobenzoyl thioglycolic acid, methyl naphthalene dithiobenzoate, 4-methyl allyl dithiobenzoate, and benzyl-*N*,*N*-dimethyldithiocarbamate was compared. The effect of stabilizer concentration and controller structure and concentration on polymerization rate and molecular weight development was analyzed. Good performance was obtained with the first three controllers, although simultaneous high polymerization rates and low polydispersities were not possible with either of them. The performance of the fourth RAFT controller was poor.

1. Introduction

Controlled/“living” radical polymerization (CLRP) processes have reached a rather mature level in the last few years. They have allowed the synthesis of polymer materials with controlled microstructures which find uses in technologically important areas, such as aerospace, nanotechnology, industrial electronics, and biomaterials [1–4]. Reversible addition-fragmentation chain transfer (RAFT) polymerization has proven to be one of the most effective CLRP processes because of its advantages over other CLRP techniques (atom-transfer radical polymerization, ATRP, and nitroxide-mediated radical polymerization, NMRP), such as the applicability of the technique to a larger range of monomer types, reaction conditions (temperature and pressure), and processes (mass, solution, emulsion, miniemulsion, and dispersion) [5–8]. Single phase (bulk and solution) RAFT polymerizations are reasonably well understood. However, in the case of heterogeneous phase polymerization processes, the physical and modeling aspects of the kinetics and molecular weight development become more difficult to handle, due to the partition of reaction components between the two phases, the uncertain assignment of the site of reaction, the possible reactions in both phases, the selection of stabilizer, particle size distribution (PSD) control issues, and the solubility and transport properties of the RAFT agent [2,3].

Supercritical carbon dioxide ($scCO_2$) has emerged as a “green” solvent for polymerization processes. It is part of the atmosphere and since it can be recycled after being used, its contribution to the greenhouse effect from polymer related processes should be indeed minimal. It can also be obtained as a byproduct from fermentation and combustion processes. It is chemically stable, non-flammable and its critical point is reached at mild conditions (31.1 °C and 73.8 bar) [9–13].

Many polymers have been synthesized in $scCO_2$, including fluoropolymers, polysiloxanes, poly(methyl methacrylate), polystyrene, and polycarbonates [11,14–16]. While the majority of vinyl monomers are soluble in $scCO_2$ at relatively moderate pressures, the same is not true for polymers of high molecular weight. Therefore, the polymerization of these monomers in $scCO_2$ usually proceeds as dispersion or precipitation polymerization processes [17–22]. As in any dispersion polymerization process, the use of stabilizers is

---

* Corresponding author. Tel.: +52 55 5622 5256; fax: +52 55 5622 5355.
E-mail address: vivaldo@unam.mx (E. Vivaldo-Lima).

0032-3861/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2009.08.036

needed. In this case the stabilizers must have CO_2-phylic and CO_2-phobic regions.

In dispersion polymerization processes, active polymer chains grow in the continuous phase until a critical size is reached and then they precipitate. The presence of a stabilizer is needed to prevent coagulation or flocculation. The stabilizers most widely used in polymerizations in $scCO_2$ contain fluorinated or silyloxy groups in the CO_2-phylic region of the molecule. These compounds are highly soluble in $scCO_2$ [23–25].

The only RAFT polymerizations of styrene and methyl acrylate (MA) carried out in $scCO_2$ reported in the literature have proceeded in homogeneous phase, in a solution of CO_2 and toluene [26,27]. Both polymerizations were mediated by cumyl dithiobenzoate as RAFT controller. In the case of RAFT polymerization of methyl methacrylate (MMA) in $scCO_2$, a dispersion process stabilized by poly(dimethylsiloxane monomethacrylate), effective control was obtained by using cyano dithiobenzoates [28,29].

In this contribution, a systematic and through study on the RAFT polymerization of styrene in $scCO_2$, using a block copolymer of poly(styrene-block-dimethylsiloxane) (PSDMS) as stabilizer, is presented. The use of four RAFT controllers, different from those used in the previous reports from the literature, the use of a different stabilizer, and the presentation of a detailed study, analyzing the effects of process conditions and initial composition of the reacting mixture on polymerization rate and molecular weight development, producing low polydispersities and high conversions, makes our study much different from the first reports on RAFT polymerization in $scCO_2$.

2. Experimental

2.1. Reagents

Styrene (Aldrich Chemical Co. Inc., 99%, S4972-4L) was washed with a 5 wt.% NaOH solution, dried with magnesium sulphate, and distilled under vacuum at 22 °C. 2,2′-Azobisisobutyronitrile (AIBN, Akzo Novel Chemicals) was recrystallized twice from methanol. Carbon dioxide (Praxair, 99.99% purity) was used as-received. S-(thiobenzoyl) thioglycolic acid (Aldrich, 99%, 157880) (see its structure in Fig. 1a), referred to as “RAFT A” in the remainder of this paper, was used as received. Methyl naphthalene dithiobenzoate (referred to as “RAFT B”), and 4-methyl allyl dithiobenzoate (referred to as “RAFT C”), whose structures are shown in Fig. 1b and c, were synthesized in our group from p-tolyl bromide and bromobenzene, respectively, using Grignard reactants. Allylbromide and 2-bromomethylnapthalene were used to introduce the R group into the RAFT controller molecule (see Fig. 6 of Ref. 8 for definition of the R and Z groups of a RAFT molecule). Benzyl-*N*,*N*-dimethyldithiocarbamate (Aldrich, 98%, 368229) (referred to as “RAFT D”, with chemical structure shown in Fig. 1d) was used in the early stages of the project, but its performance was not good. PSDMS stabilizer was synthesized in our laboratory by anionic polymerization [30–33].

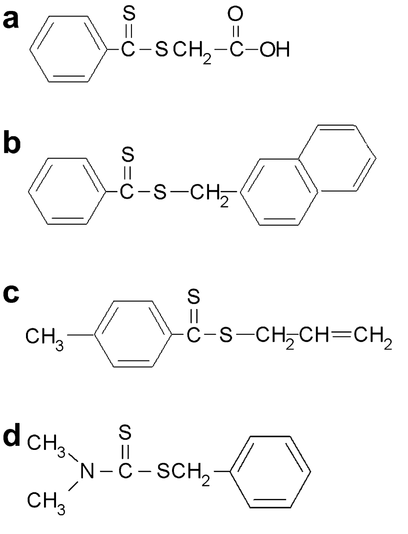

Fig. 1. Structures of the RAFT controllers used in this paper: (a) S-(thiobenzoyl) thioglycolic acid (“RAFT A”), (b) S-(naphtyl-2-methyl)-dithiobenzoate (“RAFT B”), (c) S-allyl-4-methyldithiobenzoate (“RAFT C”), and (d) benzyl-*N*,*N*-dimethyldithiocarbamate (“RAFT D”).

2.2. Synthesis of PSDMS stabilizer

Hexamethylcyclotrisiloxane monomer (Sigma Aldrich, 98%) was distilled at 135 °C, at atmospheric pressure. Butyl lithium initiator (Sigma Aldrich, 2.5 mmol/mL) was used as-received. Cyclohexane solvent was dried with sodium and benzophenone, and then distilled. All reagent manipulations were made in a tight system, purged with nitrogen. The polystyrene block was synthesized first, followed by the polyhexamethylsiloxane one. The synthetic route used for PSDMS is shown in Fig. 2a. The number-average molecular weight (M_n) ratio between the blocks was 1:9, respectively. This ratio was deducted from the ^1H NMR spectra shown in Fig. 2b. M_n of PSDMS obtained by gel permeation chromatography (GPC) was 55,000 g/mol. To ensure that the copolymer presented a diblock structure, the material was also characterized by differential scanning calorimetry (DSC). Two glass transition temperatures (T_g), one for polystyrene (100 °C), and the other for polydimethylsiloxane (-127 °C), were observed (DSC curve not shown for brevity).

2.3. Polymerization system

All the polymerizations of this paper were conducted in a 38 mL high-pressure view cell, equipped with two frontal and two lateral sapphire windows (Crystal Systems Inc.®), which allowed visual observation of the reaction mixture. A 260 Dual Syringe Pump System (Teledyne ISCO®) was used to handle the CO_2 and bring it to supercritical conditions. The reactor was charged with monomer, initiator, RAFT agent and stabilizer and a magnetic stirrer bar. Then, it was purged with a slow flow of CO_2, and pressurized with CO_2 until a given pressure, lower than the desired reaction pressure. Next, the reactor was placed into a warm bath, and heated to the desired reaction temperature. Once this temperature was reached and controlled, pressure was increased to the desired reaction pressure by loading additional CO_2. The reaction mixture was stirred using a magnetic bar. The reaction proceeded until the desired time was reached. The product was washed with methanol, and then dried at 50 °C in an oven until constant weight. Total monomer conversion was determined gravimetrically.

2.4. Polymer characterization

Monomer conversion was measured gravimetrically. Molecular weight development (M_n and M_w) was followed by size exclusion chromatography (SEC or GPC) using a Waters Alliance 2695 chromatograph. The GPC was equipped with a Shodex column bank, from KF-801 to KF-804, Waters 2414 refractive index, Waters 2996 PDA, and Viscotek 270D intrinsic viscosity detectors. Polystyrene standards from Polymer Standards Service Inc., ranging from $M_n = 392$ to 3 151 000 Da were used.

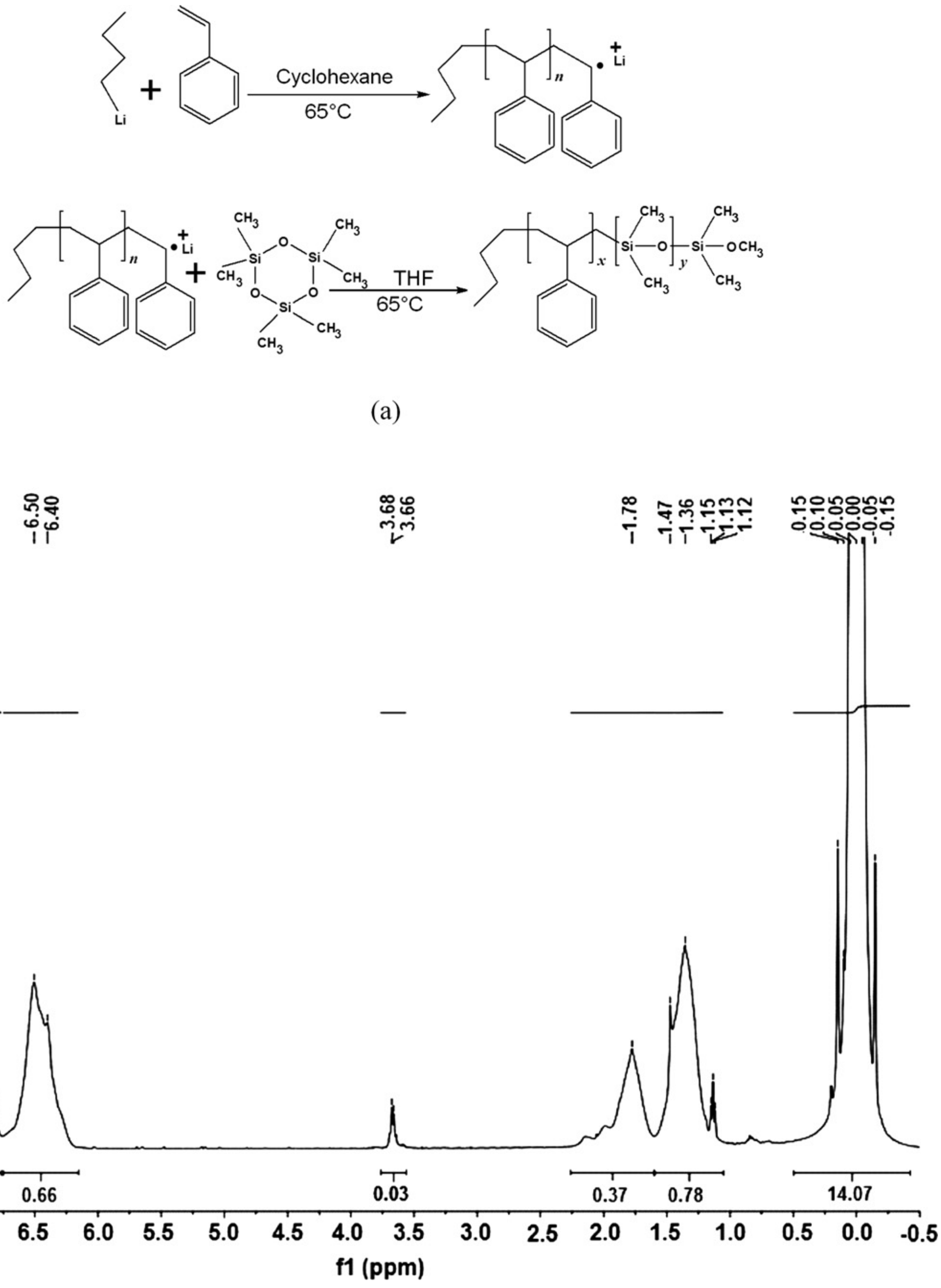

Fig. 2. Poly(styrene-b-dimethylsiloxane) used in this study as stabilizer: (a) scheme of synthesis, (b) characterization by ^{1}H NMR.

3. Results and discussion

Three studies were considered in this paper. The first study was focused on the effect of stabilizer initial concentration on polymerization rate (PR) and molecular weight development (MW-Dev) in RAFT polymerization of styrene in $scCO_2$. The concentration of PSDMS where best performance in terms of PR and MW-Dev was observed was used for the other two studies. In the second study, the effect of the structure of the RAFT controller (groups Z and R of the RAFT controller typical structure) was analyzed. Finally, once an adequate stabilizer concentration level, and the most adequate RAFT controller were chosen, in the third study the effect of the RAFT/Initiator molar ratio on PR and MD-Dev was assessed.

In all the experiments of the three studies described above, the mass of monomer was 8 g, the ratio of mass of monomer to total reaction volume was 20 wt./v%, $T = 80\,^{\circ}C$, $P = 300$ bar, and the speed of agitation was 500 rpm.

3.1. Effect of stabilizer concentration

It is well known that dispersion polymerizations require the use of effective stabilizers to form stable particles and proceed up to high conversions. The stabilizer used in this study, PSDMS, contained a CO_2-phylic block and a CO_2-phobic one, but it was necessary to determine the most adequate concentration level for the specific system studied in this paper. It is important to know the optimal stabilizer concentration, not only to avoid wasting it, but also to prevent some undesirable steric effects that may interfere with the mass transport between the phases, or adversely affect particle morphology, if the concentration is too high. The study

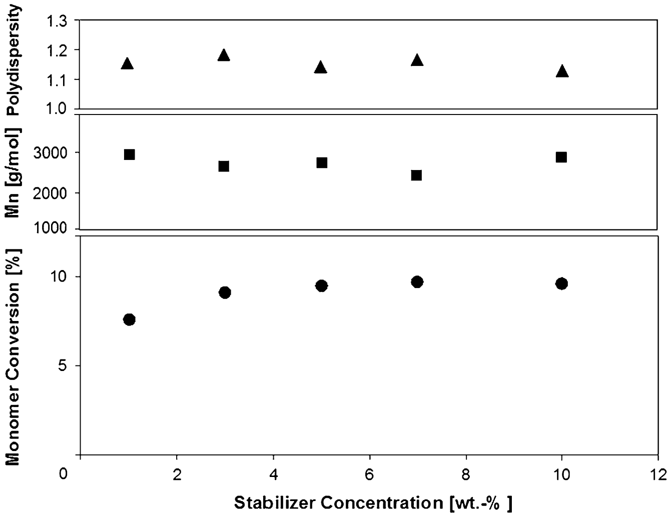

Fig. 3. Effect of stabilizer initial concentration on monomer conversion, number average molecular weight, M_n, and polydispersity in RAFT polymerization of styrene in $scCO_2$, with $T = 80\ ^\circ C$, and $P = 300$ bar.

about stabilizer concentration was carried out using RAFT A, since preliminary runs established that this controller was more effective than RAFT D. RAFT controllers A and D were readily available, since they are commercially available chemicals. In order to determine the adequate stabilizer concentration for our polymerization system, five experiments were carried out. These experiments were conducted using 8 g of styrene. The concentrations of AIBN and RAFT A were 0.0064 and 0.0128 M, respectively. The concentration of PSDMS was varied from 1 to 10 wt.%. The polymerizations in the five runs were stopped at 8 h.

It is observed in Fig. 3 that monomer conversion at 8 h of polymerization increases as the concentration of PSDMS is increased, up to a limiting value of around 6 wt.%, remaining almost constant thereafter. However, there is not much variation on the value of monomer conversion achieved in the range 3–10 wt.% of stabilizer. In the case of number average molecular weight, M_n, there seems to be no effect of stabilizer concentration since M_n remains almost constant. The polydispersity index (PDI) remains below 1.2 in all the range of stabilizer concentrations studied. These results already suggest that RAFT A may be adequate for controlled styrene polymerization in $scCO_2$. This will be analyzed in further detail in the following section of this paper.

3.2. *Effect of RAFT controller structure*

As mentioned before, four different RAFT controllers were compared in this study. The names and chemical structures of the controllers used are provided in Fig. 1. A comparison of the monomer conversions reached at 8 h of polymerization time, among the four RAFT controllers and the blank (without controller)

Table 1
Summary of results for the comparison of RAFT controllers.[a]

RAFT	STY Conversion [%]	M_n	PDI
A	9.1	2648	1.18
B	17	2537	1.30
C	20	5996	1.40
D	33	14 734	1.96
0	37.1	22 858	3.80

[a] The experiments were conducted using 8 g of Styrene; $[AIBN]_0$ and $[RAFT]_0$ were 0.0064 and 0.0128 M, respectively, $[PSDMS]_0 = 3$ wt.%. $T = 80\ ^\circ C$, $P = 300$ bar and 8 h of reaction time. RAFT 0 represents a blank experiment without RAFT agent.

Table 2
Comparison between a non-controlled polymerization system (RAFT 0) and polymerizations in the presence of RAFT D.[a]

RAFT	Reaction time [h]	STY conversion [%]	M_n	PDI
D	4	15	10 340	2.50
D	16	55	132 690	2.50
D	24	68	283 020	2.70
0	4	20	15 540	4.50
0	16	63	703 80	4.00
0	24	75	93 670	4.10

[a] The experiments were conducted using 8 g of Styrene; $[AIBN]_0$ and $[RAFT]_0$ were 0.0064 and 0.0128 M, respectively, $[PSDMS]_0$ 3 wt.%. $T = 80\ ^\circ C$, $P = 300$ bar.

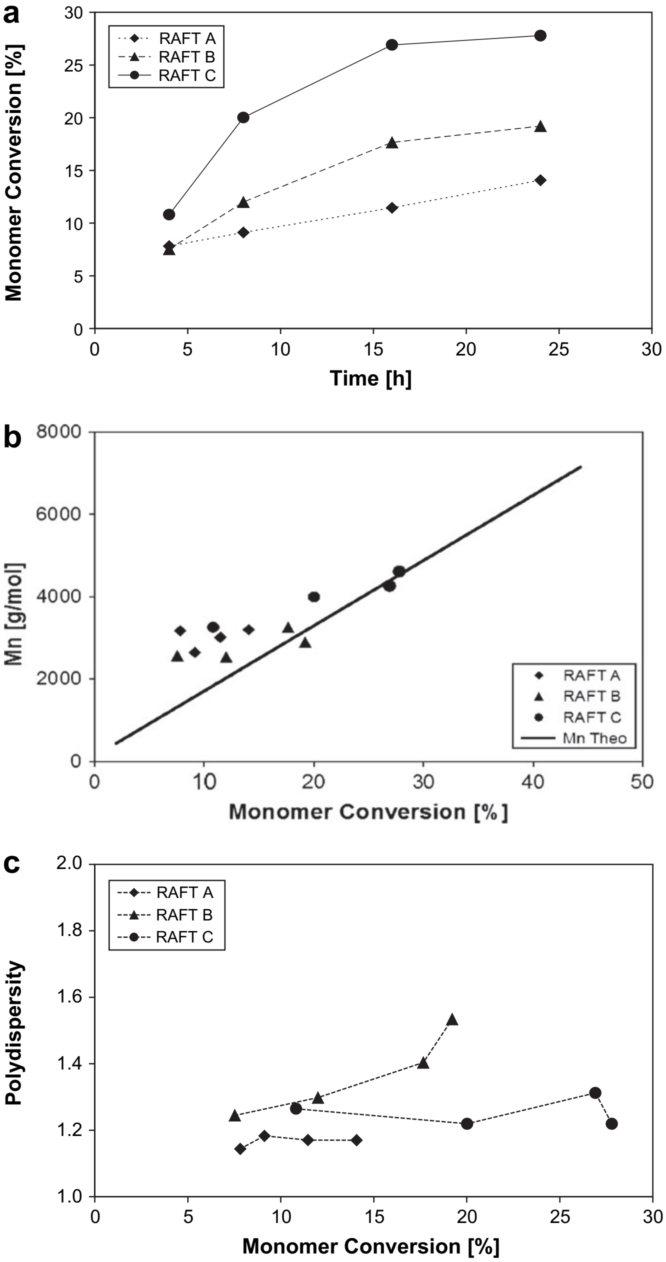

Fig. 4. Effect of the structure of the RAFT agent on: (a) monomer conversion versus time, (b) M_n versus monomer conversion, and (c) Polydispersity versus monomer conversion, in polymerization of styrene in $scCO_2$. $[AIBN]_0$ and $[RAFT]_0$ were 0.0064 and 0.0128 M, respectively; $[PSDMS]_0 = 3$ wt.%, $T = 80\ ^\circ C$, and $P = 300$ bar.

run, is shown in Table 1. As expected, the conversion reached in the blank run is the highest (around 38%). The conversion achieved with RAFT D was quite close to the conversion obtained in the blank run (around 33%). The slowest polymerization was that using RAFT A (9%). The conversions reached with controllers RAFT B and RAFT C, lied in between the other two.

Additional results at different polymerization times for the cases without controller (blank) and with RAFT D are shown in Table 2. These additional results confirm that the polydispersities obtained with RAFT D are quite high. That is why this controller was excluded from the remaining studies reported in this paper.

Once RAFT D, which was a dithiocarbamate compound, had been disregarded as controller for the polymerization of styrene in $scCO_2$, a kinetic study comparing the performance of the other three controllers was carried out. The results are shown in Fig. 4. It is observed in Fig. 4a that the fastest polymerization rate is achieved with RAFT C. The slowest polymerization rate was obtained with RAFT A, and the runs using RAFT B lied in between the other two. There does not seem to be much difference in the measured values of M_n obtained with the three controllers, as observed in Fig. 4b. There is a linear trend in the M_n versus conversion profile, but the profile does not start from the origin, which suggests that the system is not controlled at the beginning of the polymerization. The theoretical M_n profile shown in Fig. 4b was calculated as $M_{n,\text{theo}} = (([\text{Monomer}]_o - [\text{Monomer}]_t)/[\text{RAFT}]_o)\text{MW}_{\text{Monomer}}$ [34]. The PDIs are lower than 1.2 for RAFT A and around 1.3 for most of the data points of the other two controllers.

From the four controllers tested, RAFT D did not provide an adequate control level. Dithiocarbamates with similar structures such as S-benzyl *N*,*N*-diethyldithiocarbamate and S-(2-cyanopropyl) *N*,*N*-dimethyldithiocarbamate have been reported to be ineffective as RAFT controllers for bulk polymerization of styrene [35]. It is also known that the fragmentation of *N*,*N*-dialkylderivatives is difficult due to the delocalization of the radical obtained from free radical addition to the dithiocarbamate group by the nitrogen free electrons, whereas an electron-withdrawing substituent on the nitrogen would not be able to delocalize the isolated electron, and would allow fragmentation. Thus, by a change in the nitrogen substituent, the activity of dithiocarbamates can be substantially modified, and they can become very effective RAFT controllers [30–33,35]. Dithiocarbamate derivatives which have the nonbonded electron pair on the nitrogen atom included as part of an aromatic system are known to be effective RAFT controllers. Examples of such dithiocarbamates are those derived from pyrrole [36,37] and imidazole [38].

RAFT A produced the slowest polymerization rate, but it provided the best control level, and also, it had the advantage of being commercially available. RAFT B and C provided faster polymerization rates than RAFT A, and the control level achieved with them was good, but they are more expensive. The differences in performance among these three controllers can be understood by taking into consideration their chemical structures. The three controllers are dithiobenzoates. The main difference among them is the structure of the R group from the RAFT molecule (for a representation of the typical RAFT structure, refer, for instance, to Fig. 6 of Moad et al. [8]). The Z group is the same, a benzyl group. The R group will be released from the RAFT molecule, as a free radical, after the formation of the double bond, C═S, between the thiocarbonyl group and the S atom to which the R group is bonded. At this point, the solubility in $scCO_2$ of the R group is important since the locus for the initiation of new propagating chains depends on it. If chain initiation derived from the release of the R group takes place in the continuous phase, the propagating chain will grow until a critical chain length is reached, and a new particle stabilized by PSDMS is formed. The solubility in $scCO_2$ of the RAFT agent determines the phase in which the controller will be placed until the addition–fragmentation reaction takes place. The solubility of the RAFT agent may be determined by the Z group. In this study,

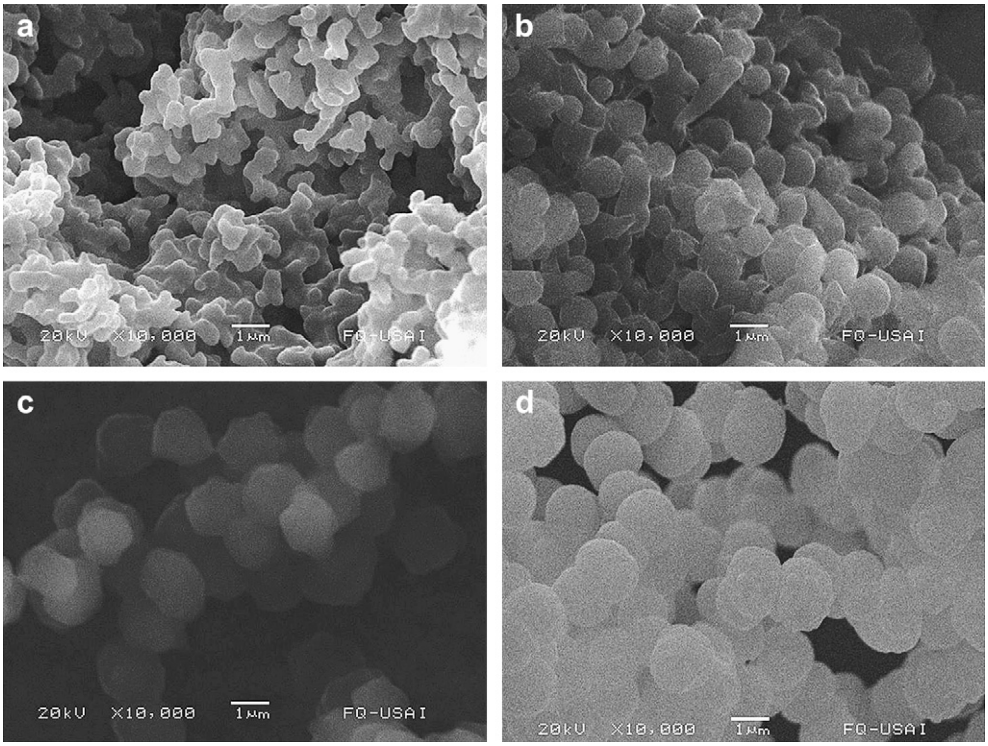

Fig. 5. Scanning electron microscopy (SEM) images of typical particles produced in RAFT polymerization of styrene in $scCO_2$. Experimental conditions: 8 g of styrene; $[\text{AIBN}]_0 = 0.0064$ M, $[\text{RAFT A}]_0 = 0.0128$ M, $[\text{PSDMS}]_0 = 3$ wt.%, $T = 80$ °C, and $P = 300$ bar. Reaction times: (a) 4 h, (b) 24 h, (c) 48 h, and (d) 72 h.

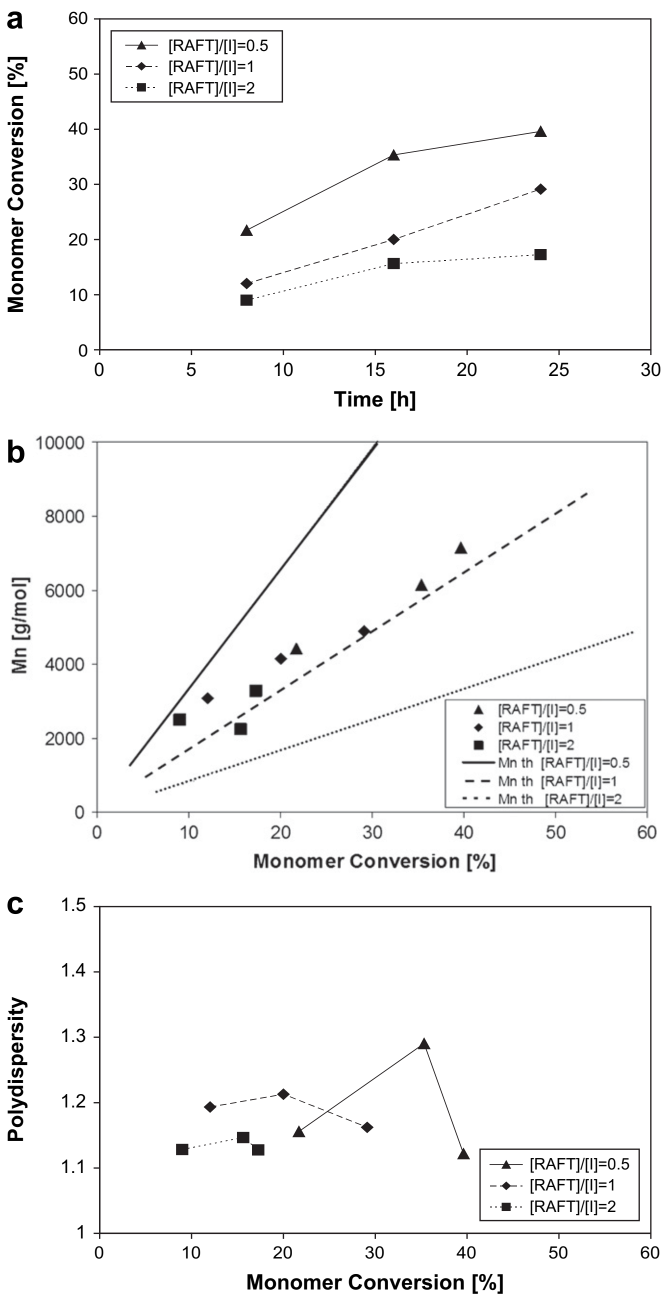

Fig. 6. Effect of the RAFT/Initiator molar ratio on: (a) monomer conversion versus time, (b) M_n versus monomer conversion, and (c) polydispersity versus monomer conversion.

because of the structure of the Z group of the dithiocompounds used as controllers, it was expected that the RAFT agents would be soluble in the dispersed phase. This was confirmed by the fact that a dispersed phase was produced early on during the polymerization and that good control (manifested as low PDIs) was achieved.

SEM images for styrene polymerization using RAFT A at different times (4, 24, 48 and 72 h) are shown in Fig. 5. It is observed that small particles but partially agglomerated are produced at low conversions (see Fig. 5a). As polymerization proceeds, the particles grow in size, but surprisingly the level of agglomeration is reduced, until well defined spherical particles are produced at 72 h of polymerization (see the progression from Fig. 5a–d). These results are not straightforward to explain. They are the result of several phenomena such as rather poor mixing, increasing viscosity of the particles as polymerization proceeds, and effectiveness of the stabilizer, taking place simultaneously. Although an increasing viscosity would promote higher rate of agglomeration, the action of the stabilizer reduces the effectiveness of coalescence, until rather hard particles are produced.

3.3. *Effect of RAFT controller concentration ($[RAFT]_o/[I]_o$)*

For this study the concentration of AIBN was kept constant (0.0128 M), the concentration of the RAFT agent (RAFT A) was varied ($[RAFT]_0/[I]_0 = 2$, 1, 0.5), $[PSDMS]_0 = 3$ wt.%, $T = 80\,°C$, and $P = 300$ bar.

It is observed in Fig. 6a that the polymerization rate is decreased as the amount of controller is increased. The amount of RAFT agent does not affect the evolution of the M_n versus conversion profile (see Fig. 6b), but it is clearly observed that better control (manifested as lower PDIs) is obtained if the ratio RAFT/Initiator is increased, as shown in Fig. 6c. All these results are consistent with the known behavior of RAFT polymerization systems. Moreover, these results suggest that the addition-fragmentation steps of the RAFT polymerization mechanism take place in the dispersed phase. Otherwise, the degree of control would have been poor, if the controller had remained in the continuous phase.

4. Concluding remarks

An experimental study on the polymerization of styrene in $scCO_2$ using PSDMS as stabilizer, AIBN as initiator, and of S-thiobenzoyl thioglycolic acid (RAFT A), Methyl naphthalene dithiobenzoate (RAFT B), 4-Methyl allyl dithiobenzoate (RAFT C), and *N*,*N*-Dimethyl benzyl dithiocarbamate (RAFT D) as controllers was carried out. PSDMS in the concentration range 3–7 wt.% worked fine as stabilizer. Spherical particles in the 1 μm range were produced. Three of the controllers (RAFTs A, B, and C) performed well as controllers, but RAFT A turned out to be the most attractive since it provided good control to the polymerization, and it is commercially available. However, as with most RAFT controlled polymerizations, the presence of the controller reduces polymerization rate.

The results obtained suggest that the addition and fragmentation reactions proceeded in the dispersed phase, mainly, which was the intended situation.

Acknowledgements

Financial support from the National Council for Science and Technology of México (CONACYT) (Projects IAMC U40259-Y and 101682, as well as Ph.D. scholarships to P.R.G.-M. and G.J.-S.), and DGAPA-UNAM (Projects PAPIIT IN104107 and IN119510), is gratefully acknowledged. The assistance from Mr. Ivan Puente-Lee (UNAM, México) with the SEM studies is also acknowledged.

References

[1] Matyjaszewski K. Comparison and classification of controlled/living radical polymerization. ACS Symposium Series No. 768. In: Matyjaszewski K, editor. Controlled/living radical polymerization. Progress in ATRP, NMP and RAFT. Washington, DC: American Chemical Society; 2000. p. 2–26.
[2] Cunningham M. Prog Polym Sci 2002;27:1039–67.
[3] Qiu J, Charleux B, Matyjaszewski K. Prog Polym Sci 2001;26:2083–134.
[4] Fukuda T, Goto A. Kinetics of living radical polymerization. ACS Symposium Series No. 768. In: Matyjaszewski K, editor. Controlled/living radical polymerization. Progress en ATRP, NMP and RAFT. Washington, DC: American Chemical Society; 2000. p. 27–39.
[5] Graeme M, Rizzardo E, Thang SH. Aust J Chem 2006;59:669–92.
[6] Braunecker WA, Matyjaszewski K. Prog Polym Sci 2007;32:93–146.

[7] Moad G, Mayadunne RTA, Rizzardo E, Skidmore M, Thang SH. Kinetics and mechanism of RAFT polymerization. ACS Symposium Series No. 854. In: Matyjaszewski K, editor. Advances in controlled/living radical polymerization, vol. 854. Washington, DC: American Chemical Society; 2003. p. 520.
[8] Moad G, Rizzardo E, Thang SH. Aust J Chem 2005;58:379.
[9] Young JL, DeSimone JM. Pure Appl Chem 2000;72(7):1357–63.
[10] Span R, Wagner W. J Phys Chem Ref Data 1996;25(6):1509–96.
[11] Kendall JL, Canelas DA, Young JL, DeSimone JM. Chem Rev 1999;99:543–63.
[12] Eckert CA, Knutson BL, Debenedetti PG. Nature 1996;373:313.
[13] Leitner W. Nature 2000;405:129.
[14] Canelas DA, DeSimone JM. Adv Polym Sci 1997;133:103.
[15] Cooper AI. J Mater Chem 2000;10:207.
[16] Sarbu T, Styranec T, Beckman EJ. Nature 2000;405:165.
[17] Charpentier PA, Kennedy KA, DeSimone JM, Roberts GW. Macromolecules 1999;32:5973.
[18] Ahmed TS, DeSimone JM, Roberts GW. Macromolecules 2006;39:15.
[19] Liu T, DeSimone JM, Roberts GW. J Polym Sci Polym Chem 2005;43:2546.
[20] Liu T, DeSimone JM, Roberts GW. Polymer 2006;47:4276.
[21] Liu T, Garner P, DeSimone JM, Roberts GW, Bothun GD. Macromolecules 2006;39:6489.
[22] Ahmed TS, DeSimone JM, Roberts GW. Macromolecules 2007;40:9322.
[23] Hsiao Y, Maury E, DeSimone JM, Mawson SM, Johnston KP. Macromolecules 1995;28:8159–66.
[24] Hsiao Y, DeSimone JM. Polym Prep 1995;36:190–1.
[25] Hsiao Y, DeSimone JM. Polym Prep 1996;74:260.
[26] Arita T, Beuermann S, Buback M, Vana P. e-Polymer 2004;003:1–13.
[27] Arita T, Beuermann S, Buback M, Vana P. Macromol Mater Eng 2005;290:283–93.
[28] Thurecht KJ, Gregory AM, Wang W, Howdle SM. Macromolecules 2007;40:2965–7.
[29] Gregory AM, Thurecht KJ, Howdle SM. Macromolecules 2008;41:1215–22.
[30] Smith SD, DeSimone JM, Huang H, York G, Dwight DW, Wilkes GL, et al. Macromolecules 1992;25:2575.
[31] Zilliox JG, Roovers JEL, Bywaters S. Macromolecules 1975;8:573.
[32] Saam JC, Gordon DJ, Lindsey S. Macromolecules 1970;3:1.
[33] Flory PJ, Semlyen JA. J Am Chem Soc 1966;88:3209.
[34] Moad G, Rizzardo E, Thang SH. Aust J Chem 2006;59(10):669–92.
[35] Mayadunne RTA, Rizzardo E, Chiefari J, Chong YK, Moad G, Thang SH. Macromolecules 1999;32:6977–80.
[36] Hua D, Bai R, Lu W, Pan C. J Polym Sci Polym Chem 2004;42:5670–7.
[37] Zhou D, Zhu X, Zhu J, Yin H. J Polym Sci Polym Chem 2005;43:4849–56.
[38] Moad G, Chiefari J, Krstina J, Postma A, Mayadunne RTA, Rizzardo E, et al. Polym Int 2000;49:993–1001.