

Reversible Addition–Fragmentation Chain Transfer Polymerization of Styrene with Benzoimidazole Dithiocarbamate as a Reversible Addition–Fragmentation Chain Transfer Agent

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Received 14 November 2004; accepted 22 July 2005

DOI 10.1002/app.23330

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Two novel dithiocarbamates [2-Y-benzoimidazole-1-carbodithioic acid benzyl esters: Y = methyl (**1b**) or phenyl (**1c**)] were synthesized and successfully used in the reversible addition–fragmentation chain transfer (RAFT) polymerization of styrene in bulk with thermal initiation. The effects of the temperatures and concentration ratios of the styrene and RAFT agents on the polymerization were investigated. The results showed that the polymerization of styrene could be well controlled in the presence of **1b** or **1c**. The linear relationships between $\ln([M]_0/[M])$ and the polymerization time (where $[M]_0$ is the initial monomer concentration and $[M]$ is the monomer concentration) indicated that

the polymerizations were first-order reactions with respect to the monomer concentration. The molecular weights increased linearly with the monomer conversion and were close to the theoretical values. The molecular weight distributions [weight-average molecular weight/number-average molecular weight (M_w/M_n)] were very narrow from 5.3% conversion up to 94% conversion ($M_w/M_n < 1.3$). © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 560–564, 2006

Key words: living polymerization; reversible addition fragmentation chain transfer (RAFT)

INTRODUCTION

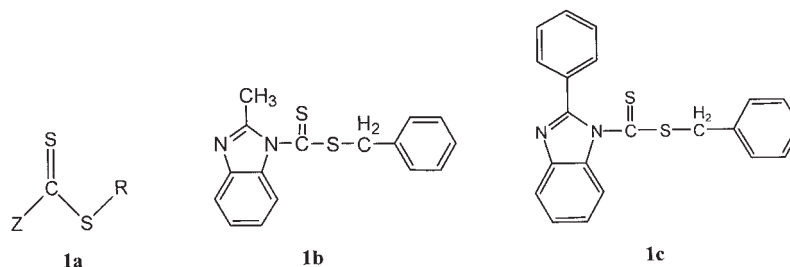
In recent years, considerable effort^{1–7} has been expended to develop free-radical polymerizations that display the essential characteristics of living polymerizations. Several processes have been reported, such as stable free polymerization,⁶ atom transfer radical polymerization,^{2–5} and reversible addition–fragmentation chain transfer (RAFT) polymerization.^{7,8} RAFT polymerization is the youngest of these new methods and appears the most versatile. The RAFT process is a polymerization in the presence of a RAFT agent [$Z-C(=S)-R$] that reacts by a series of reversible addition–fragmentation steps. There are four classes of thiocarbonylthio RAFT agents, depending on the nature of the Z group: dithioesters (Z is aryl or alkyl), trithiocarbonates (Z is substituted sulfur), dithiocarbonates (xanthates; Z is substituted oxygen), and dithiocarbamates (Z is substituted nitrogen). Dithiocar-

bamates are not only photoiniferters⁹ but also RAFT agents.¹⁰ The efficiency of dithiocarbamates in the control of polymerization depends on the molecular structure of the dithiocarbamates. Rizzardo and co-workers^{10,11} found that the electron-withdrawing groups on the nitrogen atom of dithiocarbamates can significantly enhance the activity of dithiocarbamates. Destarac et al.¹² found the key parameter for the control of the radical polymerization of acrylates, styrene (St), and vinyl acetate with novel dithiocarbamates, *N,N*-disubstituted or cyclic dithiocarbamates, as RAFT agents to be the conjugation of the lone pair of electrons of the nitrogen atom with carbonyl or aromatic groups. Recently, Pan et al.¹³ reported the free-radical polymerizations of methyl acrylate under γ -ray irradiation in the presence of dithiocarbamates with different N groups. The results indicated that the conjugation structure of the N group of the dithiocarbamates played an important role in living free-radical polymerization. However, the mechanism of the γ -ray-irradiation living free-radical polymerization has been under debate.^{13,14} In this work, we synthesized two novel dithiocarbamates [2-Y-benzoimidazole-1-carbodithioic acid benzyl esters: Y = methyl (**1b**) or phenyl (**1c**); Scheme 1] and used them as RAFT agents in the thermally initiated RAFT polymerization of St to examine the effectiveness for the controlled

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Contract grant sponsor: Science and Technology Development Planning of Jiangsu Province; contract grant number: BG2004018.

Contract grant sponsor: Suzhou City; contract grant numbers: SG0413 and SSZ0419.



Scheme 1

polymerization of St and the effect of the dithiocarbamate structure on the polymerization.

EXPERIMENTAL

Materials

Dimethyl sulfoxide (analytical reagent; Shanghai Wulian Chemicals Co., Ltd., Shanghai, China) was purified by vacuum distillation over anhydrous CaH_2 . St (analytical reagent; Shanghai Chemical Reagent Co., Ltd., Shanghai, China) was washed with an aqueous solution of sodium hydroxide (5 wt %) three times and then with deionized water until neutralization. After being dried with anhydrous magnesium sulfate, the monomer was distilled twice under reduced pressure before use. Tetrahydrofuran (THF; analytical reagent; Jiangsu Yangyuan Chemical Factory, Changshu, China), 2-methyl-benzimidazole (98%, Acros Organics, Fairlawn, NJ), 2-phenyl-benzimidazole (97%, Acros Organics), NaH (60%, powder, Merck-Schuchardt, Germany), and benzyl bromide (chemically pure; Shanghai Chemical Reagent) were used as received.

Synthesis and polymerization

Synthesis

The general procedure for the synthesis of dithioesters **1b** and **1c** was according to the literature.¹⁵ Pure **1b** was obtained as an orange oil, and the purity was greater than 99% [high-performance liquid chromatography (HPLC); 515, Waters]. Pure **1c** was obtained as a yellow powder, and the purity was greater than 98% (HPLC; 515, Waters).

Polymerization

The typical procedures were as follows. A master batch solution of 12 mL (105 mmol) of St and 62.1 mg (0.21 mmol) of **1b** was prepared, and aliquots of 1 mL were placed in polymerization ampoules. The content was purged with argon to eliminate oxygen for approximately 10 min. Then, the ampoules were flame-sealed. The polymerization reaction was performed at the appropriate temperature. At the end of the reac-

tion, each ampoule was quenched in ice water and opened. The reaction mixture was diluted with 2 mL of THF and precipitated in 250 mL of methanol. The polymer was filtered and dried at room temperature *in vacuo* until a constant weight. The conversion of the polymer was determined gravimetrically.

Characterization

The number-average molecular weights (M_n 's) and molecular weight distributions [weight-average molecular weight/number-average molecular weight (M_w/M_n)] of the polymers were determined with a Waters 1515 gel permeation chromatographer. The gel permeation chromatography (GPC) equipment was equipped with a refractive-index detector operated at 30°C with HR 1, HR 3, and HR 4 columns with a molecular weight range of 100–500,000, which was calibrated with polystyrene (PS) standard samples. THF was used as the eluent at a flow rate of 1.0 mL/min. $^1\text{H-NMR}$ spectra of the polymers were recorded on an Inova 400-MHz NMR instrument with CDCl_3 as the solvent and tetramethylsilane as the internal standard.

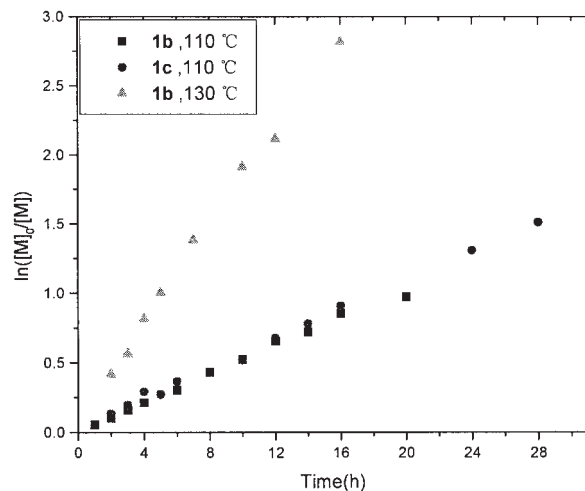


Figure 1 Kinetic plots of the polymerization of St in the presence of **1b** and **1c** ($[\text{St}]_0/[\text{RAFT agent}]_0 = 500:1$).

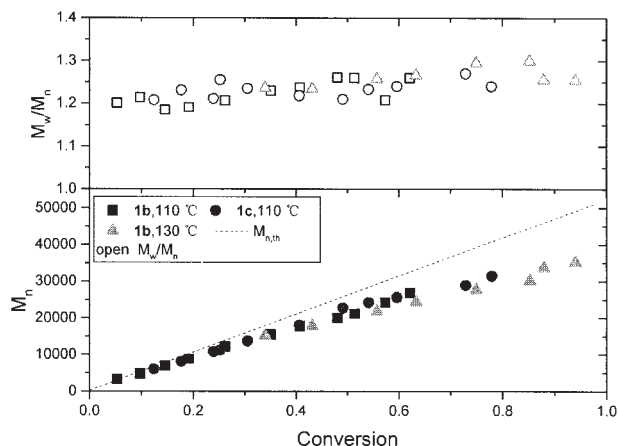


Figure 2 M_n and M_w/M_n versus the conversion for the polymerizations of St in the presence of **1b** and **1c** ($[St]_0/[RAFT\ agent]_0 = 500 : 1$).

RESULTS AND DISCUSSION

Living polymerization character

The RAFT polymerizations of St were carried out with **1b** and **1c** as RAFT agents with thermal initiation in bulk with the $[St]_0/[RAFT\ agent]_0$ molar ratio of 500:1 at 110 and 130 °C, respectively (where $[St]_0$ and $[RAFT\ agent]_0$ are the initial concentrations of St and the RAFT agent, respectively). The kinetic plots of $\ln([M]_0/[M])$ versus the polymerization time (where $[M]_0$ is the initial monomer concentration and $[M]$ is the monomer concentration) are shown in Figure 1. The linear relationships between $\ln([M]_0/[M])$ and the polymerization time indicated that the polymerizations were first-order reactions with respect to the monomer concentration and that the number of radicals remained constant during the polymerizations of St with thermal initiation. Figure 1 also shows that there was no inhibition period in the polymerization in all cases. The rate of polymerization for **1b** was almost the same as that of **1c** at the same polymeriza-

tion temperature and increased with increasing polymerization temperature. The M_n and M_w/M_n values are shown in Figure 2. The molecular weights increased linearly with the monomer conversion and were lower than the theoretical number-average molecular weights ($M_{n,th}$'s) at high conversions; this indicated some side reactions of chain transfer. The $M_{n,th}$ values were calculated with the following equation:

$$M_{n,th} = \frac{[St]_0}{[RAFT\ agent]_0} \times \text{Conversion} \times M_{\text{styrene}} + M_{\text{RAFTagent}}$$

where M_{styrene} and $M_{\text{RAFTagent}}$ are the molecular weights of St and the RAFT agent, respectively. The M_w/M_n values were very narrow from a 5.3% conversion up to a 94% conversion ($M_w/M_n < 1.3$). All the results showed that the two novel dithiocarbamates, **1b** and **1c**, were effective RAFT agents for the RAFT polymerization of St, and the substitution group of methyl or phenyl on this dithiocarbamate had no obvious effects on the effectiveness of controlled polymerization.

Effect of the $[St]_0/[RAFT\ agent]_0$ ratio

The polymerizations of St were carried out in bulk with different $[St]_0/[RAFT\ agent]_0$ molar ratios to examine their effect on the RAFT polymerization of St. The results are shown in Table I. When the $[St]_0/[RAFT\ agent]_0$ ratio changed from 200 : 1 to 800 : 1, no obvious effects of the ratio on M_w/M_n were observed. The agreement between $M_{n,GPC}$ and $M_{n,th}$ was good at a higher concentration of the RAFT agent ($[St]_0/[RAFT\ agent]_0 = 200 : 1$). The M_w/M_n values were very narrow in all cases ($M_w/M_n = 1.17\text{--}1.29$). However, the polymerization rates at a high RAFT agent concentration, such as $[St]_0/[RAFT\ agent]_0 = 200 : 1$, was lower than those with the 500 : 1 and 800 : 1 ratios. The polymerization showed slight retardation.¹⁶ Davis and coworkers^{17–19} reported that the retar-

TABLE I
Polymerization Results of St at Different $[St]_0/[RAFT\ agent]_0$ Ratios at 110 °C

RAFT	$[St]_0/[RAFT\ agent]_0$	Time (h)	$M_{n,th}$	$M_{n,GPC}$	M_w/M_n	Conversion
1b	200 : 1	4	3,300	3,300	1.18	0.14
		10	7,600	6,700	1.19	0.35
	500 : 1	4	10,300	8,800	1.19	0.19
		10	21,200	17,800	1.24	0.41
	800 : 1	4	16,000	14,600	1.21	0.19
		10	35,000	27,000	1.28	0.42
1c	200 : 1	4	3,700	3,600	1.17	0.16
		10	8,000	7,000	1.19	0.37
	500 : 1	4	13,200	11,200	1.26	0.25
		10	21,200	18,000	1.22	0.40

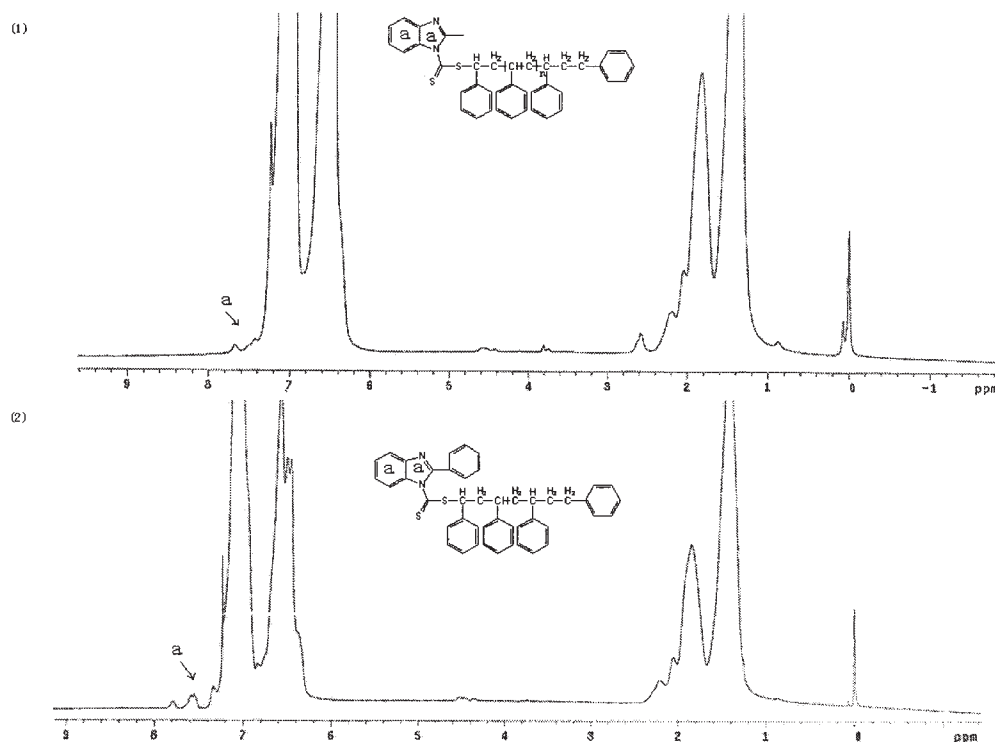


Figure 3 $^1\text{H-NMR}$ spectra of (1) PS ($M_n = 8500$, $M_w/M_n = 1.19$) with **1b** as the RAFT agent and (2) PS ($M_n = 7600$, $M_w/M_n = 1.21$) with **1c** as the RAFT agent.

dation in the RAFT polymerization was caused by the low fragmentation rate of the mediate radical. The magnitude of the retardation present in the RAFT polymerization of St was closely associated with the stability of the macro-RAFT radical, that is, its average lifetime. Monteiro and de Brouwer²⁰ offered an alternative explanation for the retardation effect in RAFT polymerization. These authors assumed that the macro-RAFT radical can undergo self-termination and termination with free macroradicals, thus slowing the rate of polymerization at enhanced levels of the initial RAFT agent.

End-group analysis and chain-extension reaction

The $^1\text{H-NMR}$ spectrum of the polymers prepared with **1b** and **1c** as RAFT agents with thermal initiation were used to obtain qualitative information on the polymer end group. Typical spectra of PS ($M_n = 3300$, $M_w/M_n = 1.20$) with **1b** as the RAFT agent and PS ($M_n = 8100$, $M_w/M_n = 1.23$) with **1c** as the RAFT agent are shown in Figure 3. The signals at $\delta = 7.4\text{--}7.8$ ppm correspond to the aromatic protons of **1b** units [Fig. 3(1)], and the signals at $\delta = 7.3\text{--}7.9$ ppm correspond to the aromatic protons of **1c** units [Fig. 3(2)]. The spectra indicate that the moiety of the RAFT agent was attached to the end of PS.

An additional way of verifying the functionality of a polymer is the chain-extension reaction. Therefore, PS capped with the RAFT moiety was used as a macro-RAFT agent to carry out the chain-extension reaction.

A typical chain-extension reaction was carried out with the addition of fresh St monomer with PS as the macro-RAFT agent ($[\text{St}]_0/[\text{macro-RAFT}]_0 = 500:1$) at 110°C for 5 h. The GPC curves of the original and extended polymer are shown in Figure 4. There was an obvious peak shift from the macro-RAFT agent to the product, and the molecular weight increased from 6900 to 25,000 (Fig. 4; **1b**) and from 11,200 to 31,600 (Fig. 4; **1c**). The peak of the original polymer disappeared, and this demonstrated that the macro-RAFT agent converted to the product. However, the molecular weight distribution of the chain-extension product was broader than before, and this may have been caused by the small amount of homopolymerization of St and the dead polymer existing in the original polymer.^{21,22} This evidence supported the idea that the RAFT polymerization of St with **1b** or **1c** as a RAFT agent under thermal initiation was well controlled and was consistent with the RAFT mechanism.

CONCLUSIONS

Two novel dithiocarbamates, **1b** and **1c**, were effective RAFT agents for the RAFT polymerization of St, and the substitution group of methyl or phenyl on these dithiocarbamates had no obvious effects on the effectiveness of controlled polymerization. The results showed that the polymerization of St could be well controlled in the presence of **1b** and **1c**. The molecular

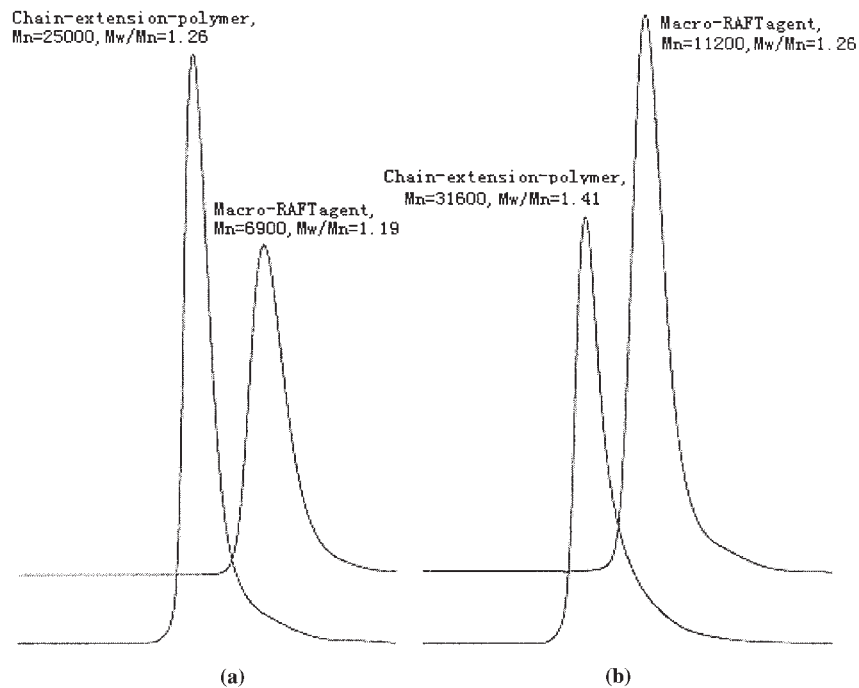


Figure 4 GPC curves of the chain-extension reaction ($[St]_0/[macro-RAFT]_0 = 500:1$, temperature = 110°C): (a) macro-RAFT agent **1b** and (b) macro-RAFT agent **1c**.

weights increased linearly with the monomer conversion and were close to the theoretical values. The M_w/M_n values were very narrow from a 5.3% conversion up to a 94% conversion ($M_w/M_n < 1.3$).

References

- Otsu, T.; Yoshida, M. *Macromol Chem Rapid Commun* 1982, 3, 127.
- Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* 1995, 28, 1721.
- Wang, J. S.; Matyjaszewski, K. *Macromolecules* 1995, 28, 7901.
- Wang, J. S.; Matyjaszewski, K. *J Am Chem Soc* 1995, 117, 5614.
- Percec, V.; Narboiu, B. *Macromolecules* 1995, 28, 7970.
- Georges, M. K.; Veregin, P. R. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* 1993, 26, 2987.
- Chiefari, J.; Chong, Y. K.; Ercole, F.; Kristina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* 1998, 31, 5559.
- Le, T. P.; Moad, G.; Rizzardo, E.; Thang, S. H. *PCT Int. Pat. Appl. WO 9801478 A1* (1998).
- Otsu, T.; Matsunaga, T.; Doi, T.; Matsumoto, A. *Eur Polym Mater* 1995, 31, 67.
- Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Moad, G.; Thang, S. H. *Macromolecules* 1999, 32, 6977.
- Chiefari, J.; Mayadunne, R. T. A.; Moad, C. L.; Moad, G.; Rizzardo, E.; Postma, A.; Skidmore, M. A.; Thang, S. H. *Macromolecules* 2003, 36, 2273.
- Destarac, M.; Charmot, D.; Franck, X.; Zard, S. Z. *Macromol Rapid Commun* 2000, 21, 1035.
- Hua, D.; Bai, R.; Lu, W.; Pan, C. *J Polym Sci Part A: Polym Chem* 2004, 42, 5670.
- Quinn, J. F.; Earner, L.; Davis, T. P.; Thang, S. H.; Rizzardo, E. *Macromol Rapid Commun* 2002, 23, 717.
- Schilli, C.; Lanzendörfer, M. G.; Müller, A. X. E. *Macromolecules* 2002, 35, 6819.
- Feldermann, A.; Coote, M. L.; Stenzel, M. H.; Davis, T. P.; Barner-Kowollik, C. *J Am Chem Soc* 2004, 126, 15916.
- Barner-Kowollik, C.; Quinn, J. F.; Morsley, D. R.; Davis, T. P. *J Polym Sci Part A: Polym Chem* 2001, 39, 1353.
- Barner-Kowollik, C.; Vana, P.; Quinn, J. F.; Davis, T. P. *J Polym Sci Part A: Polym Chem* 2002, 40, 1058.
- Barner-Kowollik, C.; Quinn, J. F.; Nguyen, T. L. U.; Heuts, J. P. A.; Davis, T. P. *Macromolecules* 2001, 34, 7849.
- Monteiro, M. J.; de Brouwer, H. *Macromolecules* 2001, 34, 349.
- Goto, A.; Fukuda, T. *Macromolecules* 1997, 30, 5183.
- Moad, G.; Chiefari, J.; Krstina, J.; Mayadunne, R. T. A.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym Int* 2000, 49, 993.