# Synthesis of block copolymers by combination of ATRP and photoiniferter processes



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#### Abstract

BACKGROUND: Block copolymers of monomers polymerizing by different mechanisms can be prepared by the transformation approach. A wide range of combinations of different polymerization modes has been reported in the literature. In this work, the transformation approach was further extended to the preparation of block copolymers by combining atom transfer radical polymerization (ATRP) and photoiniferter processes.

RESULTS: Photoactive morpholine-4-dithiocarbamate-terminated polystyrene (MDC-PS-MDC) was prepared by the reaction of dibrominated polystyrene, obtained by ATRP, with morpholine-4-dithiocarbamate sodium salt in dimethylformamide. The structure of MDC-PS-MDC was confirmed by <sup>1</sup>H NMR and UV-visible spectral analysis. The ability of MDC-PS-MDC to act as a photoiniferter for the block copolymerization of methyl acrylate was examined. The polymerization shows a 'living' character at up to 25% conversion and produces well-defined polymers with molecular weights close to those predicted from theory and relatively narrow polydispersities  $(M_w/M_n \approx 1.40)$ .

CONCLUSION: It is demonstrated that the end groups of polymers obtained by ATRP can be converted into morpholino-4-dithiocarbamate groups which act as photoiniferters. In this way, the desired mechanistic transformation between two controlled free radical polymerization methods can be achieved. © 2008 Society of Chemical Industry

**Keywords:** photopolymerization; controlled radical polymerization; atom transfer radical polymerization; iniferter system; block copolymerization

#### INTRODUCTION

A transformation reaction is an elegant way to synthesize block copolymers from monomers that polymerize with different mechanisms.<sup>1</sup> In this concept, a polymer, obtained by a particular polymerization mechanism, is functionalized either by initiation or termination steps. The polymer is isolated and purified, and finally the functional groups are converted into another kind of species capable of initiating the polymerization of the second monomer. Living polymerization techniques are essential processes for obtaining well-defined macromolecules with controlled molecular weight, polydispersity index, and architecture and terminal functionalities. A wide range of transformation reactions combining various living ionic polymerization methods have been successfully used to synthesize block copolymers that cannot be obtained by a single method.<sup>2</sup> Living ionic polymerizations have also been combined with conventional free radical polymerization.<sup>3,4</sup> However, as usual in conventional free radical polymerization, major drawbacks arise from the transfer and termination reactions which lead to undesired structures. These drawbacks essentially result in incomplete block copolymer formation. Following Otsu's iniferter concept,<sup>5–7</sup> recent developments in controlled/living radical polymerization (CLRP) methods have made it possible to extend the mechanistic interconversion between well-established ionic polymerization methods with radical processes, leading to the formation of welldefined block copolymer structures. The most widely used methods for CLRP include atom transfer radical polymerization (ATRP),<sup>8–13</sup> nitroxide-mediated radical polymerization (NMRP)<sup>14–16</sup> and reversible addition-fragmentation chain transfer polymerization (RAFT).<sup>17–20</sup>

Mechanistic transformations can be achieved not only between different polymerization methods, but also by the same mechanism using different initiating systems. For example, ATRP can be combined with NMRP, both being controlled radical polymerization methods.<sup>21–23</sup> In this way, the limitation of a particular initiating system to certain monomers can be overcome, and block copolymers from all kinds of free radical polymerizable monomers with controlled structures can be obtained.

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In this paper, we report a transformation approach for the synthesis of block copolymers by combination of ATRP and photoiniferter processes. For this purpose, dibrominated polystyrenes were first prepared by ATRP and functionalized with photoactive morpholine-4-dithiocarbamate (MDC) groups. The ability of photoactive morpholine-4-dithiocarbamateterminated polystyrene (MDC-PS-MDC) to act as a photoiniferter for the block copolymerization of methyl acrylate (MA) was examined. As will be shown, polymerization shows a 'living' character up to 25% conversion and produces well-defined polymers with molecular weights close to those predicted from theory and relatively narrow polydispersities  $(M_w/M_n \approx 1.40)$ .

#### EXPERIMENTAL Materials

Styrene (St; 99%, Aldrich) and MA (99%, Aldrich) were passed through a basic alumina column to remove the inhibitor. N, N, N', N'', N''pentamethyldiethylenetriamine (PMDETA; 99%, Aldrich), used as a ligand, was distilled before use. 2-Bromoisobutyryl bromide (98%, Aldrich), ethylene glycol (95%, Aldrich), triethylamine (99.5%, Fluka), CuBr (98%, Acros), carbon disulfide (99.5%, Merck) and (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TMDPO; Ciba) were used as received. Morpholine (99%, Merck) was stored over metallic sodium under nitrogen atmosphere for 24 h and finally distilled under reduced pressure. Tetrahydrofuran (THF; 99.8%, J.T. Baker) was dried and distilled over benzophenone-Na. Other solvents were purified by conventional procedures.

# Synthesis of morpholine-4-dithiocarbamate sodium salt (MDC<sup>-</sup>Na<sup>+</sup>)

To a 100 mL Erlenmeyer flask were added morpholine (17.40 g, 0.20 mol) and 20 mL methanol. The solution was cooled to 0 °C in an ice bath. Carbon disulfide (7.60 g, 0.10 mol) was introduced by dropwise addition through a pressure-equalizing dropping funnel over 30 min with vigorous stirring. Then a solution of NaOH (4.00 g, 0.10 mol) in 20 mL methanol was added and the mixture was stirred at 60 °C for 1 h. About three-quarters of the methanol was removed using a rotavapor. The mixture was chilled and poured into 40 mL diethyl ether. The white precipitate (sodium salt of morpholine dithiocarbamic acid) was filtered and dried at 40 °C for 2 h under vacuum. The yield was 15.70 g (84.90%).

# Synthesis of 1,2-bis(bromoisobutryloxy)ethane

1,2-Bis(bromoisobutryloxy)ethane, as bifunctional ATRP initiator, was synthesized according to the literature.<sup>24</sup>

# Preparation of dibrominated polystyrene (Br-PS-Br) by ATRP

A round-bottom flask equipped with magnetic stirrer and a lateral neck with tap was used. The system was evacuated and back-filled with dry nitrogen several times. CuBr (0.03 g, 0.22 mmol), PMDETA (45.5  $\mu$ L 0.22 mmol), **1** as an initiator (0.04 g, 0.11 mmol) and styrene (5 mL, 44 mmol) were introduced under nitrogen atmosphere. The flask was heated to 90 °C in an oil bath and stirred for 1 h. Then the mixture was diluted with THF, and passed through an alumina column to remove the complex salts. Precipitation of the polymer was performed in a ten-fold volume of methanol. The solid was then collected after filtration and drying at 40 °C in vacuum overnight (conversion: 14%;  $M_{n,th}$ : 5820;  $M_{n,NMR}$ : 5050;  $M_{n,GPC}$ : 6330;  $M_w/M_n$ : 1.17).

### Synthesis of MDC-PS-MDC

Br-PS-Br (0.50g,  $7.9 \times 10^{-2}$  mmol), MDC<sup>-</sup>Na<sup>+</sup> (0.15 g,  $7.9 \times 10^{-1}$  mmol) and dimethylformamide (7 mL) were added to the flask. The reaction mixture was degassed by three freeze-pump-thaw cycles and left *in vacuo*. The tube was then placed in a stirrer at room temperature for 48 h. The mixture was precipitated in methanol and the precipitated polymer was filtered off and dried *in vacuo*.

# Photopolymerization

A solution of MDC-PS-MDC (0.10 g,  $1.5 \times 10^{-2}$  mmol) and MA (0.80 mL, 9 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.7 mL) was irradiated with a Rayonet 'merry-goround' photoreactor equipped with 16 lamps emitting light nominally at  $\lambda > 300$  nm at room temperature. The light intensity was  $6 \times 10^{-3}$  mW cm<sup>-2</sup> as measured by a Delta Ohm model HD-9021 radiometer. After a given time, the resulting polymers were precipitated in methanol and then dried under reduced pressure. Conversion of monomer was determined gravimetrically.

# Photopolymerization with TMDPO

TMDPO  $(3.10 \times 10^{-3} \text{ g}, 0.8 \times 10^{-2} \text{ mmol})$  and monomer MA (1.19 mL, 13.3 mmol) with MDC-PS-MDC  $(0.10 \text{ g}, 2.2 \times 10^{-2} \text{ mmol})$  solution in CH<sub>2</sub>Cl<sub>2</sub> (2.6 mL) were placed in Pyrex tubes flushed with dry nitrogen. The mixtures were irradiated as described above except that a CuSO<sub>4</sub> aqueous solution was used as the photofilter in order to avoid absorption by MDC-PS-MDC. The thickness of the saturated solution of CuSO<sub>4</sub> was 1 cm. Conversion of monomer was determined gravimetrically.

# Characterization

<sup>1</sup>H NMR spectra in CDCl<sub>3</sub> with Si(CH<sub>3</sub>)<sub>4</sub> as an internal standard were recorded at room temperature at 250 and 62.5 MHz using a Bruker DPX 250 spectrometer. Fourier tansform infrared (FTIR) spectra were recorded using a Perkin-Elmer FTIR Spectrum One B spectrometer. UV spectra were recorded using a Shimadzu UV-1601 spectrometer. Molecular weights were determined using a gel permeation chromatography (GPC) instrument equipped with a Waters Styragel column (HR series 2, 3, 5E) with THF as the eluent at a flow rate of 0,  $3 \text{ mL min}^{-1}$  and a Waters 410 differential refractometer detector. Calibration was done with standard polystyrene samples.

#### **RESULTS AND DISCUSSION**

Dithiocarbamates are important control agents that have been widely used in controlled free radical polymerizations, such as photoiniferters<sup>25</sup> and RAFT agents in thermal conditions.<sup>26</sup> We have recently designed and synthesized phenacyl ester of morpholine dithiocarbamate (PMDC) which acts both as photoiniferter and RAFT agent in controlled free radical polymerization.<sup>27</sup> Detailed polymerization and spectroscopic studies revealed that, at early stages of the polymerizations, both reversible termination (iniferter) and RAFT mechanisms were operative. After PMDC is totally consumed, however, reversible termination was the dominant process in the polymerization (Scheme 1).

 $\alpha,\omega$ -Halogen end-groups of polymers, obtained by ATRP, may be altered to other functional groups by appropriate chemical reactions.<sup>28,29</sup> Thus, polystyrene having bromine at both ends (Br-PS-Br), obtained from ATRP using a bifunctional ATRP initiator, can



Scheme 2. MDC functionalization of polystyrene obtained by ATRP.

be converted into a photoactive functional photoiniferter (MDC-PS-MDC), by substitution reaction with  $MDC^-Na^+$  (Scheme 2).

This process eventually leads to polymers equipped with the same terminal functional groups as those obtained from PMDC (discussed above) and gives the possibility to switch the initiating system from ATRP to photoiniferter. The structure of MDC-PS-MDC was confirmed by <sup>1</sup>H NMR and UVvisible spectroscopies. The <sup>1</sup>H NMR spectrum of MDC-PS-MDC exhibits signals at 3.7–4.1 ppm, attributed to the methine proton next to a sulfur atom and in morpholine moieties (Fig. 1(B)). The



Scheme 1. Overall polymerization mechanism of styrene (St) with PMDC.



Figure 1. <sup>1</sup>H NMR spectra of (A) Br-PS-Br and (B) MDC-PS-MDC in CDCl<sub>3</sub>.

disappearance of the peak corresponding to the proton located at the  $\alpha$ -position of the chain end at 4.4 ppm (Fig. 1(A)) is additional evidence for the successful functionalization. Almost quantitative functionalization (more than *ca* 96%) was attained as evidenced by the comparison of the intensities of integrals belonging to protons of initial ATRP initiator (c protons) to those of the methine proton next to sulfur and in morpholine group (a', d, e protons).

The incorporation of MDC groups at polymer chain ends was also evidenced by UV absorption measurements. Figure 2 shows absorption spectra of the bromo-terminated precursor polymer, MDC<sup>-</sup>Na<sup>+</sup> and the final product, MDC-PS-MDC. It shows that the polymeric photoiniferter contains the characteristic absorption band of the MDC chromophore. In the FTIR spectrum of MDC-PS-MDC, a weak absorption at 1067 cm<sup>-1</sup> corresponding to a Cdbond;S group is also noted.<sup>30</sup>

Dithiocarbamate compounds are known to undergo decomposition in the absence of monomer.<sup>31</sup> Photoinduced decomposition of MDC-PS-MDC was confirmed by the spectral changes on UV irradiation. Representative results for the decomposition of MDC-PS-MDC are shown in Fig. 3. UV spectra were recorded after the solution had been exposed to the light of the UV lamp for subsequent intervals during the 75 min.

The utilization of MDC-PS-MDC as photoiniferter for block copolymerization with MA was tested. The copolymerization of MA (Scheme 3) was performed by UV irradiation at different time intervals with MDC-PS-MDC and [MA]<sub>0</sub>/[MDC-PS-MDC]<sub>0</sub> mole ratio of 600:1. Typical GPC profiles of these



Figure 2. Typical UV-visible spectra of MDC<sup>-</sup>Na<sup>+</sup>, Br-PS-Br and MDC-PS-MDC.



**Figure 3.** Typical UV-visible spectral changes of MDC-PS-MDC on irradiation at above 300 nm under nitrogen in  $CH_2Cl_2$ . UV spectra were taken subsequent intervals during the 75 min.



Figure 4. GPC traces for block copolymers obtained at different time intervals ( $[MDC-PS-MDC]_0/[MA]_0 = 1/600$ ).

polymerization series are shown in Fig. 4. All the GPC curves show a unimodal distribution and the elution peaks shift to the high molecular weight side, increasing with reaction time.



Scheme 3. Block copolymerization of polystyrene with MA.

**Table 1.** Polymerization conditions and results for MA polymerized under UV irradiation using MDC-PS-MDC as a macrophotoinitiator ( $M_{n,th}$ : 5820;  $M_{n,GPC}$ : 6330;  $M_w/M_n$ : 1.17)

Time (min)	Conversion <sup>a</sup> (%)	M <sub>n,th</sub> b (g mol <sup>-1</sup> )	M <sub>n,GPC</sub> <sup>c</sup> (g mol <sup>−1</sup> )	M <sub>w</sub> /M <sub>n</sub> c
30	7	9800	10100	1.53
45	20	16400	14800	1.48
60	26	19800	19800	1.42
75	25	19100	19700	1.41
	Time (min) 30 45 60 75	Time (min) Conversion <sup>a</sup> (%)   30 7   45 20   60 26   75 25	Time (min) Conversion <sup>a</sup> (Mn,th <sup>b</sup> (g mol <sup>-1</sup> ))   30 7 9 800   45 20 16 400   60 26 19 800   75 25 19 100	Time (min)Conversiona (%) $M_{n,th}^{b}$ $M_{n,GPC}^{c}$ (g mol <sup>-1</sup> )3079 80010 100452016 40014 800602619 80019 800752519 10019 700

<sup>a</sup> Determined gravimetrically.

<sup>b</sup> Calculated according to Eqn (1).

<sup>c</sup> Determined by GPC based on polystyrene standards.

The copolymerization results are listed in Table 1. The theoretical number-average molecular weight,  $M_{n,th}$ , is calculated according to

$$M_{n,th} = \% \text{ conversion} \times \frac{[MA]_0}{[MDC-PS-MDC]_0} + M_{MDC-PS-MDC}$$
(1)

where  $M_{\text{MDC-PS-MDC}}$  is the molecular weight of the polymeric photoiniferter.  $M_{n,\text{th}}$  values are in good agreement with  $M_{n,\text{GPC}}$  values, which further verifies the controlled character of the polymerization.

The controlled block copolymerization mechanism<sup>31</sup> is supported by the following evidence: firstorder kinetics up to 25% conversion shown in Fig. 5 demonstrates that the concentration of chain radicals remains constant during polymerization; a linear relationship between molecular weight and conversion is observed (Fig. 6); and the molecular weight is



**Figure 5.** Plots of (**■**) monomer conversion and ( $\Delta$ ) ln([M]<sub>0</sub>/[M]<sub>t</sub>) versus polymerization time ([MA] = 3.5 mol L<sup>-1</sup>, [MA]<sub>0</sub>/[MDC-PS-MDC]<sub>0</sub> = 600 : 1,  $\lambda_{inc.} > 300$  nm,  $I = 6 \times 10^{-3}$  mW cm<sup>-2</sup>).



**Figure 6.** Plots of GPC experimental ( $\blacksquare$ ) and theoretical (- - - -) polymer molecular weight ( $M_n$ ) values and ( $\blacktriangle$ ) polydispersity ( $M_w/M_n$ ) values *versus* monomer conversion (experimental details are the same as in Fig. 5).

controlled by the molar ratio of monomer consumed and photoiniferter used.

At later stages of polymerization, deviations from the first-order kinetics and theoretical molecular weight increase take place. A possible reason for this observation might be the occurrence of deactivation of chain ends and termination reactions, which are more pronounced at higher monomer conversion.

It was of interest to determine whether polymerizations proceeded also via the RAFT mechanism. We performed polymerization of MA using a conventional photoinitiator with MDC-PS-MDC as a macro-RAFT agent. In this case, initiating radicals are produced from the added photoinitiator and MDC-PS-MDC was expected to act only as a RAFT agent. In the experiment, the absorbance of MDC-PS-MDC was prevented by using a filter solution (see Experimental section). Thus, polymerization of MA using TMDPO, as long wavelength absorbing photoinitiator in the presence of MDC-PS-MDC under similar experimental conditions, yields polymer with 30% conversion and polydispersity of 1.7. The broader molecular weight distribution obtained indicates less control of the polymerization state when light is absorbed by the added photoinitiator. These results indicate that either propagating radicals formed from the photoinitiator do not react with dithio groups in a manner similar to classical RAFT process or that the propagating radicals are less reactive with MDC-PS-MDC than with other RAFT agents.

### CONCLUSIONS

It has been demonstrated that mechanistic transformation from ATRP to photoiniferter process can be achieved by taking advantage of end-group modification of polymers obtained by ATRP. Well-defined block copolymers of St and MA were synthesized using polystyrene with MDC end-groups as a photoiniferter under UV irradiation at ambient temperature. The controlled character of this polymerization was confirmed in both cases by the linear trend of molecular weight evolution with conversion.

#### REFERENCES

- 1 Tasdelen MA and Yagci Y, Segmented copolymers by mechanistic transformations, in *Macromolecular Engineering: Precise Synthesis, Materials Properties, Applications*, Vol. 1, ed. by Matyjaszeswki K, Gnaonou Y and Liebler L. Wiley-VCH, Manheim, pp. 541 (2007).
- 2 Yagci Y and Tasdelen MA, Prog Polym Sci 31:1133 (2006).
- 3 Yagci Y, Serhatli IE, Kubisa P and Biedron T, Macromolecules 26:2397 (1993).
- 4 Hizal G and Yagci Y, Polymer 30:722 (1989).
- 5 Otsu T, Yoshida M and Tazaki T, *Makromol Chem-Rapid* **3**:133 (1982).
- 6 Otsu T and Yoshida M, Makromol Chem-Rapid 3:127 (1982).
- 7 Otsu T, J Polym Sci Polym Chem Ed 38:2121 (2000).
- 8 Matyjaszewski K, ACS Symp Ser 854:2 (2003).
- 9 Wang JS and Matyjaszewski K, Macromolecules 28:7572 (1995).

- 10 Wang JS and Matyjaszewski K, J Am Chem Soc 117:5614 (1995).
- 11 Kato M, Kamigaito M, Sawamoto M and Higashimura T, Macromolecules 28:1721 (1995).
- 12 Matyjaszewski K and Xia JH, Chem Rev 101:2921 (2001).
- 13 Kamigaito M, Ando T and Sawamoto M, Chem Rev 101:3689 (2001).
- 14 Fukuda T, Terauchi T, Goto A, Tsujii Y and Miyamoto T, Macromolecules 29:3050 (1996).
- 15 Benoit D, Chaplinski V, Braslau R and Hawker CJ, J Am Chem Soc 121:3904 (1999).
- 16 Hawker CJ, Bosman AW and Harth E, Chem Rev 101:3661 (2001).
- 17 Ganachaud F, Monteiro MJ, Gilbert RG, Dourges MA, Thang SH and Rizzardo E, *Macromolecules* **33**:6738 (2000).
- 18 Chiefari J, Chong YK, Ercole F, Krstina J, Jeffery J, Le TPT, et al, Macromolecules **31**:5559 (1998).
- 19 Chong YK, Le TPT, Moad G, Rizzardo E and Thang SH, Macromolecules 32:2071 (1999).
- 20 Moad G, Chiefari J, Chong YK, Krstina J, Mayadunne RTA, Postma A, et al, Polym Int **49**:993 (2000).
- 21 Miura Y, Narumi A, Matsuya S, Satoh T, Duan Q, Kaga H, et al, J Polym Sci Polym Chem Ed 43:4271 (2005).
- 22 Celik C, Hizal G and Tunca U, J Polym Sci Polym Chem Ed 41:2542 (2003).
- 23 Durmaz H, Aras S, Hizal G and Tunca U, Design Monomers Polym 8:203 (2005).
- 24 Karanam S, Goossens H, Klumperman B and Lemstra P, Macromolecules 36:3051 (2003).
- 25 Bai RK, You YZ and Pan CY, *Macromol Rapid Commun* 22:315 (2001).
- 26 Barner L, Quinn JF, Barner-Kowollik C, Vana P and Davis TP, Eur Polym J 39:449 (2003).
- 27 Tasdelen MA, Durmaz YY, Karagoz B, Bicak N and Yagci Y, *β Polym Sci Polym Chem Ed* 46:3387 (2008).
- 28 Gao HF, Louche G, Sumerlin BS, Jahed N, Golas P and Matyjaszewski K, Macromolecules 38:8979 (2005).
- 29 Durmaz YY, Yilmaz G and Yagci Y, J Polym Sci Polym Chem Ed 45:423 (2007).
- 30 You YZ, Hong CY, Bai RK, Pan CY and Wang J, Macromol Chem Phys 203:477 (2002).
- 31 Quinn JF, Barner L, Barner-Kowollik C, Rizzardo E and Davis TP, *Macromolecules* **35**:7620 (2002).