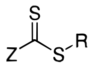
Living Polymers by the Use of Trithiocarbonates as Reversible Addition−Fragmentation Chain Transfer (RAFT) Agents: ABA Triblock Copolymers by Radical Polymerization in Two Steps

Roshan T. A. Mayadunne,* Ezio Rizzardo,* John Chiefari, Julia Krstina, Graeme Moad, Almar Postma, and San H. Thang

CSIRO Molecular Science, Bag 10, Clayton South, Victoria 3169, Australia

Received August 23, 1999
Revised Manuscript Received November 1, 1999

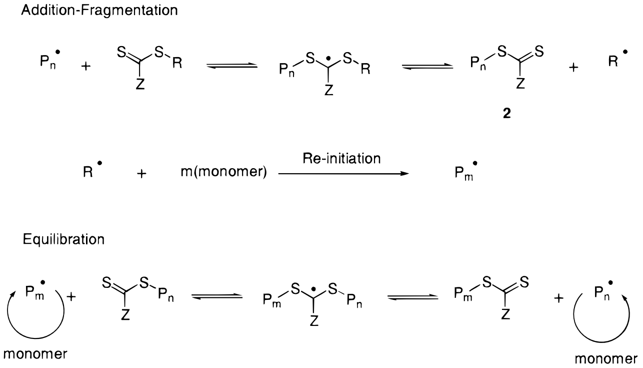
Recently, we demonstrated that thiocarbonylthio compounds of general structure (**1**) confer living characteristics to radical polymerization.[1,2] These reagents function by establishing a dynamic equilibrium between propagating radicals ($P_n^\bullet$) and dormant chains (**2**) by a mechanism of reversible addition−fragmentation chain transfer (RAFT) as shown in Scheme 1. RAFT agents (**1**) function effectively only when the substituent on sulfur (R) is a good homolytic leaving group when compared to the polymer chain P_n.[3] With appropriate choice of the RAFT agent (**1**), a wide range of polymers of predetermined molecular weight and narrow polydispersity can be prepared.[1,2,4−8] The versatility and convenience of this process offer distinct advantages over other forms of living radical polymerization.[9−12]



1

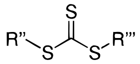
Z = aryl, alkyl, NR'$_2$, OR', SR',
R = homolytic leaving group

Scheme 1. The RAFT Process[a]



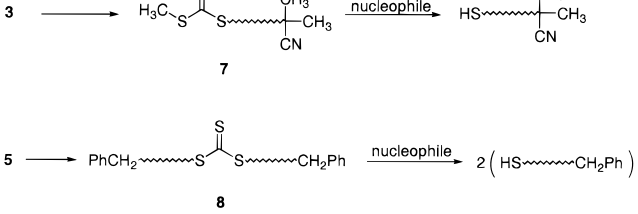
[a] R is a good homolytic leaving group and R• can initiate polymerization. Z is a group that modifies the reactivity of the thiocarbonyl group toward radical addition. P_n and P_m are polymer chains.

Our previous work has shown that trithiocarbonates are effective RAFT agents.[1,6] The outstanding feature of trithiocarbonates **1** (Z = SR) is that they can be prepared with either one (e.g., **3** and **4**) or two (e.g., **5** and **6**) good homolytic leaving groups (R″, R‴). For example, transfer agent **3** should give rise to polymers of structure **7**, whereas **5**, which can grow in two directions, should yield polymer of structure **8** (Scheme 2). An important consequence is that ABA triblock copolymers should be available in only two sequential monomer addition steps.[13] The purpose of this communication is to provide proof of this hypothesis by focusing attention on the distinct advantages of trithiocarbonates in block copolymer synthesis.



3 R″ = CH_3; R‴ = $C(CH_3)_2CN$
4 R″ = CH_3; R‴ = CH(Ph)COOH
5 R″ and R‴ = CH_2Ph
6 R″ and R‴ = $CH(CH_3)Ph$

Scheme 2. Cleavage of Polymers at the Trithiocarbonate Link



The experimental results shown in Table 1 demonstrate the effectiveness of trithiocarbonates (**3**−**6**) in controlling the polymerization of styrene, methyl acrylate (MA), and methyl methacrylate (MMA). Of particular note are the very low polydispersities that can be achieved, especially at high conversions. Indeed, the broader polydispersities ($\bar{M}_w/\bar{M}_n$ = 1.27 and 1.24) for PMMA at low conversion (Table 1) are attributed to the relatively low chain transfer constant of RAFT agents in the polymerization of methyl methacrylate.[4] As the polymerization progresses, the polydispersities reduce to 1.17 and 1.13, respectively.

Also notable (Table 1) is the good agreement between the molecular weights determined by GPC and those calculated [$\bar{M}_n$(calcd)] assuming one trithiocarbonate group per chain. A representative example showing the correspondence of ($\bar{M}_n$) and $\bar{M}_n$(calcd) as a function of conversion is shown in Figure 1. The decrease in polydispersity as the equilibrium of chains is established is evident from the plot. Although $\bar{M}_n$(calcd) is based on the assumption that all chains contain one trithiocarbonate moiety, it is important to realize that a small number of dead chains are produced by radical−radical termination.

Polymers prepared with symmetrical trithiocarbonates should have the active functionality located in the center, e.g., **8** (see Scheme 2). A way to confirm this is to cleave the polymer chains at the trithiocarbonate function. This can be achieved readily with mild nucleophiles such as primary or secondary amines (Scheme 2).[14] When PMA ($\bar{M}_n$ = 66 900 and $\bar{M}_w/\bar{M}_n$ = 1.09) prepared using **5** was treated with ethylenediamine in THF at room temperature, PMA of $\bar{M}_n$ = 37 900 and $\bar{M}_w/\bar{M}_n$ = 1.16 was obtained. The fact that the molecular weight halved with no appreciable change in polydispersity shows that the length of the two chains are equal

---

* To whom correspondence should be addressed. Telephone: +613 9545 2500. Fax: +613 9545 2446. E-mail: ezio.rizzardo@molsci.csiro.au.

10.1021/ma991451a CCC: $19.00

Table 1. Molecular Weight/Conversion Data for Polymers Formed by Polymerization of Various Monomers in the Presence of Trithiocarbonate Compounds[a]

monomer[b] (concn in benzene, °C)	RAFT agent (M × 10^2)	initiator[c] (M × 10^2)	time (h)	$\bar{M}_n$[d]	$\bar{M}_n$ (calcd)[e]	$\bar{M}_w/\bar{M}_n$	conv.[f] (%)
styrene (bulk, 100)	**3** (2.93)	thermal[g]	20	11 800	11 140	1.06	36
styrene (bulk, 110)	**5** (2.92)	thermal[g]	16	17 200	20 100	1.19	65
styrene (bulk, 100)	**6** (2.92)	thermal[g]	20	13 900	11 890	1.06	38
styrene (bulk, 110)	**3** (2.93)	thermal[g]	48	27 800	27 880	1.09	91
styrene (bulk, 110)	**4** (2.93)	thermal[g]	48	29 200	28 590	1.07	92
MA (2.22 M, 60)	**3** (0.17)	AIBN (0.073)	4	65 400	62 310	1.06	55
MA (2.22 M, 60)	**5** (0.17)	AIBN (0.073)	4	66 900	60 630	1.09	54
MMA (7.02 M, 60)	**3** (1.12)	AIBN (0.73)	4	24 100	24 000	1.27	38
			16	57 000	59 700	1.17	>95
MMA (7.02 M, 80)	**3** (1.12)	VAZO-88 (0.74)	4	30 000	29 500	1.24	47
			8	59 300	59 680	1.13	>95

[a] Reaction mixtures were prepared to give the concentrations shown, degassed through three freeze–thaw–evacuate cycles, sealed under vacuum, and heated in a constant-temperature bath for the stated time. [b] Abbreviations: MMA (methyl methacrylate) and MA (methyl acrylate). [c] Abbreviations: AIBN (2,2′-azobis(2-cyanopropane)) and VAZO-88 (1,1′-azobis(1-cyclohexanecarbonitrile)). [d] Molecular weight data were obtained by gel permeation chromatography (GPC) with 10^6, 10^5, 10^4, 10^3, 500, and 100 Å Waters ultrastyragel columns connected in series. Tetrahydrofuran (1.0 mL/min) was used as eluent. Samples for GPC were isolated by evaporation of monomer and solvent (no fractionation or precipitation was performed). The system was calibrated with narrow polydispersity polystyrene standards, and molecular weights are reported as polystyrene equivalents. [e] The following formula was used to calculate the theoretical molecular weight: M_n(calcd) = ([monomer]/[CTA]) × conversion × MW of monomer. This expression does not include the small number of chains formed from the initiator. It also requires complete consumption of the chain transfer agent. [f] Conversions were determined gravimetrically following evaporation of monomer and solvent. Conversions were those obtained for the times indicated and are not limiting conversions. [g] No added initiator.

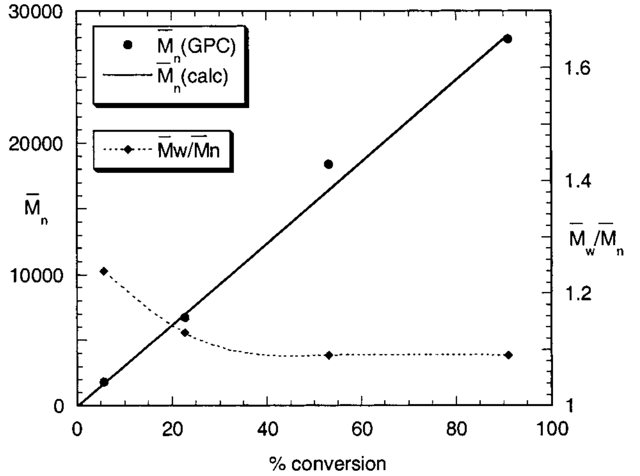


Figure 1. Evolution of molecular weight and polydispersity with conversion during the polymerization of styrene (bulk) performed at 110 °C in the presence of *S*-methyl *S*-(2-cyanoisopropyl) trithiocarbonate **3** (0.0293 M) as the chain transfer agent. See footnote e of Table 1 for M_n (calcd).

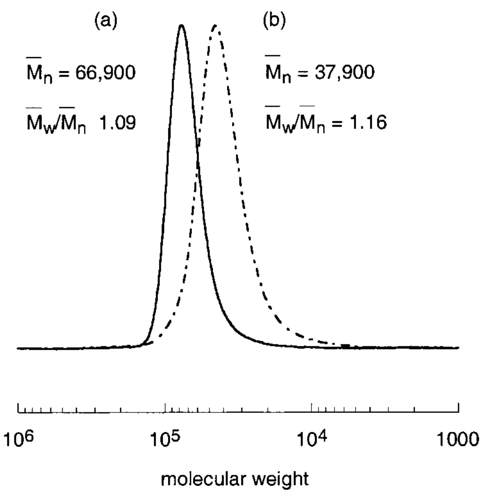
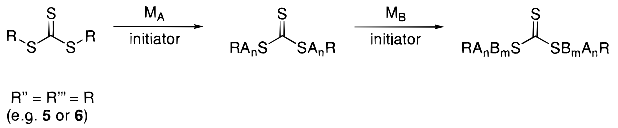


Figure 2. GPC traces of (a) PMA prepared using **5** and (b) the same PMA treated with ethylenediamine in THF at room temperature (see text).

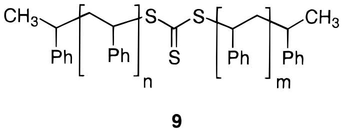
(Figure 2). On the other hand, when PMA ($\bar{M}_n$ = 65 500 and $\bar{M}_w/\bar{M}_n$ = 1.06) prepared using trithiocarbonate **3** was treated in the same manner, no significant change in molecular weight and polydispersity was observed, as is expected of a polymer of structure **7**.

Having the trithiocarbonate function located in the middle of polymer chains allows insertion of monomer at this site and, thus, the advantage of forming ABA triblock copolymers in two steps (see Scheme 3). To demonstrate this, we have synthesized polystyrene-*block*-poly(*n*-butyl acrylate)-*block*-polystyrene. Polystyrene (**9**) of $\bar{M}_n$ = 20 100 and $\bar{M}_w/\bar{M}_n$ = 1.11, prepared in the presence of **6** was chain-extended with *n*-butyl acrylate to afford the ABA triblock copolymer with $\bar{M}_n$ = 161 500 and $\bar{M}_w/\bar{M}_n$ = 1.16 (see Figure 3). The ABA triblock would thus be composed of polystyrene end segments ($\bar{M}_n$ = 10 100) on either side of poly(*n*-butyl acrylate) ($\bar{M}_n$ = 141 400).

Scheme 3[a]



[a] M_A and M_B are different monomers, and A_n and B_m are their respective polymers.



9

The preparation of trithiocarbonates is simple and high-yielding. Primary or secondary dialkyl trithiocarbonates are synthesized by treating aqueous KOH and carbon disulfide with an alkyl halide in the presence of a phase-transfer catalyst.[15] Tertiary trithiocarbonates can be synthesized according to a procedure developed recently in our laboratory.[16]

In conclusion, these results demonstrate that trithiocarbonates can be employed as effective RAFT agents.

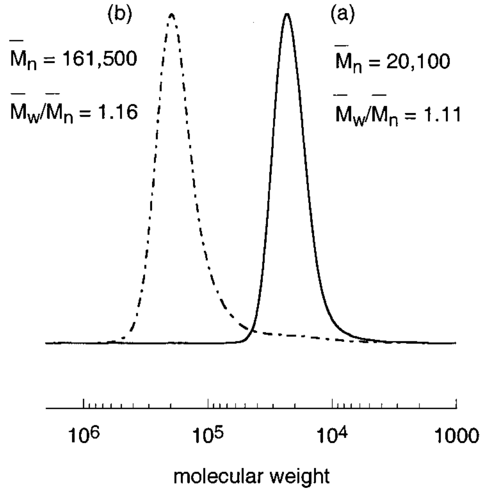


Figure 3. GPC traces for (a) PSt **9** ($\bar{M}_n = 20\,100$, $\bar{M}_w/\bar{M}_n = 1.11$), prepared in bulk at 110 °C using *S*,*S*-di(1-phenylethyl) trithiocarbonate **6** (0.0173 M) as the chain transfer agent and (b) poly(styrene-*block*-*n*-butyl acrylate-*block*-styrene) ($\bar{M}_n = 161\,500$, $\bar{M}_w/\bar{M}_n = 1.16$) prepared by chain extension of PSt **9** (0.0016 M) with *n*-butyl acrylate (2.79 M), AIBN (0.073×10^{-2}M) at 60 °C for 8 h.[17]

In the presence of these transfer agents, homopolymers and block copolymers of controlled molecular weight and narrow polydispersity can be prepared. Important ABA triblock copolymers of predetermined molecular weight are accessible in two steps from these compounds. Extension of this technology to the synthesis of polymers of more complex architectures (e.g., stars) will be reported in a forthcoming paper.

Acknowledgment. We are grateful to Drs. C. Berge, M. Fryd, and R. Matheson of DuPont Performance Coatings for their support of this work and for valuable discussion.

References and Notes

(1) Le, T. P.; Moad, G.; Rizzardo, E.; Thang, S. H. PCT Int. Appl. WO 9801478 A1 980115; *Chem. Abstr.* **1998** *128*, 115390.
(2) Chiefari, J.; Mayadunne, R. T. A.; Moad, G.; Rizzardo, E.; Thang, S. H. PCT Int. Appl. WO 9931144 A1 990624; *Chem. Abstr.* **1999** *131*, 45250.
(3) The leaving group ability of R (Scheme 1) increases with increasing stability and bulk of radical R•. Thus, CH_3 and $C(CH_3)_2CN$ are examples of very poor and very good homolytic leaving groups, respectively.
(4) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, 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*, 5559−5562.
(5) Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Thang, S. H. *Macromol. Symp.* **1999**, *143*, 291−307.
(6) Rizzardo, E.; Chiefari, J.; Moad, G.; Mayadunne, R. T. A.; Thang, S. H. *Polym. Prepr.* **1999**, *40*, 342−343.
(7) Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Moad, G.; Thang, S. H. *Macromolecules* **1999**, *32*, 6977−6980.
(8) Chong, Y. K.; Le, T. P.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1999**, *32*, 2071−2074.
(9) Matyjaszewski, K. *ACS Symp. Ser.* **1998**, *685*, 2−30.
(10) Colombani, D. *Prog. Polym. Sci.* **1997**, *22*, 1649−1720.
(11) Otsu, T.; Matsumoto, A. *Adv. Polym. Sci.* **1998**, *136*, 75−137.
(12) Rizzardo, E.; Moad, G. In *The Polymeric Materials Encyclopaedia: Synthesis, Properties and Applications*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; Vol. 5, p 3834.
(13) Bis(dithioester)s also provide a route to ABA triblocks in two steps.[8] The advantage of trithiocarbonates is that they are more readily available.
(14) For leading references on the reactions of dithio compounds, see: Kato, S.; Ishida, M. *Sulfur Rep.* **1988**, *8*, 155. Mayer, R.; Scheithauer, S. In *Houben-Weyl Methods of Organic Chemistry*; Beuchel, K. H., Falbe, J., Hagemann, H., Hanack, M., Eds.; Thieme: Stuttgart, Germany, 1985; Vol. E, p 891.
(15) Lee, A. W. M.; Chan, W. H.; Wong, H. C. *Synth. Commun.* **1988**, *18*, 1531−1536.
(16) Moad, G.; Rizzardo, E.; Thang, S. H. PCT Int. Appl. WO 9905099 A1 990204; *Chem. Abstr.* **1999** *130*, 154069. Thang, S. H.; Chong, Y. K.; Mayadunne, R. T. A.; Moad, G.; Rizzardo, E. *Tetrahedron Lett.* **1999**, *40*, 2435−2438.
(17) As described in our previous publications, the amount of impurity polymer (homo- and diblock impurity) produced is dependent on the number of initiator-derived chains and not the amount of initiator used in the experiment. In ascertaining the amount of initiator derived chains, based on the rate of decomposition of the initiator, allowance must also be made for the efficiency of the initiator. Thus, in summary: [initiator-derived chains] = [initiator decomposed] × [initiator efficiency] × 2 = [diblock impurity] + [homopolymer impurity].

MA991451A