

A More Versatile Route to Block Copolymers and Other Polymers of Complex Architecture by Living Radical Polymerization: The RAFT Process

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Over the past few years, methods for achieving living¹ radical polymerization have proliferated.² However, the use of these methods in the synthesis of block copolymers and other structures of complex architecture has been limited by the fact that the processes are not compatible with certain monomers or reaction conditions, or both. Thus, recent work suggests that nitroxide-mediated polymerization, although it can be successfully used for making block copolymers based on styrene and derivatives,³ appears to have less utility for other systems.^{4,5} Atom transfer radical polymerization⁶ has limitations with monomers or initiators containing acid functionality (e.g., methacrylic acid⁷) and provides products contaminated with metal ions. Although these and other problems may sometimes be mitigated by appropriate selection of the reagents and reaction conditions, there is, nonetheless, a clear need for a more versatile process.

Recently, we reported a new living radical polymerization (reversible addition–fragmentation chain transfer, the RAFT process) that offers exceptional versatility in providing polymers of predetermined molecular weight and very narrow polydispersity (usually <1.2, sometimes <1.1).^{8,9} This is achieved by performing the polymerization in the presence of certain dithio compounds (e.g., dithiobenzoates **1a–d**) which act as highly



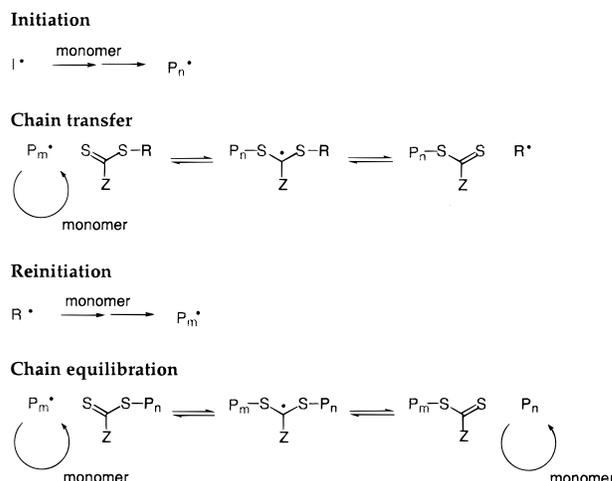
- 1**
- 1a** R = CH₂Ph
1b R = CH(CH₃)Ph
1c R = C(CH₃)₂Ph
1d R = C(CH₃)(CN)CH₂CH₂CO₂H

efficient reversible addition–fragmentation chain transfer agents and provide the polymerization with living characteristics.

In this paper, we report on the use of the RAFT process in the synthesis of block copolymers.¹⁰ One advantage of the method which we wished to exploit is its compatibility with a wide range of monomers, including functional monomers. Thus, narrow polydispersity block copolymers have been prepared with monomers containing acid (e.g., acrylic acid), hydroxy (e.g., 2-hydroxyethyl methacrylate), and tertiary amino [e.g., 2-(dimethylamino)ethyl methacrylate] functionality.⁹

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Scheme 1. A Block Synthesis

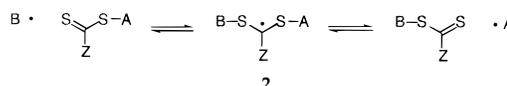


The sequence of events for a polymerization carried out in the presence of **1** can be envisioned as follows (Scheme 1). In the early stages of the polymerization, the reagent [S=C(Z)S–R] is rapidly transformed into a polymeric thiocarbonylthio compound [S=C(Z)S–P_n] by reaction with a propagating radical (P_m·). The radical liberated (R·) reacts with a monomer to form a new propagating radical (P_n'·).

Chain extension of the polymeric thiocarbonylthio compound [S=C(Z)S–P_n] occurs by the same process. The reversible addition–fragmentation sequence in which the S=C(Z)S– moiety is transferred between dormant and active chains maintains the living character of the polymerization. Because the majority of chains in the product polymer possess the S=C(Z)S– group, polymerization can be continued in the presence of a second monomer to give a block copolymer.

The experimental protocol for polymer synthesis by RAFT polymerization is described in greater detail elsewhere.⁸ Polymerizations can be carried out in bulk, solution, emulsion, or suspension using standard reaction conditions. Representative procedures are provided in the Notes.^{11,12}

Scheme 2



One requirement for forming a narrow polydispersity AB block copolymer in a batch polymerization is that the first-formed polymeric thiocarbonylthio compound (S=C(Z)S–A) should have a high transfer constant in the subsequent polymerization step to give the B block.¹³ This requires that the leaving group ability of propagating radical A· is comparable to or greater than that of the propagating radical B· under the reaction conditions (cf. Scheme 2). When A is a poly(acrylate ester) or a polystyrene chain, the transfer constants of S=C(Z)S–A in MMA polymerization appear to be very low. This is attributed to the styryl- or acrylyl-propagating radicals being poor leaving groups with respect to a methacrylyl-propagating radical causing the adduct radical (**2**) to partition strongly in favor of starting materials. It follows that, when preparing a block copolymer, for

Table 1. Molecular Weight Data for AB Diblock Copolymers

dithioester	monomer A ^a	\bar{M}_n^b	\bar{M}_w/\bar{M}_n	monomer B ^a	\bar{M}_n^b	\bar{M}_w/\bar{M}_n	solvent ^{a,c}
1a	St	20 300	1.15	DMA	43 000	1.24	benzene
1a	St	20 300	1.15	MeSt	25 400	1.19	benzene
1b	BA	33 600	1.13	AA	52 400 ^d	1.19	DMF
1b	MA	24 100	1.07	EA	30 900	1.10	benzene
1c	MMA	3 230	1.17	MAA	4 720 ^d	1.18	DMF
1c	MMA	17 400	1.20	St	35 000	1.24	bulk
1c	BzMA	1 800	1.13	DMAMEA	3 500	1.06	EtOAc
1c	BzMA	1 800	1.13	MAA	2 400 ^d	1.09	DMF
1d	EO	750	1.04	St	7 800	1.07	bulk
1d	EO	750	1.04	BzMA	10 800	1.10	benzene

^a Abbreviations: AA, acrylic acid; BA, butyl acrylate; EA, ethyl acrylate; BzMA, benzyl methacrylate; DMA, *N,N*-dimethylacrylamide; DMAEMA, 2-(dimethylamino)ethyl methacrylate; EO, ethylene oxide; MeSt, *para*-methylstyrene; MA, methyl acrylate; MAA, methacrylic acid; MMA, methyl methacrylate; St, styrene; DMF, *N,N*-dimethyl formamide; EtOAc, ethyl acetate. ^b Molecular weight data were obtained by gel permeation chromatography (GPC) with 10⁶, 10⁵, 10⁴, 10³, 500 and 100 Å Waters Ultrastaygel 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). Systems calibrated with narrow polydispersity polystyrene standards and molecular weights are reported as polystyrene equivalents. ^c Solvent used in synthesis of B block. ^d Prior to GPC analysis, (meth)acrylic acid groups were converted to methyl (meth)acrylate units with tetrabutylammonium hydroxide and methyl iodide in tetrahydrofuran at 80 °C.

Table 2. Molecular Weight Data for ABA Triblock Copolymers

dithioester	monomer B ^a	\bar{M}_n^b	\bar{M}_w/\bar{M}_n	monomer A ^a	\bar{M}_n^b	\bar{M}_w/\bar{M}_n	solvent ^c
3	BMA	35 500	1.09	St	87 600	1.08	bulk
3	BMA	35 500	1.09	MMA	112 200	1.14	benzene
3	MMA	23 000	1.16	HEMA ^d	28 500	1.18	THF ^d

^{a-c} See footnotes a–c of Table 1. ^d Tetrahydrofuran.

which one block is based on a methacrylate monomer and the other on a styrene or an acrylate monomer, the methacrylate block should be prepared first.

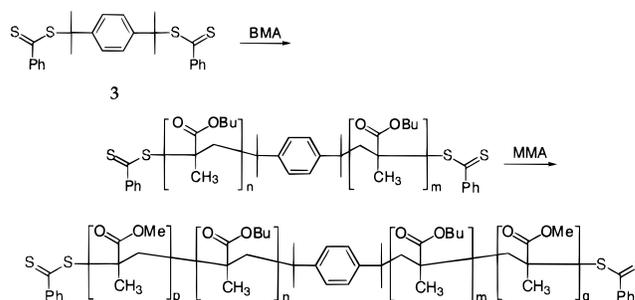
In the absence of chain transfer (to solvent, initiator, or monomer), the total number of chains formed will be equal to (or less than) the moles of dithio compound employed *plus* the moles of initiator-derived radicals generated during the course of the polymerization. In block synthesis, these additional initiator-derived chains are a source of homopolymer impurity. The level of impurities can be controlled by appropriate selection of the reaction conditions.¹⁴ For maximum purity, it is desirable to use as low a concentration of initiator as practicable and to choose solvents and initiators which give minimal chain transfer. As with conventional radical polymerization, the rate of RAFT polymerization is determined by the initiator concentration. In practice, it is usually not difficult to achieve block copolymers with no detectable homopolymer impurity (<5%) while still achieving an acceptable rate of polymerization.

Examples of AB block copolymers formed by RAFT polymerization are shown in Table 1. The procedure has been used in the synthesis of a wide range of hard–soft, hydrophilic–hydrophobic, and other block copolymers containing various functionality, as mentioned above.

A method for synthesizing copolymers which vary in composition along their length is to rely on disparate monomer reactivity ratios, and the consequent composition drift with conversion, to create a gradient or tapered copolymer.^{15,16} For example, copolymerization of a 1:0.91 (mole ratio) mixture of MMA and BA ($r_{\text{MMA}} \approx 1.7$ and $r_{\text{BA}} \approx 0.2$)¹⁷ in the presence of cumyl dithiobenzoate (**1c**) provides a narrow polydispersity copolymer with a gradient in composition of [MMA]/[BA] from ca. 1:0.45 to ca. 2:1.¹⁸ The overall composition of the copolymer was the same as that of a copolymer prepared in the absence of **1c**.

Two strategies may be adopted for triblock synthesis. The first is to simply add further monomer to a preformed AB diblock. To establish this process, a poly-

Scheme 3



(benzyl methacrylate-*block*-dimethylaminoethyl methacrylate) ($\bar{M}_n = 3500$; $\bar{M}_w/\bar{M}_n = 1.06$) was converted to poly(benzyl methacrylate-*block* 2-(dimethylamino)ethyl methacrylate-*block*-*tert*-butyl methacrylate) ($\bar{M}_n = 8250$; $\bar{M}_w/\bar{M}_n = 1.12$).

The second approach, which is suited to ABA triblock synthesis, is to start with a difunctional transfer agent (e.g., **3**) so that the two arms are grown simultaneously as shown in Scheme 3. Examples of the use of this strategy to form hard–soft–hard ABA triblocks are provided in Table 2 and Figure 1c.

More complex architectures (stars, grafts) are also possible by using the appropriate precursor containing multiple thiocarbonylthio groups.⁸ For example, the compounds **4** and **5**, respectively (see Scheme 4) are precursors to tetrafunctional and hexafunctional star polymers. Polymerization gives a narrow polydispersity product, and NMR analysis shows that all dithioester groups have reacted.

Blocks with polymers formed by other (nonradical) mechanisms can also be synthesized by applying the RAFT process. Thus, the acid functional dithioester (**1d**) was coupled with poly(ethylene oxide) monomethyl ether (**6**) with the aid of dicyclohexyl carbodiimide (DCC) to provide a polymeric dithioester (**7**) which was then used in block synthesis with either styrene or benzyl methacrylate (Scheme 5). The block copolymers (e.g., **8**) had very narrow polydispersity (see Table 1) and

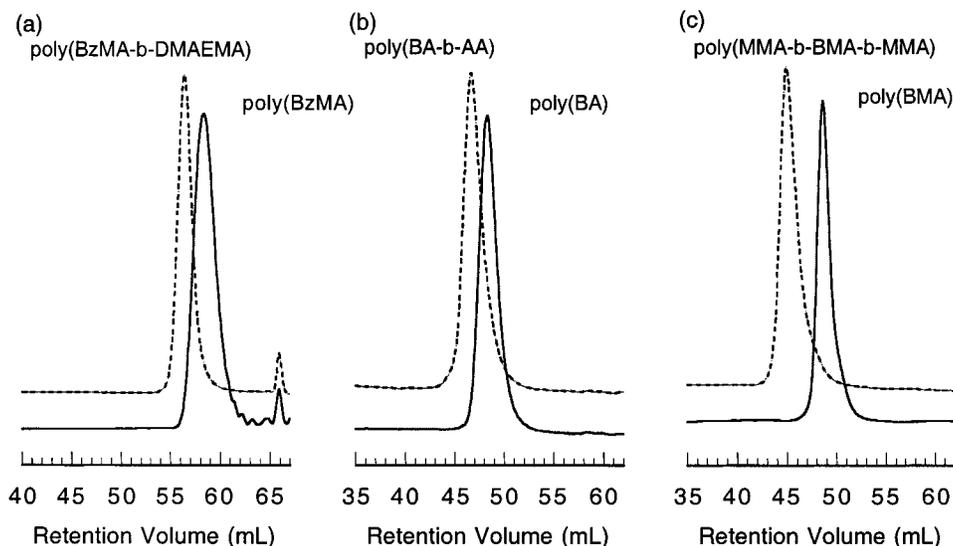
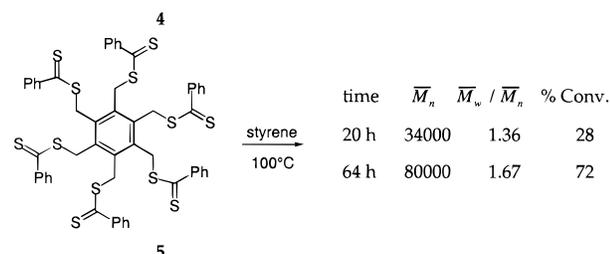
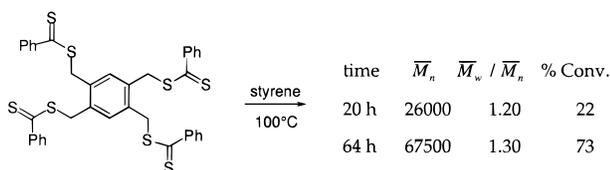
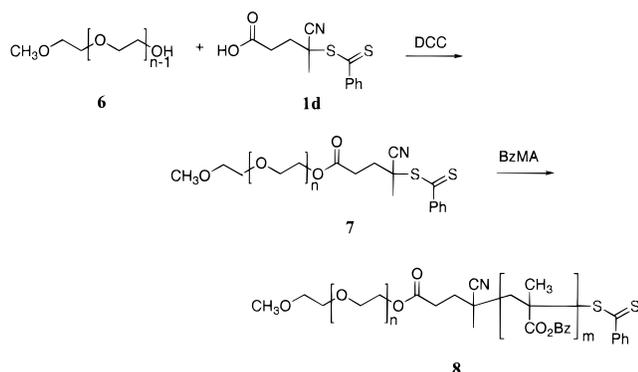


Figure 1. GPC traces for (a) poly(benzyl methacrylate) and poly(benzyl methacrylate-*block* 2-(dimethylamino)ethyl methacrylate),¹² (b) methylated poly(butyl acrylate-*block*-acrylic acid), and (c) poly(butyl methacrylate) and poly(methyl methacrylate-*block*-butyl methacrylate-*block*-methyl methacrylate).¹¹ For details on molecular weight refer to Tables 1 or 2. For details of GPC analysis see footnotes b and d of Table 1.

Scheme 4



Scheme 5



contained no detectable EO homopolymer impurity. Previous attempts to use living radical polymerization to make poly(styrene-*block*-ethylene oxide) (e.g., atom transfer radical polymerization,¹⁹ nitroxide-mediated polymerization,²⁰ or through the use of photoinitiators^{21,22}) have met with only limited success (low yield or a product of broad polydispersity or both).

The structure of block copolymers (see Tables 1 and 2) has in each case been proved by chromatographic or spectroscopic analysis or both (¹H NMR and UV/vis).

The GPC traces shown in Figure 1 provide three examples of the clean conversion of thiocarbonylthio-terminated polymers into block copolymers. Parts a and b of Figure 1 show examples of diblocks of differing molecular weight and composition. The B blocks are composed of monomers that have traditionally been considered difficult (DMAEMA¹² and AA). Figure 1c shows an ABA triblock.¹¹ In each case, the polymerizations providing the final block was taken to high conversion.

The examples discussed above serve to demonstrate the versatility of RAFT polymerization as a process for the synthesis of block copolymers and other polymers of complex architecture. Further details will be provided in forthcoming publications.

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References and Notes

- (1) The use of the adjective "living" to describe a radical polymerization which displays the attributes of a living polymerization is preferred over other terms that have been advocated in this context (e.g., "controlled", "living/controlled", "pseudo living", or "living polymerization with reversible deactivation"), even though some side reactions (radical-radical termination) must inevitably complicate the process.
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- (10) Portions of this work were presented at the IUPAC World Polymer Congress, Gold Coast, Australia in July 1998. Thang, S. H.; Chong, Y. K.; Ercole, F.; Le, T. P. T.; Moad, G.; Rizzardo, E. In *World Polymer Congress Preprints*; RACI, Polymer Division: Brisbane, 1998; p 142.
- (11) Synthesis of poly(methyl methacrylate-*block*-butyl methacrylate-*block*-methyl methacrylate). B block: A solution of AIBN (2.5 mg), *n*-butyl methacrylate (3.8 mL), 1,4-bis-(dithiobenzoylprop-2-yl)benzene (**7**) (93.5 mg) in benzene (1.2 mL) was placed in an ampule, and the contents were degassed, sealed, and heated at 60 °C for 16 h to give poly(*n*-butyl methacrylate) (conversion, 49%). A block: A solution of the above poly(*n*-butyl methacrylate) (300 mg; precipitated from methanol to remove residual initiator), AIBN (0.51 mg), and methyl methacrylate (0.75 mL) in benzene (0.25 mL) was degassed, sealed, and heated at 60 °C for 16 h to provide the triblock copolymer (conversion of methyl methacrylate, >95%). GPC data for these polymers are shown in Table 2 and Figure 1c.
- (12) Synthesis of poly(benzyl methacrylate-*block* 2-(dimethylamino)ethyl methacrylate). A block: A solution of cumyl dithiobenzoate (**1c**) (2 g), azobis(isobutyronitrile) (101 mg) in benzyl methacrylate (15 mL), and benzene (5 mL) was degassed through three freeze-thaw-evacuate cycles, sealed under vacuum, and heated in a constant-temperature bath at 60 °C for 88 h. B block: A solution of dithiobenzoate-terminated poly(benzyl methacrylate) (0.4 g), azobis(isobutyronitrile) (4 mg), and 2-(*N,N*-dimethylamino)ethyl methacrylate (0.4 g) in ethyl acetate (2 mL) was degassed through three freeze-thaw-evacuate cycles, sealed under vacuum, and heated in a constant-temperature bath at 60 °C for 24 h. Removal of the solvent provided the diblock copolymer. Details of molecular weight are provide in Table 1 and Figure 1a.
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- (18) MMA/BA (mole ratio, 1:0.91) copolymerization in benzene (33% v/v) in the presence of **1c** (0.008 M) with AIBN initiator (0.002 M). At 22% conversion, $\bar{M}_n = 16\,800$, $\bar{M}_w/\bar{M}_n = 1.08$, and the cumulative $[MMA]/[BA] = 1:0.45$ from $^1\text{H NMR}$. At 93% conversion, $\bar{M}_n = 75\,400$, $\bar{M}_w/\bar{M}_n = 1.21$, and the cumulative $[MMA]/[BA] = 1:0.8$.
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