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Living Free Radical Polymerization with Reversible Addition–Fragmentation Chain Transfer (RAFT Polymerization): Approaches to Star Polymers

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ABSTRACT: The synthesis of multiarm star polymers by radical polymerization with reversible addition–fragmentation chain transfer (RAFT) is described. When the precursor RAFT agents to star polymers are trithiocarbonate derived, fragmentation of the radical intermediate can lead to different products depending on the leaving abilities of the two groups attached to sulfur. To demonstrate this, two types of RAFT agents, ones that allow growth of arms away from the core and the other attached to the core during propagation, were designed, and an example of each was synthesized. While both star RAFT agents gave excellent molecular weight control and low polydispersities (typically <1.2), the one that grows its arms away from the core offers polymers free from star–star coupled products. Thus, the direction of fragmentation should be considered when designing efficient star RAFT agents. The living nature of the arms of these polymers was demonstrated by extending the arms with a different monomer to afford a star block copolymer. The RAFT agents described are easily synthesized from commercially available reagents by a simple experimental procedure.

Introduction

Multiarm polymers including stars, microgels, and dendritic polymers have attracted considerable attention in recent years.¹ Much of this interest originates from the discovery that these polymers have lower bulk and solution viscosities compared to those of linear analogues of the same molecular weight.^{2–5} The reason for this decrease is attributed to the greater dependence of the viscosity on the molecular weight of each arm as compared to the total molecular weight of the star polymer. The rheological behavior of well-defined star-shaped polymers has been extensively studied in recent years.⁶ Multiarm polymers are also capable of containing a higher degree of end group functionality compared to linear polymers of similar molecular weight, and this is useful in many specialized applications. Several recent reviews have been written on the syntheses of these types of polymers and their properties in dilute solution.^{7,8}

Although preparation of star polymers has been documented as early as 1948 by Schaefgen and Flory,⁹ the preparation of well-defined multiarm polymers remained a challenge until the advent of living polymerization techniques. This is because precise control of the polymerization is crucial to the synthesis of such multiarm polymers. With the discovery of living anionic polymerization, Morton and co-workers in 1956¹⁰ were able to take advantage of the method to synthesize well-defined four-armed polystyrenes for the first time by neutralizing living poly(styryllithium) with tetrachlorosilane. Although the product was a mixture of four- and three-arm stars, this work eventually led to many

researchers taking on the challenge. As a consequence, the use of anionic living polymerization for the preparation of star polymers dominates the current literature.

Regardless of the method of polymerization (ionic, metathesis, group transfer, or radical), preparations of star polymers described in the literature can be categorized into two broad approaches, namely, (i) the arms first and (ii) the core first approaches. In the “arms first” approach the linear arms of the star polymer are synthesized first followed by binding of the arms to form the core. The binding of the arms is achieved by using either a difunctional monomer (e.g., divinylbenzene) or a multifunctional terminating agent (e.g., tetrachlorosilane). The “core first” method involves the synthesis of a multifunctional initiator (the core) followed by the extension of arms by monomer addition.

The applicability of living/controlled radical polymerization techniques in the synthesis of star polymers is well documented in the literature.¹¹ Of those that use the arms first approach, atom transfer radical polymerization (ATRP),¹² nitroxide-mediated polymerization,¹³ and iniferter techniques¹⁴ with divinylbenzene as a binder of the core are prominent. Difunctional monomers have often been used to produce styrene microgels,¹⁵ which are star polymers with unlimited arms and have more than 40% mass concentrated in the core. Methods to prepare microgels using reversible addition–fragmentation chain transfer (RAFT) polymerization¹⁶ were reported recently.

The core first approach dominates the preparation of star polymers by free radical processes. Matyjaszewski and co-workers have explored the efficiency of a number of multifunctional initiators in the polymerizations of styrene, methyl acrylate, and methyl methacrylate by atom transfer radical polymerization (ATRP).¹² Star polymers with up to eight arms and dendrimer type multiarm polymers^{17–19} have been prepared using ATRP recently. Pugh et al.,²⁰ Sawamoto et al.,^{21,22} Gnanou et

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al.,²³ and Hawker et al.¹⁷ have also contributed much to this area. Use of nitroxide-mediated living polymerization in the construction of star polymers has been recently reviewed by Hawker et al.²⁴

In other related work, star polymers have been synthesized by the use of multifunctional iniferters (initiator transfer agent terminator). Kuriyama and Otsu have described the preparation of four-arm methyl methacrylate star polymers with the use of a tetrafunctional iniferter.¹⁴ The technique relies on photolytic bond homolysis of a weak carbon–sulfur bond. Upon initiation, the carbon-centered radical propagates by addition to monomer and is subsequently terminated by radical–radical coupling with the original sulfur-centered radical to afford dormant polymer. Use of mercaptans such as pentaerythritol tetramercaptopropionate and other polymercato esters as chain transfer agents is also documented.²⁵

Limitations of current radical polymerization methods in the preparation of multiarm polymers are numerous. One of the most prominent drawbacks with all of the “core first” radical polymerization techniques is star–star coupling at relatively low monomer conversion.²³ This would result in high molecular weight polymer contaminants and may require strenuous methods of purification of the end products. ATRP related methods,²⁶ which rely on core first technique, can be limited to particular types of monomers due to incompatibilities between the initiating system (e.g., organic halide/copper halide/2,2′-bipyridine) with monomer (e.g., (meth)acrylic acid). A comparison of available controlled radical polymerization processes, highlighting the advantages and disadvantages in each, is the subject of a recent review.²⁷

Recently, we demonstrated that thiocarbonyl thio compounds could be used to confer living character to radical polymerization.^{28–30} The thiocarbonyl thio compounds reported include dithioesters,³¹ xanthates,³² dithiocarbamates,^{33,34} and trithiocarbonates.³⁵ In this paper we demonstrate how the process can effectively be used to synthesize star polymers.

Experimental Section

General. Monomers were purified by passage through activity I neutral alumina (to remove inhibitors) followed by fractional distillation and then flash distilled immediately prior to use. Gel permeation chromatography (GPC) was used to establish the molecular weight and molecular weight distribution (polydispersity) of the polymers. A Waters Associates liquid chromatograph equipped with differential refractometer and a set of six Ultrastaygel columns (10⁶, 10⁵, 10⁴, 10³, 500, and 100 Å) was used. Tetrahydrofuran (1.0 mL min^{−1}) was used as eluent. The molecular weights are reported as polystyrene equivalents. Samples for GPC analysis were isolated by evaporation of monomer. No precipitation or fractionation was performed prior to GPC analysis. Flash chromatography was performed using Merck Kieselgel 60 (230–400 mesh ASTM). Glass backed Whatman MK6F pre-coated silica microscopic slide plates with PF₂₅₄ nm indicator were used for thin-layer chromatography. The NMR spectra were recorded on a Bruker AC 200 MHz spectrometer. Tetramethylsilane (TMS) and residual CHCl₃ were used as internal standards for ¹H and ¹³C NMR spectra, respectively.

Synthesis of RAFT Agents. 2,4,5-Tris([methylsulfanyl]carbonothioyl)sulfanyl)methylbenzylmethyl Trithiocarbonate (**1**). 1,2,4,5-Tetrakis(bromomethyl)benzene (0.45 g, 1 mmol) dissolved in 15 mL of THF was added over 30 min to a partially soluble suspension of sodium methyl trithiocarbonate (see below) (0.88 g, 6 mmol) in THF (7 mL). The solution was allowed to stir for 12 h before adding 20 mL of water and 20

mL of ethyl acetate. The organic phase was separated and the aqueous layer extracted with ethyl acetate (2 × 20 mL). The solution of combined organic phases was washed with brine (20 mL), dried with MgSO₄, and filtered, and the solvent was evaporated under reduced pressure. The crude product (yellow crystalline) was purified by flash chromatography on silica, using 20% ethyl acetate in petroleum spirits as eluent, to afford the title compound (0.47 g, 76%). ¹H NMR: δ 2.8 (12H, SCH₃), 4.6 (8H, benzyl CH₂), 7.4 (2H, ArH).

Pentaerythritoltetrakis(3-(S-benzyltrithiocarbonyl)propionate) (2). Triethylamine (4.04 g, 40 mmol) in 10 mL of CHCl₃ was added dropwise to a stirred solution of pentaerythritol (3-mercaptopropionate) (2.44 g, 5 mmol) and carbon disulfide (3.04 g, 40 mmol) in CHCl₃ (15 mL) at room temperature. The solution gradually turned deep yellow during the addition. The solution was allowed to stir for an additional 1 h. Benzyl bromide (3.76 g, 22 mmol) dissolved in 10 mL of CHCl₃ was added dropwise, and the solution was stirred for a further 2 h. The mixture was poured into a cold solution of 10% aqueous HCl and extracted three times with ethyl acetate to afford a thick yellow oil. The oil was purified by column chromatography using 30% ethyl acetate in petroleum spirits as eluent to obtain the title compound (4.22 g, 73%). ¹H NMR: δ 2.9 (8H, CH₂), 3.6 (8H, CH₂), 4.2 (8H, CH₂), 4.6 (8H, benzyl CH₂), 7.3 (20H, ArH).

Sodium Methyltrithiocarbonate. Carbon disulfide (9.1 g, 0.12 mol) in diethyl ether (100 mL) was added dropwise over 30 min to a suspension of sodium methanethiolate (7 g, 0.1 mol) in diethyl ether (300 mL) at room temperature. The solution was stirred for 2 h and the solvent removed. The residue was extracted three times with ethyl acetate to afford the product (13.4 g, 92%). The crude product was used without further purification.

Styrene Polymerizations. A typical preparation (entries 5 and 6, Table 1) of star polystyrene using RAFT agents is as follows: The RAFT agent (**2**) (42.19 mg, 36.6 × 10^{−6} mol) was dissolved in 5.0 mL of freshly flash distilled styrene. Aliquots of 2.0 mL of this solution were placed in glass ampules, degassed three times with freeze, evacuate, thaw cycles, and flame-sealed. The glass tubes were heated at 110 °C for 6 and 20 h and opened, and the contents were dissolved in THF. The mixture was transferred to a round-bottom flask, and the volatiles were removed to constant weight to afford star polystyrene in 25% and 63% conversion, respectively. The polymer samples were subsequently analyzed by GPC.

MA Polymerizations. A typical preparation (entries 11–13, Table 1) of star poly(methyl acrylate) is as follows: Two stock solutions, (1) RAFT agent (**2**) (49.08 mg, 42.6 × 10^{−6} mol) in 5.0 mL of methyl acrylate and (2) 3 mg of AIBN in 20.0 mL of benzene, were prepared. Aliquots of 1.0 mL of stock solution 1 and 4.0 mL of stock solution 2 were placed in each glass ampule, degassed three times with freeze, evacuate, thaw cycles, and flame-sealed. The glass tubes were heated at 60 °C for 4, 8, and 16 h. The tubes were opened, the contents were dissolved in THF and transferred to a round-bottom flask, and the volatiles were removed to constant weight to afford polymers with conversions 34%, 50%, and 79%, respectively. The polymer samples were subsequently analyzed by GPC.

Star Block Copolymers. A typical preparation of *star*-(PMA-block-PS)₄ block copolymer is as follows. A sample four-arm polystyrene (*M*_n 25 550, *M*_w/*M*_n 1.18) (107 mg, 4.19 × 10^{−6} mol) (see Table 3) prepared according to the above procedure was dissolved in 2.0 mL of MA and labeled stock solution 1. An aliquot of 1.0 mL of this solution was added to an ampule containing 4.0 mL of stock solution 2, prepared by dissolving AIBN (3 mg) in 20.0 mL of benzene. The mixture was degassed three times with freeze, evacuate, thaw cycles and flame-sealed. The glass tubes were heated at 60 °C for 4 and 8 h; the volatiles were removed and dried to constant weight. The polymer samples were analyzed by GPC, and the results are shown in Table 3.

Cleavage of Arms of Star Polymers. A typical procedure for entry 1 in Table 2 is as follows. A sample of *star*-PS (100 mg) was dissolved in 5 mL of THF and piperidine (~100 μL) added. The solution was stirred at room temperature for 10

Table 1. Molecular Weight/Conversion Data for Star Polymers Formed by Polymerization of Various Monomers in the Presence of Compounds 1 and 2^a

entry	monomer ^b (concn in benzene, °C)	dithio compd (M × 10 ³)	initiator ^c (M × 10 ²)	time (h)	M _n ^d	M _n (calcd) ^e	M _w /M _n	conv ^f (%)
1	styrene (bulk, 110)	1 (7.3)	thermal ^g	6	24 300	30 800	1.09	24
2				22	54 800	89 000	1.08	71
3				30	57 000	103 500	1.07	83
4				48	70 700	117 000	1.08	94
5	styrene (bulk, 110)	2 (7.3)	thermal ^g	6	25 600	31 700	1.18	25
6				20	63 900	78 700	1.08	63
7				30	77 800 ⁱ	102 800	1.07 ^j	82
8				48	92 000 ⁱ	119 700	1.07 ^j	96
9	MA (2.22 M, 60)	1 (0.43)	AIBN (0.073)	4	161 000 ⁱ		1.64	51
10				16	250 800 ⁱ		1.94	76
11	MA (2.22 M, 60)	2 (1.70)	AIBN (0.073)	4	37 200	38 900	1.10	34
12				8	53 700	57 700	1.08	50
13				16	73 000	89 400	1.14 ^h	79

^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: (monomers) MMA = methyl methacrylate, MA = methyl acrylate. ^c Abbreviations: AIBN = 2,2'-azobis(2-cyanopropane); VAZO-88 = 1,1'-azobis(1-cyclohexanecarbonitrile). ^d 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). System 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: $M_n(\text{calc}) = ([\text{monomer}]/[\text{CTA}]) \times \text{conversion} \times \text{MW of monomer}$. The above 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 a limiting conversion. ^g No added initiator. ^h Includes low molecular weight tail. ⁱ Trimodal distributions. ^j The values shown are excluding the low molecular weight hump.

Table 2. Molecular Weight Data for Linear Polymers Formed by Cleaving the Arms of Star Polymers Using Piperidine at Room Temperature

entry	polymer	M _n	M _n (calcd)	M _w /M _n	conv (%)
1	star P(Sty) 8	63 900	78700	1.08	63
2	linear P(Sty) 10	18 750	4 × 18750 + 660 = 75660	1.19	quantitative recovery
3	star P(MA) 9	101 200	130000	1.19	29
4	linear P(MA) 11	30 500	4 × 30500 + 660 = 122660	1.37	quantitative recovery

Table 3. Molecular Weight/Conversion Data for star-(PMA-block-PS)₄ Prepared Using 9

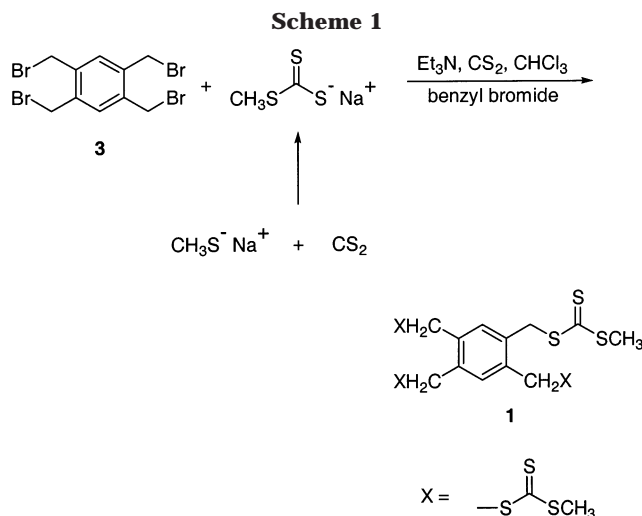
entry	monomer (concn in benzene, °C)	dithio compd (M × 10 ³)	initiator (M × 10 ²)	time (h)	M _n	M _w /M _n	conv (%)
1	first block styrene (bulk, 110)	2 (7.3)	thermal	6	25 550	1.18	25
2	second block MA (2.22 M, 60)	first block (0.42)	AIBN (0.073)	4	87 700	1.24	26
3				8	129 600	1.23	46

h, and the volatiles were removed under reduced pressure. The crude residue after drying to constant weight was analyzed by GPC.

Results and Discussion

Syntheses of RAFT Agents. The challenge in the preparation of star polymers by radical polymerization with RAFT rests in part on the successful design and synthesis of the multiarmed RAFT agents. Some of the important factors to consider are steric congestion at the reactive sites (the thiocarbonyl group), the ways in which fragmentation could occur, the various types of impurity star and/or linear polymer that can result based on the envisaged mechanism, and the ease of synthesis of the chain transfer agents.

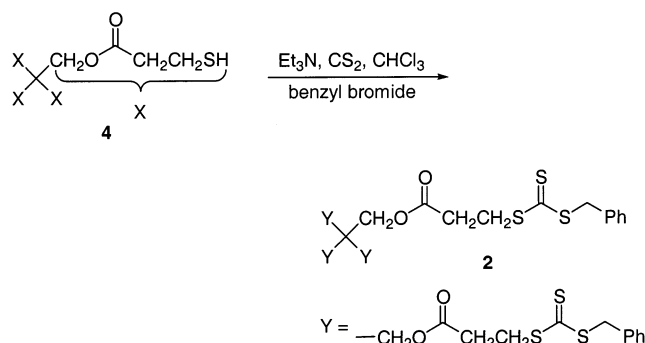
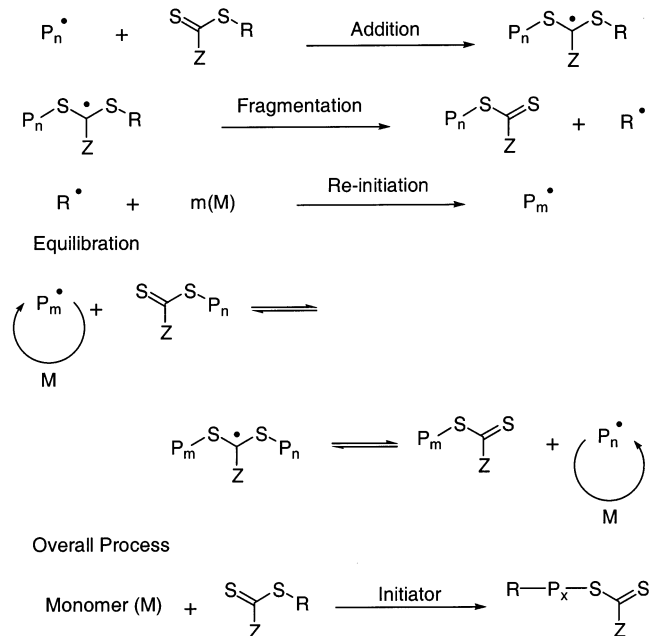
Taking these factors into consideration, we have synthesized the RAFT agents **1** and **2**, both having the trithiocarbonate moiety as the active function and a benzyl moiety as the leaving group. The methods used for the syntheses of these chain transfer agents are simple and use inexpensive commercial reagents, and the reactions are high yielding. Scheme 1 illustrates the one-pot procedure used to synthesize compound **1** in 76% yield. It is important, in carrying out this reaction, to add the tetrabromobenzyl compound (**3**) to a suspension of the sodium salt of the methyl trithiocarbonate over the period specified in the procedure, as it would



ensure all four arms being functionalized. The sodium salt of the methyl trithiocarbonate can be either prepared in situ or presynthesized as it is stable at room temperature for extended periods of time.

Similarly, the one-pot preparation of compound **2** involves the addition of carbon disulfide to a solution of the commercially available tetrathiol **4** and triethylamine (Scheme 2). Alkylation of the resulting am-

Scheme 2

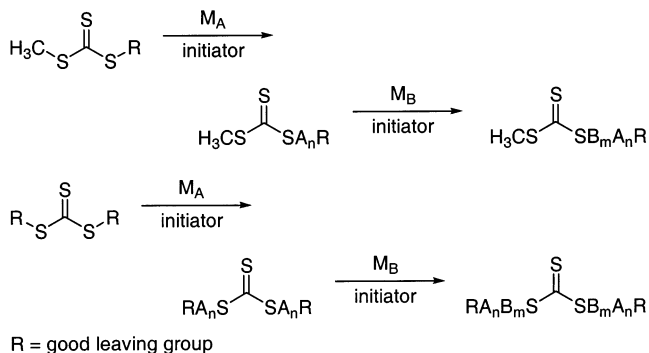
Scheme 3. RAFT Process^a

^a M is monomer; R is a radical that can initiate polymerization; P_n, P_m, and P_x are polymer chains.

monium salt with benzyl bromide affords the desired tetraarm RAFT agent (2) in good yield.

Mechanism of RAFT Polymerization. Radical polymerization with reversible addition–fragmentation chain transfer (RAFT) is a living process reported recently.^{28–35} The mechanism by which the process imparts living character to the polymerization is shown in Scheme 3 and is carried out by simply introducing a suitable thiocarbonylthio compound to an otherwise conventional radical polymerization. During the first stages of the polymerization the RAFT agent (ZC=SSR) is consumed by propagating radicals by an addition–fragmentation mechanism. The fragmented radical (R[•]) reinitiates polymerization, resulting in new propagating radicals which then take part in the equilibrium established between the dormant polymer and active chains. The equilibration process allows all chains produced to grow in a uniform manner, resulting in narrow polydispersity polymers. The nature of the Z and R groups is crucial to the success of the polymerization. The results of an investigation on their effects will be published shortly.^{36,37}

Various types of effective RAFT agents have been reported to date. These include dithioesters, dithiocarbamates, and trithiocarbonates.^{28–35} Of these, trithiocarbonates were shown to have useful structural char-

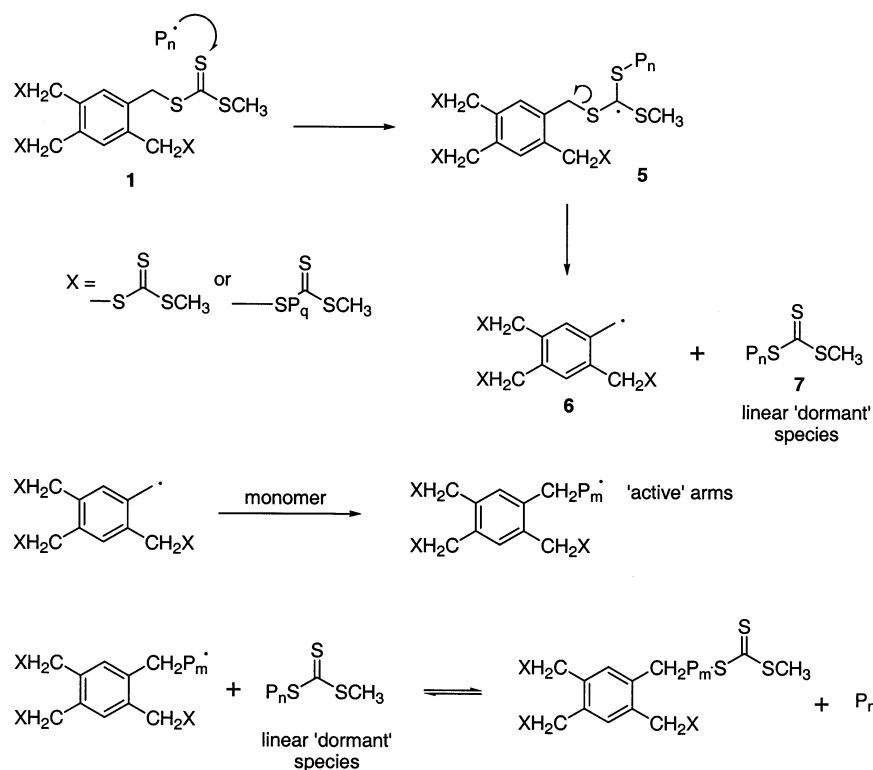
Scheme 4^a

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

acteristics as they can accommodate either one or two leaving groups attached to the sulfur atoms (Scheme 4). Depending on the leaving ability of these groups, polymers having a trithiocarbonate moiety incorporated in the middle of the polymer or at the terminus can be synthesized. The ability to prepare ABA triblock copolymers in two steps from those that have two good leaving groups is one of the advantages of trithiocarbonates reported recently.³⁵ When used in the preparation of star polymers, the ability to control the way in which the RAFT agent can fragment can be used to advantage. This allows the preparation of star polymers of controlled molecular weight and narrow polydispersity, free from star–star coupled impurities.

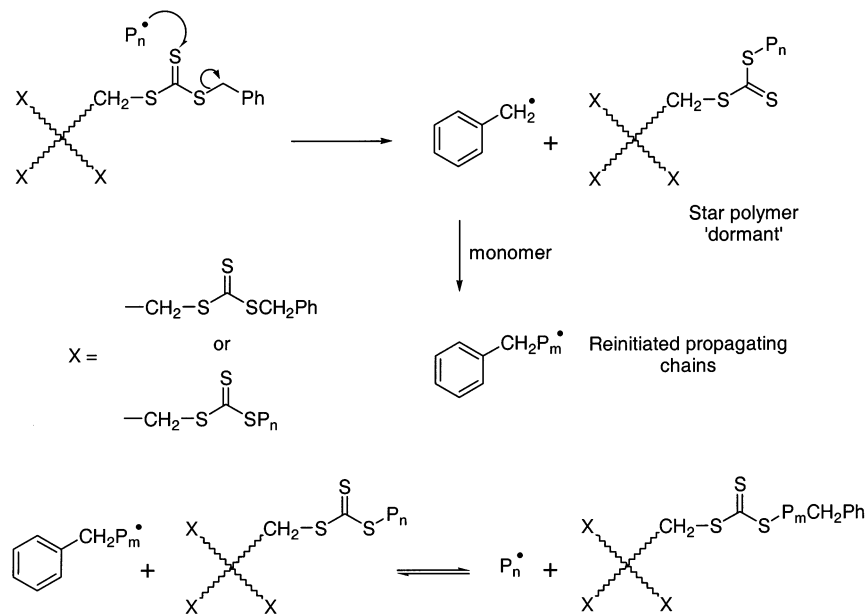
Polymerizations. As briefly described above (see Scheme 4), control in the direction of fragmentation can be used to advantage in the syntheses of star polymers with trithiocarbonates. Because each arm is tied at the core of the molecule (compounds 1 and 2), the way in which fragmentation of the intermediate radical occurs is important as one would result in a propagating radical attached and the other detached from the core of the molecule. The direction of fragmentation of the intermediate following radical attack at the thiocarbonyl group is controlled by the leaving ability of the groups attached to the two sulfur atoms of the trithiocarbonate moiety. The leaving ability of a group is dependent on the combination of a number of factors such as thermodynamic (bond strength of the forming and the breaking bond), steric (presence of bulky substituents), electronic effects of the substituents directly attached to the leaving carbon center (electron withdrawing and releasing abilities of groups), and the stability of the radical formed. From experience^{38,39} it is known that methyl radicals, being primary, are poor leaving groups relative to secondary benzyl radicals. The latter radicals also have the effect of being stabilized by the aromatic ring through electron delocalization; however, they are sufficiently reactive to undergo addition reactions which makes them suitable as initiators in radical polymerizations. Having detailed the mixture of complex factors that influence fragmentation, in RAFT polymerization, it is the relative stability/leaving ability of the adding vs the fragmenting (leaving) radicals that is important.^{32,36,37,40} As described earlier, rapid consumption of the RAFT agent is crucial to the success of the reaction.

The first type of the proposed RAFT agents, e.g. 1 where the leaving group following fragmentation is bound to the central core of the polymer, is shown in Scheme 5. The resulting intermediate radical 5, formed by addition at the sulfur of the thiocarbonyl group,

Scheme 5^a

^a P_n , P_m , and P_q are polymer chains.

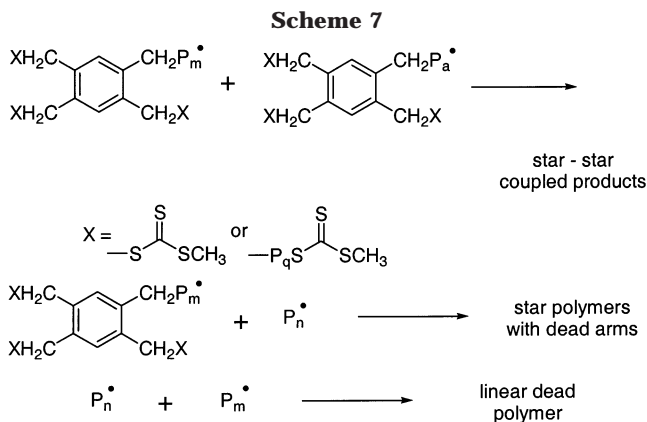
Scheme 6



fragments at the benzyl–sulfur bond since methyl radicals are relatively poor radical leaving groups, as described earlier. Upon fragmentation the benzylic radical **6** adds to monomer, resulting in a propagating arm attached to the core. Propagation ceases either upon exchange of a trithiocarbonate moiety from living linear dormant chains, as illustrated in Scheme 5 (or from a dormant chain attached to the core, in which case resulting in another propagating arm), or by radical–radical termination. While the former process allows equal chances for arms to grow to similar length, the latter process is minimized by design by having a low concentration of radicals in solution, as required by the

concept of “living” radical polymerization. Thus, it is clear that at any one moment in time each polymer arm of such a transfer agent may be “active” (propagating) or “dormant” (capped with the trithiocarbonate moiety).

On the other hand, the second type of multiarm RAFT agent shown in Scheme 6, e.g. **2**, following fragmentation results in a benzyl radical detached from the core. Again, fragmentation of the $\text{CH}_2\text{—S}$ bond is highly unfavorable compared to the S—benzyl bond. Thus, unlike with the previous case, the benzyl radicals that reinitiate polymerization do so away from the star polymer and result in linear propagating chains. With the linear propagating chains in equilibrium with the



arms of the star polymer, the arms of the polymer grow in a controlled manner. What is important to note with these types of RAFT agents is that the arms of the star polymer at all times are dormant, and growth of arms always occurs away from the core as linear propagating species.

Mechanistically, the number of possible side reactions that can produce impurity polymers from growing arms attached to the core is greater than the alternative method, i.e., growing arms away from the core. Since termination reactions cannot be totally eliminated in radical polymerization, most of these impurities are as a result of such reactions, despite careful selection of reaction conditions. With star RAFT agents similar to **1**, two types of active propagating species, ones that are attached to the core and linear chains resulting from continuous initiation, can exist at a given moment in time. Radical–radical termination resulting from these species can thus produce star–star coupled polymers, star polymers with dead arms, and linear dead polymers (see Scheme 7). In addition, linear polymer capped with the trithiocarbonate moiety is also a byproduct (see Scheme 5). On the other hand, with RAFT agent **2** the dead polymer produced as a result of termination is limited to only linear polymer. Neither star–star coupled products nor linear species capped with the active functionality are possible with such RAFT agents.

Typical GPC chromatograms for the polymerization of styrene using RAFT agent **1** are shown in Figure 1. Initial formation of relatively broader polydispersity star polymer (Figure 1, trace a) and the subsequent narrowing of the polymer arms as RAFT equilibration takes effect are clearly noticeable from the GPC chromatograms and from the results in Table 1. The polydispersity, despite the multimodal distributions, remains low at 1.07, including the leading hump, and 1.21 with both impurities taken into account at near quantitative conversion (48 h). The leading hump (on the high molecular weight end) in the 48 h trace (Figure 1) is approximately double the peak molecular weight (M_p) of the main peak and is attributed to star–star coupled products as discussed before. The possibility of coupling more than two cores with one another does exist; however, statistically this has a very low probability and, if any occurs, may not be detected by GPC. The tailing hump in the low molecular weight end of the chromatogram is believed to be due to linear dormant chains and polymer from radical–radical termination of linear propagating radicals.

The GPC chromatograms resulting from polymerization of styrene in the presence of RAFT agent **2** show

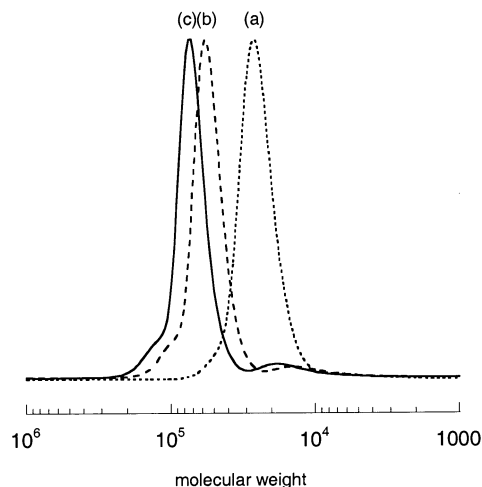


Figure 1. GPC chromatograms for the polymerization of styrene in the presence of RAFT agent **1**: (a) $M_n = 24\,300$, $M_w/M_n = 1.09$, 6 h (Table 1, entry 1); (b) $M_n = 54\,800$, $M_w/M_n = 1.08$, 22 h (Table 1, entry 2); (c) $M_n = 70\,700$, $M_w/M_n = 1.07$, 48 h (Table 1, entry 4).

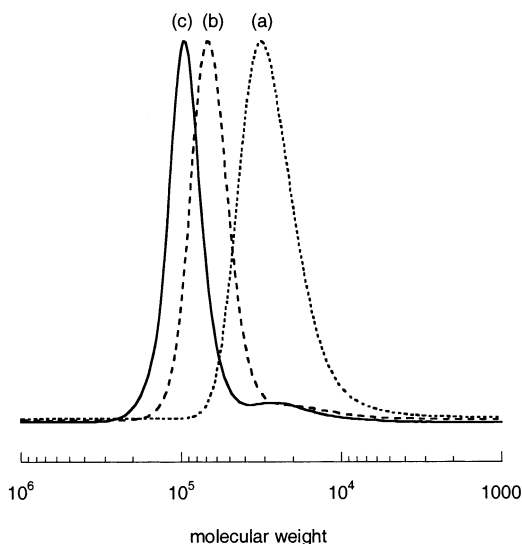


Figure 2. GPC chromatogram for the polymerization of styrene in the presence of RAFT agent **2**: (a) $M_n = 25\,600$, $M_w/M_n = 1.18$, 6 h (Table 1, entry 5); (b) $M_n = 63\,900$, $M_w/M_n = 1.08$, 20 h (Table 1, entry 6); (c) $M_n = 92\,000$, $M_w/M_n = 1.07$, 48 h (Table 1, entry 8). The M_n and M_w/M_n values stated are measured excluding the low molecular weight peak.

much cleaner product polymers as expected (Figure 2). Judging from the peak shapes, formation of star–star coupled byproducts is not evident. The only impurity that exists in the crude mixture is the low molecular weight species, formed by the continuous radical–radical termination of linear propagating radicals during the polymerization.

Free radical polymerizations of methyl acrylate with RAFT agents often yield good control and afford polymers with low polydispersity that are free from impurities at moderate conversions. However, if the polymerizations are allowed to proceed to higher conversions (over 60% approximately), the resulting polymer often becomes contaminated with a broadly dispersed byproduct, approximately twice the molecular weight of the main narrow peak. It becomes pronounced at low concentrations of RAFT agent with the polymerization carried to high conversion. Increasing the concentration of the RAFT agent has the effect of total elimination of

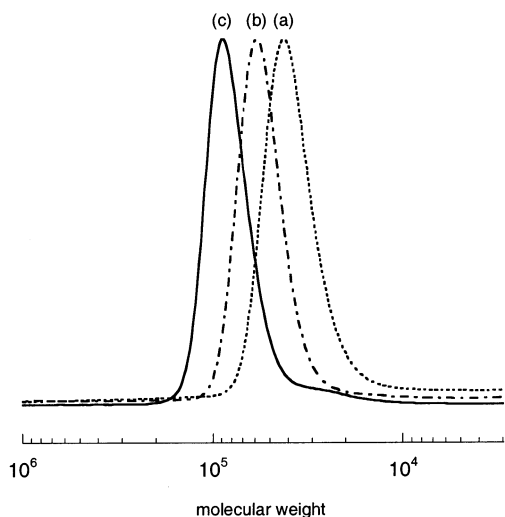


Figure 3. GPC chromatogram for the polymerization of methyl acrylate in the presence of RAFT agent **2**: (a) $M_n = 37\,200$, $M_w/M_n = 1.10$, 4 h (Table 1, entry 11); (b) $M_n = 53\,700$, $M_w/M_n = 1.08$, 8 h (Table 1, entry 12); (c) $M_n = 73\,000$, $M_w/M_n = 1.14$, 16 h (Table 1, entry 13).

this impurity at the expense of lowering molecular weight of the resulting polymer. The mechanism of this side reaction is yet to be defined; however, a fraction of the byproduct is believed to result from radical–radical termination of propagating species. In some cases it has been established that the hump contains the dithioester chromophore (unpublished results), indicating the presence of dormant chains among the dead chains.

With the star RAFT agent **2** we have observed the byproduct to be on the low molecular weight side of the chromatogram and approximately half the molecular weight of the star polymer (or twice the molecular weight of each arm of the star polymer). Since with RAFT agent **2** the growth of arms always occurs as linear species, radical–radical combination would result in dead polymer with half the molecular weight of the 4-arm star polymer (or twice the molecular weight of each arm). The low molecular weight impurity polymer is minimized by increasing the concentration of the RAFT agent while keeping the monomer and initiator concentrations constant. The GPC chromatograms of products obtained are shown in Figure 3, and the data are listed in Table 1 (entries 11–13). Polymerization of MA in the presence of RAFT agent **1** and taken to over 50% conversion affords product polymers having trimodal distributions due to star–star coupling (Table 1, entries 9 and 10).

A living polymerization is characterized by narrow polydispersity products, linear increase in molecular weight with conversion, predictability of molecular weight based on the ratio of monomer consumed to the amount of RAFT agent used, and the ability to extend the chains by sequential addition of monomer. First, the star polystyrene and poly(methyl acrylate) prepared using star RAFT agents have low polydispersity which narrows with conversion of monomer (Table 1). The GPC chromatograms of some of the results are shown in Figures 1–3. Second, a linear increase in molecular weight with conversion was observed for each of the multiarm RAFT agents **1** and **2** during polymerization of both styrene and methyl acrylate. A typical plot for the polymerization of styrene in the presence of star RAFT agent **2** is shown in Figure 4.

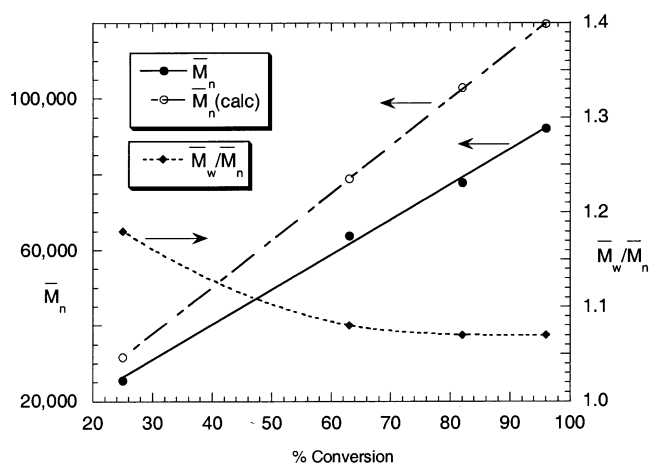
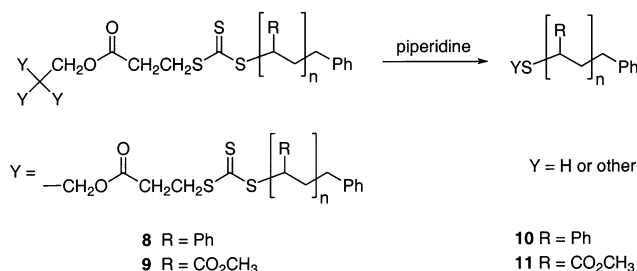


Figure 4. Evolution of molecular weight with conversion for the polymerization of styrene in the presence of RAFT agent **2** (Table 1, entries 5–8).

Scheme 8



The most notable observation from Figure 4 is the marked deviation of the GPC molecular weight from the theoretical molecular weight. The latter is calculated based on the formula $M_n(\text{calc}) = \{[\text{monomer}]/[\text{RAFT agent}]\} \times \text{MW}(\text{monomer}) \times \text{fractional conversion} + \text{MW}(\text{RAFT agent})$. From Figure 4, the difference between the two values is observed to widen with the increase in the molecular weight of the polymer. In our earlier publications,^{28–35} RAFT polymerization with monofunctionalized RAFT agents has been demonstrated to be “living”. RAFT polymerizations with multifunctional RAFT agents **1** and **2** also satisfy the conditions of a living polymerization. They offer narrow polydispersity polymers, have a linear molecular weight–conversion profile, and have the ability to form star block copolymers with sequential addition of monomer (see below). The exception is that the difference between the predicted and the measured molecular weight increases with the molecular weight of the polymer. The difference in physical characteristics of star-shaped polymers (such as lower hydrodynamic volumes of the star polymers compared to linear polymer) and the linear polystyrene standards used to evaluate their molecular weights is the most likely explanation for this discrepancy.

One way to verify the absolute molecular weight of the star polymers is to cleave the arms and characterize the resulting linear polymer against standards. As the trithiocarbonate link can be cleaved with strong nucleophiles, two samples of star polymers, one a polystyrene **8** of M_n 63 900, $M_n(\text{calc})$ 78 700 (M_w/M_n 1.08) and the other a poly(methyl acrylate) **9** of M_n 101 200, $M_n(\text{calc})$ 130 000 (M_w/M_n 1.19), in separate experiments were treated with piperidine (Scheme 8). The GPC molecular weight of linear polystyrene **10** isolated from the first of these experiments was 18 750 with M_w/M_n 1.19

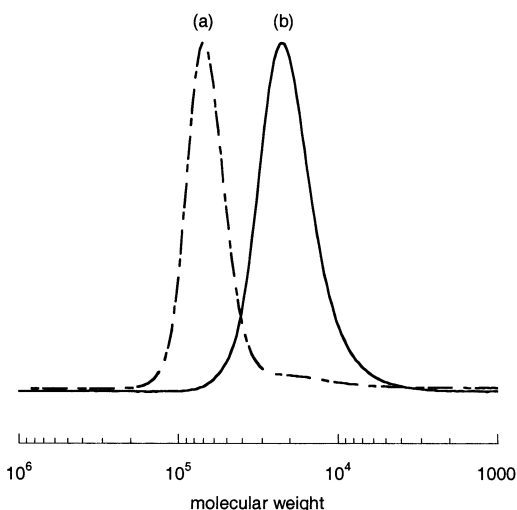


Figure 5. GPC chromatograms of (a) the star polystyrene **8** prepared using **2**: $M_n = 63\,900$, $M_n(\text{calc}) = 78\,700$, $M_w/M_n = 1.08$ (Table 2) and (b) after treatment of polystyrene **8** with piperidine: $M_n = 18\,750$ ($4 \times M_n + M_w$ of core = $4 \times 18\,750 + 660 = 75\,660 \sim M_n(\text{calc})$ of a), $M_w/M_n = 1.19$ (Table 2).

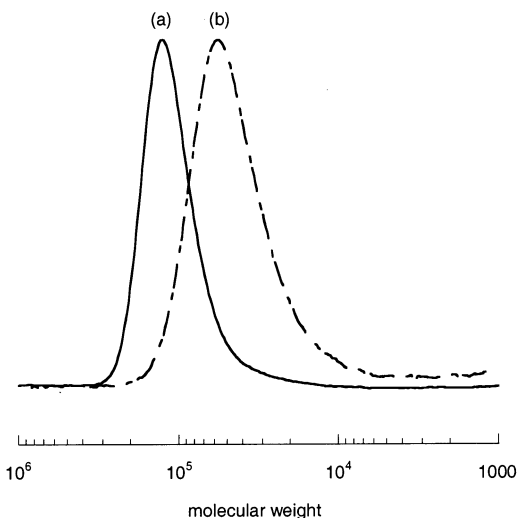


Figure 6. GPC chromatograms of (a) the star poly(methyl acrylate) **9** prepared using **2**: $M_n = 101\,200$, $M_n(\text{calc}) = 130\,000$, $M_w/M_n = 1.19$ (Table 2) and (b) after treatment of poly(methyl acrylate) **9** with piperidine: $M_n = 30\,500$ ($4 \times M_n + M_w$ of core = $4 \times 30\,500 + 660 = 122\,660 \sim M_n(\text{calc})$ of a), $M_w/M_n = 1.37$ (Table 2).

(Figure 5, Table 2). The linear poly(methyl acrylate) **11** in the second experiment was of M_n 30 500 and M_w/M_n 1.37 (Figure 6, Table 2).

The conclusions that can be reached from the above experiments are twofold. First, in each case the molecular weight of the linear product polymer following treatment with piperidine multiplied by the number of arms of the star polymer, four in the above case, is in good agreement with the predicted molecular weight ($M_n(\text{calc})$) of the corresponding star polymer, calculated on the basis of the consumption of monomer. This explains the observed discrepancy between the observed GPC molecular weight and $M_n(\text{calc})$ of star polymers shown in Figure 4. Second, while one would expect the polydispersity of a star polymer to be narrower compared to a linear molecule of similar M_n (see below), the narrow polydispersity before and after cleavage in each experiment demonstrates that all arms of the star polymer have grown to similar molecular weight.

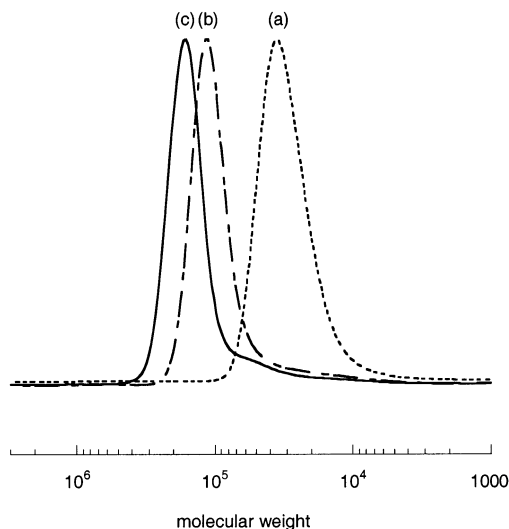


Figure 7. GPC chromatograms of (a) the star-(PS) **9** prepared using **2**, (b) *star*-(PMA-*block*-PS)₄ prepared using **9** heated with AIBN and MA for 4 h (Table 3), and (c) *star*-(PMA-*block*-PS)₄ prepared using **9** heated with AIBN and MA for 8 h (Table 3).

In fact, the small difference in the molecular weight distributions of the linear polymer arms, following cleavage, compared to the star polymer can be attributed to the averaging effect of small differences in molecular weights of the arms. This was predicted in 1948 by Flory et al. and suggested the approximate relationship M_w/M_n (of the star polymer) = $1 + 1/f$, where f is the number of arms of the star polymer.⁹

Having established that all arms of the star polymer have grown to similar molecular weight, we set out to demonstrate that these arms can be extended by sequential addition of monomer. A star block copolymer consisting of an outer polystyrene segment and an inner poly(methyl acrylate) core using the star RAFT agent **2** was synthesized for this purpose (Table 3, Figure 7). Because, according to the mechanism, monomer insertion occurs from the core in RAFT agents of the kind **2**, the outer block, polystyrene was synthesized first. Subsequently, the arms of star polystyrene of M_n 25 550 and M_w/M_n 1.18 were extended with the insertion of methyl acrylate from the core to afford *star*-(PMA-*block*-PS)₄ of M_n 87 700 and polydispersity 1.24 in 4 h. If the polymerization is continued to 8 h, a star block copolymer of M_n 129 600 and polydispersity 1.23 is obtained.

Conclusion

We have demonstrated that multiarm star polymers of defined molecular weights can be synthesized using radical polymerization with reversible addition–fragmentation chain transfer. The two ways in which such polymers can be prepared involve the growth of arms attached to or detached from the core. While good molecular weight control is achieved using both types of RAFT agents, the latter type was shown to afford star polymers uncontaminated with high molecular weight byproducts. The absolute molecular weights of the star polymers were evaluated by cleaving the arms and analyzing products against linear standards. Narrow polydispersities following scission of arms also demonstrates all arms of the polymer have grown to similar chain length. The living nature of the arms of the star polymers was demonstrated by extending the arms of a star polymer with sequential addition of monomer with excellent molecular weight control. The RAFT

agents used to prepare the star polymers are synthesized easily using freely available commercial reagents.

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