

Synthesis of Branched Methacrylic Copolymers: Comparison between RAFT and ATRP and Effect of Varying the Monomer Concentration

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ABSTRACT: The statistical copolymerization of methyl methacrylate (MMA) with varying amounts of a disulfide-based dimethacrylate (DSDMA) branching comonomer in toluene at 90 °C can lead to highly branched soluble methacrylic copolymers under appropriate conditions. This model system is utilized in order to examine the following points: (i) the relative merits of using reversible addition-fragmentation chain transfer (RAFT) polymerization and atom transfer radical polymerization (ATRP) in such syntheses; (ii) the effect of varying the number of DSDMA units per primary chain; (iii) the effect of varying the initial monomer concentration. Kinetic studies of the linear RAFT and ATRP homopolymerizations conducted in the absence of any DSDMA confirmed their living character at 10, 30, and 50 wt % [MMA]₀, where the former monomer concentration approximately corresponds to the critical overlap concentration, c^* , for linear poly(methyl methacrylate) (PMMA) chains with a mean degree of polymerization of 50. HPLC analysis of the monovinyl and divinyl comonomers confirms that there is statistical incorporation of the DSDMA brancher into the growing poly(methyl methacrylate) chains. Cleavage of both RAFT- and ATRPsynthesized branched copolymers prepared at 50 wt % [MMA]₀ using tributylphosphine affords linear primary chains with narrow molecular weight distributions; thus these retro-syntheses demonstrate the retention of living character under branching conditions and suggest little or no chain transfer to polymer. In principle, macroscopic gelation can be avoided provided that the number of fully reacted divinyl branching comonomers per primary chain is less than unity. Taking into account the respective efficiencies of the RAFT chain transfer agent and the ATRP initiator, this hypothesis holds for both ATRP and RAFT branching copolymerizations conducted in the presence of DSDMA at 50 wt % [MMA]₀ but fails at 10 wt % [MMA]₀. Thus, soluble branched copolymers can be prepared at 10 wt % [MMA]₀ containing up to five fully reacted DSDMA units per primary chain using RAFT chemistry and up to three fully reacted DSDMA units per primary chain with the ATRP formulation; no gelation is observed even when the overall conversion of vinyl groups exceeds 96%. These observations strongly suggest that intramolecular cyclization is prevalent at this lower monomer concentration, regardless of the precise nature of the polymerization chemistry. In contrast, intermolecular branching between primary chains is evidently favored at 50 wt % [MMA]₀, since this concentration substantially exceeds c^* . In summary, although there are no doubt some subtle differences between branched copolymers synthesized via RAFT and ATRP chemistry, physical factors are arguably much more important than the precise nature of the living radical polymerization chemistry; in particular, systematic variation of the monomer concentration clearly leads to fundamentally different behavior.

Introduction

Free radical copolymerization of a monovinyl monomer with a small amount of divinyl monomer usually leads to gelation: an insoluble gel network is obtained when there is an average of two or more branch points per chain. Assuming equal comonomer reactivities, no intramolecular cyclization and perfectly mono-disperse primary chains, classical Flory–Stockmayer theory predicts that the condition for the *onset* of gelation should be 0.50 units of fully reacted divinyl branching comonomer per primary chain.^{1–3} However, in a recent series of papers, ^{4–18} Sherrington and co-workers have empirically shown that *macroscopic* gelation can be avoided provided that the number of fully

reacted divinyl branching comonomers per primary chain is less than unity. This concept follows from the following simple argument: cross-linking N chains together to form a single giant molecule requires at least N - 1 fully reacted divinyl comonomers. For macroscopic gelation, N is large in the high molecular weight limit so (N - 1)/N, or the minimum number of divinyl comonomers per primary chain, x, tends to unity. Using this hypothesis, the Strathclyde group developed a facile, robust onepot synthetic route for the synthesis of various soluble branched copolymers using conventional free radical polymerization (FRP) chemistry in solution,⁴⁻¹⁵ emulsion,¹⁶ or suspension.^{17,18} In their original paper, a thiol chain transfer agent is used to reduce the mean primary chain length and hence suppress gelation in the branching copolymerization of methyl methacrylate with but-2-ene-1,4-diacrylate.⁴ This FRP approach was later extended by both Sherrington's group⁵⁻¹⁰ and other research groups to

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Scheme 1. Synthesis of Linear Poly(methyl methacrylate) by RAFT Polymerization (Left) Using Cumyl Dithiobenzoate (CDB) as Chain Transfer Agent and 1,1'-Azobiscyclohexanecarbonitrile (ACCN) Initiator, and ATRP (Right) Using 3-Methylphenyl Bromoisobutyrate Initiator, Copper(I) Chloride Catalyst and *N*-(*n*-Propyl)-2-pyridylmethanimine Ligand at 90°C in Toluene^{*a*}



^a The initial monomer concentration [MMA]₀ was varied from 10 to 50 wt. % for both RAFT and ATRP syntheses.

include various other monovinyl and divinyl comonomers,^{19–22} as well as anionic polymerization,²³ cationic polymerization,²⁴ group transfer polymerization,^{25,26} or controlled/"living" radical polymerizations (CLRP) such as atom transfer radical poly-merization^{26–34} (ATRP) and reversible addition–fragmenta-tion chain transfer (RAFT) polymerization.^{35–46} According to a number of reports, branching copolymerizations conducted under RAFT conditions usually exhibit strongly non-ideal behavior in that the number of fully reacted divinyl branching comonomers per primary chain can significantly exceed unity.^{35,38,39,42} On the other hand, at least three research groups have reported that ATRP copolymerizations conform to the Sherrington hypothesis that gelation can be avoided if x is less than unity.^{28,30,31,47} In addition, Gao and co-workers studied the ATRP copolymerization of methyl acrylate with a divinyl cross-linker and found that the nature of the divinyl cross-linker, the cross-linker/initiator molar ratio, the reactant concentrations, the ATRP initiator efficiency and the molecular weight distribution of the primary chains all influenced the gel point. 47-51 This latter set of studies has been recently reviewed.52

In a recent model study, Li and co-workers⁵⁴ quaternized a near-monodisperse poly[(2-dimethylamino)ethyl methacrylate] (PDMA) homopolymer using a bifunctional reagent, bis(2-iodoethoxy)ethane (BIEE) to produce highly branched copolymers. Branching behavior was compared both above and below the coil overlap concentration, c^* , in order to assess the effect of the concentration of the linear primary PDMA chains in determining the relative probabilities of intramolecular cyclization and intermolecular cross-linking. According to ¹H NMR studies, many more BIEE molecules could be reacted per primary chain without causing gelation when the $[PDMA]_o$ was below c^* . This observation strongly suggests that intramolecular cyclization is prevalent under these conditions, as expected. Moreover, Bannister et al. demonstrated that linear primary chains are mainly formed initially during the ATRP copolymerization of a monovinyl methacrylic monomer with a dimethacrylate branching comonomer, with extensive branching being essentially confined to the latter stages of this copolymerization.³¹ Thus, to a zeroth-order approximation, it is reasonable to equate the effect of *homopolymer* concentration in such model quaternization reactions to the effect of *monomer* concentration in branching copolymerizations. This insight allows rationalization of much of the otherwise rather confusing literature data on branching copolymerizations.^{35,38,55} Thus, syntheses of branched copolymers conducted under relatively dilute monomer concentrations (i.e., below or close to *c**) are necessarily much more wasteful of the divinyl branching comonomer, because neighboring polymer coils do not interpenetrate each other in solution and are effectively isolated.⁴⁶ Moreover, such low monomer concentrations are generally more typical of RAFT syntheses^{35,38,55} than ATRP syntheses.^{28–31,47,48}

Recently, Zhu and co-workers⁵⁶ compared RAFT, ATRP and conventional FRP for the statistical copolymerization of oligo-(ethylene glycol) monomethacrylate with oligo(ethylene glycol) dimethacrylates in the bulk. The reaction kinetics and gelation behavior were studied in detail using strain-controlled rheometry: it was found that microgel formation occurred for the FRP formulation well below the gel point, whereas macroscopic gelation was obtained for the RAFT and ATRP formulations without any evidence for prior microgel formation. This difference was attributed to the suppression of intramolecular cyclization in the RAFT and ATRP syntheses due to their much slower copolymer chain growth, which allows sufficient relaxation and diffusion to ensure evolution of a more ordered copolymer network.

In the present work, we have studied the homopolymerization of methyl methacrylate (MMA) in toluene at 90 °C by both ATRP and RAFT, respectively (see Scheme 1). In particular, the effect of varying the initial monomer concentration ([MMA]₀) on the kinetics and controlled/living character of such homopolymerizations was examined in detail. This information was then used to study the branching copolymerization of methyl methacrylate (MMA) with a disulfide-based dimethacrylate comonomer (DSDMA) using both ATRP and RAFT at [MMA]₀ = 50, 30, and 10 wt % (see Scheme 2). The latter monomer concentration approximately corresponds to the c^* calculated for linear (primary) PMMA chains with a mean target degree of polymerization, DP, of 50 (see Supporting Information for this calculation). Scheme 2. Synthesis of Branched Copolymers by Statistical Copolymerization of Methyl Methacrylate (MMA) with a Disulfide-Based Dimethacrylate (DSDMA) Comonomer at 90°C in Toluene by (a) RAFT Chemistry Using Cumyl Dithiobenzoate as a Chain Transfer Agent and ACCN Initiator and (b) ATRP Using 3-Methylphenyl Bromoisobutyrate Initiator, Copper(I) Chloride Catalyst, and *N-(n*-Propyl)-2-pyridylmethanimine Ligand



Experimental Section

Materials. All monomers, solvents, and other reagents were purchased from Aldrich at the highest purity available and used as received, unless otherwise stated. Methyl methacrylate (MMA, 99%) was passed through an activated basic alumina column (Brockmann I) to remove inhibitor before use. 1,1'-Azobiscyclohexanecarbonitrile (ACCN, 99%) was recrystallized from methanol. Cumyl dithiobenzoate (CDB),⁵⁷ the disulfide-based dimethacrylate comonomer (DSDMA; see Scheme 2)⁴⁶ and *N*-(*n*-propyl)-2-pyridylmethanimine (*n*-Pr)⁵⁸ were synthesized following previously reported methods.

Synthesis of 3-Methylphenyl Bromoisobutyrate (MP-Br) Initiator. 3-Methylphenol (13.52 g, 0.125 mol, 1.0 equiv), distilled triethylamine (52.2 mL, 0.375 mol, 3.0 equiv), and 4-(dimethylamino)pyridine (1.53 g, 12.5 mmol, 0.1 equiv) were dissolved in 250 mL of dry dichloromethane in a 1 L two-neck round-bottomed flask under a nitrogen atmosphere. This flask was immersed in an ice bath for 15 min, and then 2-bromoisobutyryl bromide (34.49 g, 0.15 mol, 1.2 equiv) was added dropwise to the stirred solution using an addition funnel over 1 h. The resulting heterogeneous mixture was stirred at 20 °C for 24 h and then filtered to remove the triethylamine hydrobromide byproduct. This solution was washed three times with a saturated aqueous solution of sodium hydrogen carbonate (500 mL) and three times with deionized water (500 mL). The purified organic solution was dried using anhydrous MgSO₄, and the dichloromethane was removed under reduced pressure. The crude brown product was then purified by column chromatography using silica gel as stationary phase and a 1:15 ethyl acetate/petroleum ether mixed eluent as mobile phase. The final ATRP initiator (3-methylphenyl bromoisobutyrate; MP-Br) was obtained as a slightly yellow liquid (32.1 g, 87%) and was stored in a freezer under nitrogen prior to use. ¹H NMR (CD₂Cl₂): δ 7.37 (t, 1H), 7.17 (d, 1H), 7.01 (d, 2H), 2.45 (s, 3H), 2.14 (s, 6H); an assigned ¹H NMR spectrum of this compound is shown in the Supporting Information. MS (EI+): m/z = 256 Da. Anal. Calcd for C₁₁H₁₃BrO₂: C, 51.38; H, 5.10; Br, 31.08. Found: C, 51.61; H, 5.25; Br, 31.09.

Synthesis of Linear Poly(methyl methacrylate) Homopolymer by RAFT. The protocol used for the RAFT synthesis of a linear poly(methyl methacrylate) homopolymer with a target DP of 50 was as follows. Cumyl dithiobenzoate (CDB, 0.654 g, 2.4 mmol) and methyl methacrylate (MMA, 12.01 g, 120.0 mmol) monomer were weighed into a 50 mL Schlenk flask, degassed using three freeze-pump-thaw cycles and refilled with nitrogen. Anhydrous toluene (13.8 mL, 50 wt %) was added via a N2-purged glass syringe and the mixture was purged with nitrogen for 10 min. 1,1'-Azobiscyclohexanecarbonitrile (ACCN, 0.117 g, 0.48 mmol, CDB/ACCN molar ratio = 5:1) initiator was added last under a positive pressure of nitrogen before the flask was immersed in a preheated oil bath at 90 °C. Aliquots (typically 0.20 mL) were periodically extracted for GPC analysis and ¹H NMR studies of the monomer conversion. In the latter case, spectra were recorded in CDCl₃ and the signals due to the residual vinyl protons of MMA monomer at δ 5.63 and 6.19 were compared with the methyl proton signals due to both the homopolymer and MMA monomer (δ 3.40–4.00). After 30 h, the polymerization was terminated by exposure to air and cooling the reaction flask temperature with liquid nitrogen. Toluene was removed under reduced pressure and the crude homopolymer was dissolved in minimal THF before precipitating (twice) into excess n-hexane to remove any unreacted monomer. Finally, the homopolymer was dried for 24 h in a vacuum oven at 50 °C to produce a light pink powder. For the linear polymerizations conducted at lower MMA concentrations, additional ACCN initiator (0.117 g, 0.48 mmol) was injected after 24 h when $[MMA]_0 = 30$ wt % and after both 24 and 48 h when $[MMA]_0 = 10$ wt %.

Synthesis of Linear Poly(methyl methacrylate) Homopolymer by ATRP. The protocol used for the ATRP synthesis of a linear poly(methyl methacrylate) homopolymer with a target DP of 50 with $[MMA]_0 = 50$ wt % was as follows. The 3-methylphenyl bromoisobutyrate initiator (MP–Br, 0.617 g, 2.4 mmol), Schiff base ligand *N*-(*n*-propyl)-2-pyridylmethanimine (*n*-Pr, 0.712 g, 4.8 mmol), and methyl methacrylate (MMA, 12.01 g, 120.0 mmol) were weighed into a 50 mL Schlenk flask, degassed using three freeze–pump–thaw cycles, and refilled with nitrogen. Anhydrous toluene (13.8 mL, 50 wt %) was added via a N₂-purged glass syringe and the mixture was purged with nitrogen for 10 min. Copper(I) chloride (0.238 g, 2.4 mmol) catalyst was added last under a positive pressure of nitrogen before the flask was immersed in a preheated oil bath at 90 °C. Aliquots (typically 0.20 mL) were periodically extracted for GPC analysis and ¹H NMR studies of the monomer conversion. In the latter case, spectra were recorded in CDCl₃ and the signals due to the residual vinyl protons of MMA monomer at δ 5.63 and 6.19 were compared with the methyl proton signals due to both the polymer and MMA monomer (δ 3.40 to 4.00). After 20 h, the polymerization was terminated by exposure to air and cooling the reaction flask temperature with liquid nitrogen. The reaction mixture was passed through a silica column with THF as eluent to remove the spent catalyst. The solution was concentrated under reduced pressure before precipitating (twice) into excess *n*-hexane to remove any unreacted monomer. Finally, the purified homopolymer was dried for 24 h in a vacuum oven at 50 °C to produce an off-white powder.

Synthesis of Poly(methyl methacrylate)-Based Branched Copolymers by RAFT or ATRP. The experimental protocol for the synthesis of branched copolymers was very similar to that used for the linear polymerizations, except that various amounts of DSDMA branching comonomer were also added to the formulations. Copolymerizations were conducted at 90 °C and aliquots were periodically withdrawn for ¹H NMR, HPLC, and GPC characterization of monomer conversions and polymer molecular weights. For [MMA]₀ = 10 wt %, such copolymerizations required up to 96 h (RAFT) or 168 h (ATRP) at 90 °C in order to ensure that high conversions (>95%) were achieved.

Reductive Cleavage of Branched Copolymers Using Tributylphosphine. The PMMA₅₀–DSDMA_{0.90} branched copolymers prepared by either RAFT or ATRP (0.200 g, 0.038 mmol disulfide bonds) were dissolved in 3.0 mL THF containing an approximately 20-fold excess of tributylphosphine (Bu₃P; 15.3 mg, 0.757 mmol) and deionized water (680 μ L, 0.038 mmol). These reaction solutions were stirred at room temperature under a nitrogen atmosphere for 24 h, concentrated under reduced pressure, precipitated in *n*-hexane, filtered, and finally dried for 24 h in a vacuum oven at 50 °C. The isolated colorless polymers were then analyzed by GPC (see below). Branched copolymers containing higher proportions of DSDMA comonomer were cleaved using a correspondingly higher amount of Bu₃P such that the Bu₃P/disulfide molar ratio was always fixed at 20.

Characterization of Branched Copolymers. ¹H NMR spectra were recorded in either CDCl₃ or CD₂Cl₂ using a Bruker AC 400 MHz spectrometer. The molecular weight distributions of the branched copolymers were examined using a PL-GPC50 integrated GPC system from Polymer Laboratories. Both linear and branched copolymers were characterized at 30 °C using the following GPC setup: THF eluent containing 2% v/v triethyla-mine at a flow rate of 1.0 mL min⁻¹; two 5 μ m (30 cm) "Mixed C" columns from Polymer Laboratories; a WellChrom K-2301 refractive index detector operating at 950 ± 30 nm, a Precision detector PD 2020 light scattering detector (with scattering angles of 90° and 15°), and a BV400RT viscosity detector. Molecular weights of the branched copolymers were determined by the triple detection method using PL Cirrus Multi online software (version 2.0) supplied by Polymer Laboratories. A series of 10 near-monodisperse linear poly(methyl methacrylate) calibration standards (M_p from 1280 to 330000 g mol⁻¹) were purchased from Polymer Laboratories and employed with the above refractive index detector for the analysis of the linear PMMA₅₀ homopolymer and the Bu₃P-degraded branched copolymers. A mean refractive index increment (dn/dc) of 0.079 was taken from the literature for these branched copolymers.⁵⁹ For kinetic studies, aliquots (typically 0.20 mL) were extracted from the (co)polymerizing solutions, diluted with THF as required and ultrafiltered using 0.22 μ m Teflon filters prior to

GPC analysis. All such copolymers were analyzed in THF at a concentration of 5.0 g/L.

Kinetic Studies of Comonomer Depletion by HPLC. The following HPLC protocol has been used to monitor the depletion of the MMA monomer and DSDMA branching agent from both RAFT and ATRP copolymerizing solutions. The Waters 2695 Separations Module HPLC setup comprised Waters Spherisorb S5 ODS2 analytical HPLC column (125 mm × 4.6 mm), a Waters UV detector set at 220 nm, and a Waters HPLC pump operating at a flow rate of 1.0 mL min⁻¹. The HPLC eluent was a gradient mobile phase initially comprising a mixture of 40%THF and 60% deionized water. The THF content was increased from 40% to 75% over 15 min and maintained at 75% THF for a further 10 min. This protocol not only allowed good discrimination between MMA (which elutes at 2.86 min) and DSDMA (which elutes at 7.19 min) but also ensured good separation from the other species that were present in the copolymerizing solution (i.e., ACCN, toluene and copolymer for the RAFT formulations; transition metal complex, toluene and copolymer for the ATRP formulations). Thus, this UV HPLC protocol allowed convenient monitoring of the progressive depletion of both MMA and DSDMA branching comonomers from copolymerizing solutions.

Results and Discussion

In order to make a meaningful comparison between RAFT and ATRP under branching conditions, we sought to hold constant as many experimental parameters as possible. MMA was chosen as the model methacrylic monomer since there are many papers describing MMA-based branched co-polymers.^{4–8,10,14,16,18,26,32,35,44,60,61} Moreover, PMMA homopolymer is very convenient for GPC analyses, since a wide range of near-monodisperse PMMA calibration standards are available at relatively low cost. The DSDMA divinyl comonomer is an extremely useful model branching agent as it allows facile retrosynthesis of the primary chains via selective cleavage of its disulfide bonds under mild reductive conditions.^{28,42,46,60} A relatively high polymerization temperature of 90 °C was selected to ensure a fairly rapid rate of propagation under RAFT conditions.⁶² This temperature was also known to afford good control over the solution polymerization of MMA in toluene according to a well-documented ATRP formulation.^{58,63} Numerous previous RAFT³⁹ and ATRP³¹ studies had indicated that a target degree of polymerization (DP) of 50 for the primary chains should be sufficient to obtain a high degree of branching within a reasonable time scale. For the RAFT formulation, CDB was selected for its well-known excellent control over the polymeri-zation of methacrylic monomers,^{64,65} both in terms of its high chain transfer efficiency and also the narrow molecular weight distributions of the final polymers. ACCN was chosen as the radical initiator for its relatively long half-life (approximately 10 h in toluene at 90 °C).⁶⁶ A subset of our earlier published RAFT data (previously reported in ref 54) has been included in this manuscript in order to facilitate close comparison with that obtained using the ATRP formulation. A phenolic-based ATRP initiator⁶³ was selected for its relatively high initiator efficiency in the polymerization of methacrylic monomers⁶³ and the N-(npropyl)-2-pyridylmethanimine ligand⁵⁸ was utilized since it was known to solubilize (and stabilize) the Cu-based catalyst in toluene at 90 °C.

Linear Homopolymerizations Conducted at Various [MMA]₀**.** The kinetics of MMA homopolymerization at 90 °C using either ATRP or RAFT was studied at [MMA]₀ = 10, 30, and 50 wt % for a fixed DP = 50. Monomer conversions were determined by ¹H NMR spectroscopy and molecular weights were obtained by THF GPC, see Table 1. As expected, a linear relationship was obtained for the evolution of molecular weight with monomer conversion for both ATRP

 Table 1. Summary of Final Monomer Conversions, GPC Molecular Weights and Polydispersities of Linear Poly(methyl methacrylate)

 Homopolymers Prepared in Toluene at 90°C at Three Different [MMA]₀ by Either RAFT Using a Cumyl Dithiobenzoate Chain Transfer Agent

 (at Relative Molar Ratios of [MMA]₀:[CDB]:[ACCN] = 50:1.0:0.2) or by ATRP Using 3-Methylphenyl Bromoisobutyrate Initiator, Copper(I)

 Chloride and N-(n-Propyl)-2-pyridylmethanimine (at Relative Molar Ratios of [MMA]:[MP-Br]:[CuCl]:[n-Pr] = 50:1:1:2)^a

formulation	[MMA] ₀ (wt %)	conversion ^{b} (%)	time (h)	M_n^c	$M_{\rm w}/M_{\rm n}$	¹ H NMR efficiency ^d (%)	GPC efficiency ^{d} (%)
ATRP	50	99.5	20	5800	1.19	90.2	90.4
ATRP	30	99.9	48	5900	1.27	88.9	89.2
ATRP	10	94.6	168	5800	1.19	86.5	86.0
RAFT	50	96.1	30	5600	1.23	89.6	90.4
RAFT	30	97.0	48	5900	1.25	86.9	86.6
RAFT	10	95.5	96	6000	1.29	84.2	84.8

^{*a*} RAFT CTA and ATRP initiator efficiencies are calculated at each [MMA]₀. ^{*b*} Monomer conversions were determined by ¹H NMR spectroscopy. ^{*c*} Molecular weight data were obtained by THF GPC using a series of poly(methyl methacrylate) calibration standards. ^{*d*} "Efficiency" refers to either initiator efficiency (ATRP) or chain transfer agent efficiency (RAFT).



Figure 1. Evolution of number-average molecular weight and polydispersity with monomer conversion for the linear homopolymerization of methyl methacrylate: (a) via RAFT using cumyl dithiobenzoate as a chain transfer agent at a relative molar ratio of [MMA]:[CDB]:[ACCN] 50:1.0:0.2, and (b) via ATRP using 3-methylphenyl bromoisobutyrate as initiator, copper(I) chloride and N-(n-propyl)-2-pyridylmethanimine as catalyst at a relative molar ratio of [MMA]:[MP–Br]:[CuCl]:[*n*-Pr] 50:1:1:2 using various [MMA]₀ in toluene at 90 °C (the straight lines represent the calculated theoretical M_n values, assuming 100% CTA or initiator efficiency).

and RAFT formulations, see Figure 1. This suggests that reasonably good living character is achieved, regardless of the initial monomer concentration. The ATRP initiator and the RAFT chain transfer agent (CTA) efficiencies were calculated to be 90% by end group analysis of their respective aromatic ¹H NMR signals. Almost identical efficiencies were estimated from THF GPC (calibrated using a series of near-monodisperse PMMA standards).

At high monomer concentration (i.e., $[MMA]_0 = 50 \text{ wt }\%$), a linear semilogarithmic plot indicating first-order kinetics with respect to monomer was obtained for both RAFT and ATRP formulations (see Figure 2). Using RAFT, a relatively constant radical flux during the polymerization was achieved by addition of further ACCN initiator after approximately every two halflives in order to ensure that high monomer conversions were achieved at $[MMA]_0 = 10$ and 30%. For the ATRP syntheses conducted at the two lowest [MMA]₀, negative deviations from first-order kinetics were observed, suggesting that termination reactions were more prevalent under these conditions. Nevertheless, very high monomer conversions were still obtained after 48 h for $[MMA]_0 = 30$ wt % and after 168 h for $[MMA]_0 =$ 10 wt %. Homopolymers with narrow polydispersities and molecular weights close to those targeted were obtained at each of the three monomer concentrations using both RAFT and ATRP formulations (see Table 1). Regardless of the monomer concentration, the final conversions achieved by RAFT were typically 96-97% whereas monomer conversions obtained by ATRP were slightly higher at $\sim 99\%$, particularly at [MMA]₀ = 50 wt %.

Calculation of CDB Chain Transfer Agent and MP-Br Initiator Efficiencies. The CDB chain transfer agent and MP-Br initiator efficiencies are crucial parameters that dictate the actual primary chain length of the branched copolymers. These efficiencies were calculated using ¹H NMR and GPC from linear RAFT and ATRP homopolymerizations (where the target DP was 50 in both cases). ¹H NMR spectra of the resulting purified linear homopolymers were recorded in CD_2Cl_2 in order to compare the three methyl ester protons of the PMMA (at δ 3.6) with either the ten aromatic protons due to CDB (RAFT formulation) or the four aromatic protons due to the MP-Br (ATRP formulation). For example, for the linear ATRP homopolymerization conducted at $[MMA]_0 =$ 50 wt %, an experimental methyl ester/MP-Br molar ratio of 165.5: 4 (theoretical molar ratio is 150: 4) was determined at a final monomer conversion of 99.5%, which indicates an initiator efficiency of 90.2%. The MP-Br efficiency can also been calculated by comparing the GPC number-average molecular weight obtained for the linear homopolymer (vs PMMA standards) with its theoretical value. This alternative approach yielded an initiator efficiency of 90.4%, which is in very good agreement with the NMR value. Calculation of the CTA efficiency for this specific RAFT formulation has been described previously.⁴⁶ Table 1 summarizes the RAFT CTA and ATRP initiator efficiencies calculated for the three different monomer concentrations examined in this study. Reduced efficiencies were obtained at lower monomer concentrations. However, even at $[MMA]_0 = 10$ wt %, these efficiencies were around 85%.



Figure 2. Semilogarithmic plot for the homopolymerization of methyl methacrylate in toluene at 90 °C, with $[MMA]_0 = 10, 30, and 50$ wt %: (a) via RAFT using cumyl dithiobenzoate as a chain transfer agent at a relative molar ratio of [MMA]:[CDB]:[ACCN] 50:1.0:0.2, and (b) via ATRP using 3-methylphenyl bromoisobutyrate as initiator, copper(I) chloride and *N*-(*n*-propyl)-2-pyridylmethanimine as catalytic system at a relative molar ratio of [MMA]:[MP-Br]:[CuCl]:[*n*-Pr] = 50:1:1:2.



Figure 3. Conversion vs time plot for the consumption of disulfide-based dimethacrylate branching agent (DSDMA, triangles) and methyl methacrylate monomer (MMA, circles) as determined using HPLC, and overall vinyl bond conversion determined by ¹H NMR (squares) during the synthesis of a copolymer with targeted composition PMMA₅₀–DSDMA_{0.90}. (a) RAFT copolymerization mediated by cumyl dithiobenzoate (CDB) in toluene at 90 °C and (b) ATRP copolymerization using MPBr/CuCl/*n*-Pr at a relative molar ratio of 1/1/2 as initiator/catalytic system in toluene at 90 °C.

HPLC Studies of the Depletion of the Monovinyl and **Divinyl Comonomers during Branching Copolymerizations** by RAFT or ATRP Conducted at $[MMA]_0 = 50$ wt % for a Targeted Composition of PMMA₅₀-DSDMA_{0.90}. One of the inherent assumptions in Flory's mean field theory is equal monomer reactivities in the statistical copolymerization of the monovinyl monomer with the divinyl comonomer. If this assumption is valid, then microgels cannot be formed at low conversions by preferential consumption of the divinyl monomer. Moreover, if the reactivity of the divinyl monomer is comparable to that of the monovinyl monomer, then there is only a very low probability that the former species remains unreacted at the end of the copolymerization. In order to assess whether the copolymerization of MMA with DSDMA was truly statistical, ¹H NMR was used to evaluate the overall vinyl monomer conversion and UV HPLC was utilized to determine the depletion of MMA and DSDMA during both RAFT and ATRP syntheses (the vinyl signals of the two comonomers overlap in the ¹H NMR spectra, whereas using a gradient eluent allows very good discrimination between these two species and hence a robust HPLC protocol). Linear calibration curves were used to quantify the concentration of each comonomer after sampling the copolymerizing solution at various times. Figure 3 shows the change in total vinyl group

conversion with reaction time (calculated by ¹H NMR) and also the individual consumptions of MMA and DSDMA comonomers (determined by UV HPLC) obtained with both RAFT⁴⁶ and ATRP formulations at $[MMA]_0 = 50$ wt % for a target copolymer composition of PMMA₅₀-DSDMA_{0.90}.

In each case the DSDMA branching agent is consumed significantly faster than the MMA. On the other hand, the probability of this divinyl monomer becoming incorporated into the copolymer chains is twice that of the monovinyl monomer. As soon as one of the vinyl bonds of the DSDMA reacts, it is removed from the reaction solution and can no longer be detected by UV HPLC. According to a recent study in our group,³¹ the remaining fraction of unreacted divinyl monomer, p, in a statistical conversion of vinyl bonds is connected to the overall fractional conversion of all double bonds, F, by the following simple relation: $p = (1 - F)^2$. This theoretical curve is plotted in Figure 4, along with the experimental data shown in Figure 3 for DSDMA. The relatively good fit indicates that the DSDMA copolymerizes statistically with MMA using either $RAFT^{46}$ or ATRP chemistry. Thus equal comonomer reactivity, which is an important assumption in Flory-Stockmayer theory, appears to be valid for this particular model system.³

Table 2 summarizes the overall vinyl conversions as judged by ¹H NMR and the weight-average molecular weights and polydispersities obtained using a light scattering detector for branched copolymerizations conducted using either ATRP or RAFT at 10 wt %, $[MMA]_0 = 30$ wt % and 50 wt %. Following the work of Bannister et al.,³¹ we calculate (see the last two columns) both n_b (using the formula $n_b = (M_n^{-1}/M_n^{-b}) - 1$), a parameter that corresponds to the average number of DSDMA comonomer units per copolymer molecule and also the ratio $(M_n^{-b} - M_n^{-1})/M_n^{-1}$, which equals unity when an infinite gel network is produced. Here M_n^{-1} corresponds to the number-average molecular weight of the linear homopolymer and M_n^{-b} corresponds to the number-average molecular weight of the linear homopolymer and M_n^{-b} corresponds to the number-average molecular weight of the linear homopolymer and M_n^{-b} corresponds to the number-average molecular weight of the linear homopolymer and M_n^{-b} corresponds to the number-average molecular weight of the linear homopolymer and M_n^{-b} corresponds to the number-average molecular weight of the linear box because the section of the branched copolymer at the equivalent overall vinyl double bond conversion. We emphasize that all of the entries shown



Figure 4. Fraction of unreacted DSDMA, p, vs fraction conversion of double bonds, F, obtained for the DSDMA data shown in Figures 3a and 3b. The dash line is the reasonable fit obtained for these data, assuming that $p = (1 - F)^2$, the triangles represent the DSDMA depletion for the RAFT technique and the squares represent the DSDMA depletion for the ATRP technique.

in Table 2 were repeated at least twice, with generally good experimental reproducibility being observed.

Branched Copolymerization at $[MMA]_0 = 10$ wt % Using **DSDMA.** A series of branched PMMA₅₀-DSDMA_x with DSDMA/CDB or DSDMA/MP-Br molar ratios varying from 1.0 to 5.0 were conducted at an initial monomer concentration of 10 wt %, which corresponds to the critical overlap concentration, c^* , estimated for PMMA₅₀ (see entries 1-6 in Table 2). Close inspection of these entries confirms that both RAFT and ATRP formulations tolerate high proportions of DSDMA brancher per primary chain without causing gelation: up to three DSDMA branchers can be present under ATRP conditions and up to five DSDMA branchers using RAFT chemistry. Given the relatively high monomer conversions achieved in both cases, most of the DSDMA brancher must therefore be wasted in intramolecular cyclization side-reactions, which are assumed to be negligible in Flory-Stockmayer theory. The ATRP formulation seems to be somewhat less non-ideal: macroscopic gelation was finally observed at a DSDMA/MP-Br molar ratio of 5.0, whereas the RAFT branched copolymer prepared under the equivalent conditions remained soluble. In principle, this suppression of gelation may be related to the reinitiation required for the RAFT copolymerization, because this could increase the number of primary chains. In general, copolymerizations conducted at around c^* (i.e., $[MMA]_0 = 10$ wt %) produced relatively low molecular weight branched copolymers compared to those conducted at higher monomer concentrations (see later). This observation can be attributed to increased participation of the DSDMA in wasteful intramolecular cyclizations, rather than intermolecular branching. However, the lower overall vinyl conversions that can be achieved under these conditions most likely also play a role, since the extent of branching is very sensitive to the overall conversion.³¹

Branched Copolymerization at $[MMA]_0 = 30$ wt % Using DSDMA. Although relatively few experiments were conducted under these conditions, the data shown in Table 2 (see entries 7 to 10) indicate that both ATRP and RAFT

Table 2. Summary of Final Monomer Conversions, GPC Molecular Weights (Determined Using the Triple Detection Method) and Polydispersities Obtained for PMMA₅₀-DSDMA_x Branched Copolymers Prepared by Either ATRP or RAFT in Toluene at 90°C at Various [MMA]₀

formulation	target copolymer composition	[MMA] ₀ wt %	conversion ^a (%)	$M_{\mathrm{n}}{}^{b}$	$M_{ m w}^{\ \ b}$	$M_{ m w}/M_{ m n}^{\ b}$	n_b^c	$(M_{\rm n}{}^{\rm b} - M_{\rm n}{}^{\rm l})^d / M_{\rm n}{}^{\rm l}$		
ATRP	PMMA ₅₀ -DSDMA _{1.0}	10	97.6	39 600	54 800	1.38	5.88	0.85		
ATRP	PMMA ₅₀ -DSDMA _{3.0}	10	96.7	59 000	126 300	2.14	9.34	0.90		
ATRP	PMMA ₅₀ -DSDMA ₅₀	10	96.9	macroscopic gelation						
RAFT	PMMA ₅₀ -DSDMA _{1.00}	10	96.7	10 200	17200	1.69	0.79	0.42		
RAFT	PMMA ₅₀ -DSDMA _{3.00}	10	96.1	18 600	69 700	3.74	2.28	0.68		
RAFT	PMMA ₅₀ -DSDMA _{5.00}	10	96.4	43 800	608 700	13.89	6.70	0.87		
ATRP	PMMA ₅₀ -DSDMA _{1.25}	30	99.1	43 900	92 300	2.10	6.51	0.87		
ATRP	PMMA ₅₀ -DSDMA _{1,50}	30	98.9		macroscopic gelation					
RAFT	PMMA ₅₀ -DSDMA _{1,50}	30	98.7	209 200	4 508 800	21.56	34.92	0.97		
RAFT	PMMA ₅₀ -DSDMA _{1.60}	30	98.5		macroscopic gelation					
ATRP	PMMA ₅₀ -DSDMA _{0.60}	50	99.1	17100	58 300	3.41	1.93	0.65		
ATRP	PMMA ₅₀ -DSDMA _{0.70}	50	98.9	19 600	72 400	3.69	2.37	0.70		
ATRP	PMMA ₅₀ -DSDMA _{0.80}	50	98.8	32 200	121 200	3.77	4.54	0.82		
ATRP	PMMA ₅₀ -DSDMA _{0.85}	50	98.9	45 000	199 000	4.42	6.71	0.87		
ATRP	PMMA ₅₀ -DSDMA _{0.90}	50	99.0	71 800	437 700	6.09	11.38	0.92		
ATRP	PMMA ₅₀ -DSDMA _{0.95}	50	98.5		macroscopic gelation					
RAFT	PMMA ₅₀ -DSDMA _{0.60}	50	96.2	8800	41 400	4.70	0.55	0.33		
RAFT	PMMA ₅₀ -DSDMA _{0.70}	50	96.5	12000	68 300	5.67	1.11	0.51		
RAFT	PMMA ₅₀ -DSDMA _{0.80}	50	97.3	13900	331 500	23.92	1.42	0.58		
RAFT	PMMA ₅₀ -DSDMA _{0.85}	50	96.1	28 700	1 1 26 700	39.29	4.07	0.79		
RAFT	PMMA ₅₀ -DSDMA _{0.90}	50	96.6	92 000	3 324 900	36.14	15.2	0.94		
RAFT	PMMA ₅₀ -DSDMA _{0.95}	50	96.1		ma	croscopic gela	tion			

^{*a*}Monomer conversions were determined by ¹H NMR spectroscopy. ^{*b*}Molecular weight data were obtained by THF GPC using a triple detection system comprising refractive index, viscosity and light scattering (15° and 90°) detectors. ^{*c*} n_b is the average number of fully reacted DSDMA branching comonomers per copolymer molecule. ${}^d(M_n^{\ b} - M_n^{\ l})/M_n^{\ l} = 1$ is the condition for the formation of an infinite gel network. $M_n^{\ b}$ and $M_n^{\ l}$ are the number-average molecular weight of, respectively, weight of the branched copolymer and the linear homopolymer, respectively.

formulations behave less non-ideally at this higher monomer concentration. Thus, ATRP can now tolerate only \sim 1.25 DSDMA units per primary chain, with gelation occurring if 1.50 DSDMA units are utilized. Similarly, the RAFT formulation remains soluble (while very close to gelation) at 1.50 DSDMA units per chain, but gelation is observed if 1.60 DSDMA units are utilized. It is perhaps also noteworthy that the ATRP syntheses are marginally less non-ideal than those conducted under RAFT conditions.

Branched Copolymerizations Conducted at $[MMA]_0$ = 50 wt % Using DSDMA. At high monomer concentration, i.e., well above c*, RAFT or ATRP copolymerization of MMA with DSDMA enables a range of soluble highly branched copolymers to be obtained simply by varying the initial DSDMA/CDB or DSDMA/MP-Br molar ratio, respectively. When such molar ratios are increased from 0.60 to 0.90 (see entries 11-16 and 17-22 in Table 2 for ATRP and RAFT formulations, respectively), the weightaverage molecular weight and polydispersity both increase dramatically. Moreover, the average number of fully reacted branching comonomer units per copolymer molecule, $n_{\rm b}$, increases with the amount of DSDMA introduced and $(M_n^{b} M_n^{\rm l}/M_n^{\rm l}$ approaches unity (indicating the formation of an infinite gel network) in both cases for the targeted composition of PMMA₅₀-DSDMA_{0.90}. More specifically, $(M_n^{b} M_n^{-1}/M_n^{-1} = 0.92$ or 0.94 for the ATRP and RAFT formulations respectively, see entries 15 and 21 in Table 2. These values are comparable to those calculated by Bannister et al.³¹ for the ATRP branched copolymerization of 2-hydroxypropyl methacrylate with ethylene glycol dimethacrylate just below the gel point. Macroscopic gelation is observed at high comonomer conversions for both RAFT and ATRP when the proportion of DSDMA per primary chain is increased from 0.90 to 0.95. The targeted PMMA₅₀-DSDMA_{0.90} formulation lies very close to the gel point for both formulations. Taking into account the CDB (or MP-Br) efficiency of around 90%, this approximately corresponds to one fully reacted DSDMA branching agent per primary chain, which is consistent with near-ideal behavior according to Sherrington's hypothesis, if not Flory-Stockmayer theory. In the rest of this manuscript, the terms "ideal" and "non-ideal" are used solely in the context of the former postulate, rather than the latter theory.

Figure 5 compares the evolution of weight-average molecular weight (M_w) with comonomer conversion for the linear PMMA₅₀ and the PMMA₅₀-DSDMA_{0.90} branched copolymer obtained using the RAFT and ATRP (see Figure 5b) formulations at $[MMA]_0 = 50$ wt %. In both cases the *onset* of branching, which corresponds to the initial deviation from linearity, is observed at around 70% comonomer conversion. Beyond this conversion, the branched copolymer $M_{\rm w}$ increases rapidly for the RAFT formulation but a less dramatic change is observed under ATRP conditions. However, the final $M_{\rm w}$ obtained in the latter case is still comparable to that reported by Li et al.²⁸ and Bannister et al.³¹ for branching compositions very close to gelation using the same target degree of polymerization of 50 for the primary chains (which in these earlier examples comprised poly-(2-hydroxypropyl methacrylate), rather than PMMA).

Figures 6 and 7 show the evolution of the GPC curves for the nominal targeted composition of PMMA₅₀–DSD-MA_{0.90} obtained at [MMA]_o = 50 wt % using (a) the light scattering detector and (b) the refractive index detector for the RAFT and the ATRP formulations, respectively. The former detector is clearly much more sensitive to the presence of high molecular weight copolymer, as expected.^{28,31,39} For the RAFT formulation (see Figure 6a), bimodal



Figure 5. Evolution of weight-average molecular weight (M_w) with total vinyl group conversion for the synthesis of branched PMMA₅₀– DSDMA_{0.90} copolymers via RAFT (\blacklozenge) and via ATRP (\blacklozenge) using an initial monomer concentration [MMA]₀ = 50 wt % (light scattering detector). The M_w of the linear homopolymers prepared in the absence of DSDMA branching agent are also shown for the RAFT formulation (\blacktriangle), and the ATRP formulation (\blacksquare) (refractive index detector).

distributions are observed even at relatively low comonomer conversions (26.6%) and these features persist up to very high monomer conversions. In contrast, the same detector indicates unimodal distributions over a wide range of conversions for the ATRP formulation.

The refractive index detector (see Figures 6b and 7b) is much more sensitive to the presence of linear primary chains, which can still be detected even at high comonomer conversions (the characteristic peak retention time for linear PMMA₅₀ homopolymer prepared in the absence of any DSDMA is approximately 16 min in the refractive index chromatograms shown in Figures 6b and 7b). This observation is consistent with a recent Monte Carlo simulation study, which predicts that a significant proportion of linear chains remain at the end of these copolymerizations due to the purely statistical nature of the branching process.⁶⁷

The last three chromatograms shown in Figure 7a suggest continued evolution of the molecular weight with comonomer conversion. However, there may also be some evidence for an artificial cut-off at such low retention times, which suggests possible formation of an unanalyzable microgel fraction. This hypothesis is supported by inspection of the GPC traces recorded using the refractive index detector: the curves at 95.0%, 97.5%, and 99.0% comonomer conversion are almost identical (see Figure 7b), whereas a high molecular weight shoulder might be expected (as observed in Figure 6a for the corresponding RAFT-synthesized branched copolymer). The presence of a microgel fraction is also consistent with the observation that the branched copolymers obtained at high conversions are very difficult to filter prior to GPC analysis. However, further studies are required to examine this hypothesis. It is perhaps worth emphasizing that the rate of polymerization obtained with the ATRP formulation conducted at $[MMA]_0 = 50$ wt % is approximately three times faster than that obtained with the RAFT formulation under the same conditions. In principle, such kinetic differences could be an important consideration when rationalizing our experimental observation of subtle differences between the RAFT and ATRP formulations. In the case of RAFT, the slower chain growth should allow greater diffusion of the branched copolymer chains, whereas for ATRP significantly less relaxation of the growing copolymer chains is possible. Further studies are required to examine this possibility.



Figure 6. GPC traces recorded at various monomer conversions for the RAFT synthesis of branched $PMMA_{50}-DSDMA_{0.90}$ copolymer in toluene at 90 °C with a $[MMA]_0 = 50$ wt % using (a) a 90° light scattering detector and (b) a refractive index detector calibrated with PMMA standards.



Figure 7. GPC traces recorded at various monomer conversions for the ATRP synthesis of branched PMMA₅₀–DSDMA_{0.90} copolymer in toluene at 90 °C with a $[MMA]_0 = 50$ wt % using (a) a 90° light scattering detector and (b) a refractive index detector calibrated with PMMA standards.



Figure 8. Schematic representation of the retrosynthesis from branched copolymer to linear primary chains by disulfide bond cleavage using reduction using tributylphosphine (Bu₃P): (left) GPC traces recorded using the refractive index detector and the light scattering detector for the PMMA₅₀–DSDMA_{0.90} branched copolymer prepared by RAFT at [MMA]₀ = 50 wt %; (right) GPC traces recorded using the refractive index detector of the degraded polymer chains obtained after reductive cleavage of disulfide bonds by Bu₃P and the PMMA₅₀ homopolymer prepared in the absence of any DSDMA branching agent.

In summary, there certainly appears to be some subtle differences in the evolution of molecular weight in the ATRP and RAFT branching copolymerizations conducted at 50 wt %. However, close inspection of Table 2 confirms that it is essential to utilize a relatively high monomer concentration (i.e., well above c^*) if near-ideal Sherrington-type behavior is desired, regardless of whether a ATRP or RAFT formulation is selected for the branching copolymerization. This is primarily because intermolecular branching can only be really efficient if individual primary chains (which exist as

random coils in solution) are able to interpenetrate each other, otherwise intramolecular cyclization will inevitably be favored.

Reductive Cleavage of Disulfide Bonds in PMMA₅₀–DSD-MA_{0.90} Branched Copolymers Using Tributylphosphine. Selective reductive cleavage of the disulfide bonds in PMMA₅₀– DSDMA_{0.90} branched copolymers prepared at $[MMA]_0 =$ 50 wt % using tributylphosphine (Bu₃P) leads to the formation of low polydispersity primary chains, as judged by gel permeation chromatography. The molecular weight distributions of these degraded chains are comparable to either RAFT-synthesized or



Figure 9. Schematic representation of the retrosynthesis from branched copolymer to linear primary chains by disulfide bond cleavage using reduction using tributylphosphine (Bu₃P): (left) GPC traces recorded using the refractive index detector and the light scattering detector for the PMMA₅₀–DSDMA_{0.90} branched copolymer prepared by ATRP at [MMA]₀ = 50 wt %; (right) GPC traces recorded using the refractive index detector of the degraded polymer chains obtained after reductive cleavage of disulfide bonds by Bu₃P and the PMMA₅₀ homopolymer prepared in the absence of any DSDMA branching agent.



Figure 10. Schematic representation of the retrosynthesis from branched copolymer to linear primary chains by disulfide bond cleavage using reduction using tributylphosphine (Bu₃P): (left) GPC traces recorded using the refractive index detector and the light scattering detector for the $PMMA_{50}-DSDMA_{5,00}$ branched copolymer prepared by RAFT at $[MMA]_0 = 10$ wt %; (right) GPC traces recorded using the refractive index detector of the degraded polymer chains obtained after reductive cleavage of disulfide bonds by Bu₃P and the PMMA₅₀ homopolymer prepared in the absence of any DSDMA branching agent.

ATRP-synthesized linear poly(methyl methacrylate) homopolymers prepared in the absence of any DSDMA branching agent, see Figures 8 and 9. This confirms that good control over the copolymerization is achieved under branching conditions and that the polydisperse highly branched chains simply comprise randomly coupled, near-monodisperse primary chains, as expected. It also suggests that chain transfer to polymer must be negligible in such branched copolymer syntheses, since such side-reactions would necessarily involve the formation of new C-C bonds that could not be cleaved by the Bu₃P.

Figure 10 shows the GPC traces of the PMMA₅₀–DSD-MA_{5.00} branched copolymer synthesized under RAFT conditions at $[MMA]_0 = 10$ wt % and its linear counterpart obtained after reductive cleavage with Bu₃P. The cleaved thiol-containing PMMA has a slightly higher molecular weight than the corresponding PMMA homopolymer prepared in the absence of any DSDMA. This is not unexpected, since the former species contains an additional five copolymerized DSDMA repeat units.

Conclusions

Linear homopolymerization of MMA in toluene at 90 °C using either RAFT or ATRP chemistry has relatively good controlled/ living character for monomer concentrations ranging from 10 to 50 wt %. At the lowest monomer concentration investigated, our RAFT formulation required periodic addition of further initiator to maintain an appropriate radical flux and hence achieve high monomer conversions. Our ATRP formulation also produced homopolymers with narrow polydispersities in very high yields but required a reaction time of 1 week at 90 °C. RAFT CTA and ATRP initiator efficiencies were comparable for a given initial monomer concentration and varied from $\sim 90\%$ at [MMA]₀ = 50 wt % to ~85% at $[MMA]_0 = 10$ wt %. Combined ¹H NMR and UV HPLC studies confirmed that the DSDMA divinyl comonomer reacts statistically with MMA during branched copolymerizations conducted with either RAFT or ATRP formulations. The approximately equal reactivities of these two comonomers reduces the possibility of microgel formation during the early stages of the copolymerization and also minimizes the probability of any unreacted DSDMA remaining at high comonomer conversion. Taking into account the RAFT CTA or ATRP initiator efficiency, our results confirm that branching copolymerizations conducted at high monomer concentration (i.e., 50 wt %) cannot tolerate more than one DSDMA unit per primary chain if gelation is to be avoided at high conversion. Highly branched copolymers with compositions that lie close to the gel point (such as PMMA₅₀-DSDMA_{0.90}) have been chemically degraded to their constituent primary chains by reductive cleavage of the disulfide bonds in the DSDMA branching comonomer. For both RAFT and ATRP formulations, this affords low polydispersity primary chains with molecular weights that are comparable to PMMA homopolymers prepared under identical conditions in the absence of any DSDMA. When branching copolymerizations are conducted at

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 $[MMA]_0 = 10$ wt % (i.e., at around the critical overlap concentration c^* for linear PMMA chains of DP 50) a relatively high proportion of branching agent can be tolerated without causing gelation; up to three DSDMA units per primary chain for the ATRP formulation and up to five DSDMA units per primary chain for the RAFT formulation. This strongly suggests that the majority of the DSDMA actually participates in intramolecular cyclizations, rather than forming intermolecular branches. ¹H NMR studies (data not shown here) confirm the presence of these "excess" DSDMA units in the branched copolymers. GPC studies of the disulfide-cleaved copolymers prepared at 10 wt % indicate slightly highly molecular weights for the thiol-functionalized primary chains, as expected. In summary, we have demonstrated that the initial monomer concentration is an important parameter in determining the nature of the products of the branched copolymerization of MMA and DSDMA under both RAFT and ATRP conditions. The DSDMA branching comonomer forms intermolecular branches at both high and low monomer concentration but reacts preferentially via intramolecular cyclization under the latter conditions. Although there are certainly some subtle differences between RAFT- and ATRPsynthesized branched copolymers, the initial monomer concentration seems to be much more important than the precise nature of the polymerization chemistry in determining the microstructure of the branched copolymer products.

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Supporting Information Available: Calculation of *c*^{*} for a linear PMMA₅₀ homopolymer; ¹H NMR spectra for the MP-Br initiator and DSDMA branching comonomer. This material is available free of charge via the Internet at http://pubs.acs.org.

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