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Synthesis of Highly Branched Methacrylic Copolymers: Observation of Near-Ideal Behavior using RAFT Polymerization

Julien Rosselgong,[†] Steven P. Armes,*[,†] William Barton,[‡] and David Price[‡]

[†]*Dainton Building, Department of Chemistry, The University of Sheffield, Sheffield, South Yorkshire, S3 7HF, United Kingdom, and* [‡]*Lubrizol Corporation, Hazelwood Research Center, Derby, DE5 61QN, United Kingdom*

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ABSTRACT: We report the synthesis of model highly branched methacrylic copolymers by copolymerizing methyl methacrylate (MMA) with a disulfide-based dimethacrylate (DSDMA) branching comonomer via reversible addition−fragmentation chain transfer (RAFT) in toluene at 90 °C using 1,1′-azobiscyclohexanecarbonitrile initiator and a cumyl dithiobenzoate (CDB) chain transfer agent. Selective cleavage of the disulfide bonds in the DSDMA branching comonomer using tributylphosphine leads to the formation of low polydispersity primary chains, as judged by gel permeation chromatography. The molecular weight distribution of these degraded chains is comparable to a RAFT-synthesized linear poly(methyl methacrylate) homopolymer prepared in the absence of any DSDMA brancher. This confirms that good control over the RAFT copolymerization is achieved under branching conditions and that the polydisperse highly branched chains simply comprise randomly coupled near-monodisperse primary chains, as expected. Moreover, HPLC analysis of the copolymerizing solution confirms that the consumption of DSDMA comonomer is close to that expected for a statistical copolymerization. The CDB efficiency is estimated to be 90% by GPC and ^{1}H NMR spectroscopy. Taking this into account and allowing for the incomplete comonomer conversions (typically 96−97%), our systematic variation of the proportion of DSDMA per primary chain indicates that this RAFT formulation conforms closely to classical Flory−Stockmayer theory. This near-ideal behavior is in marked contrast with earlier literature reports of strongly nonideal behavior, presumably because of significant levels of intramolecular cyclization. Our hypothesis is that this unwanted side reaction, which consumes the DSDMA brancher without leading to intermolecular branching, is suppressed in the present study because of the relatively high comonomer concentration (50% w/w) used in our RAFT syntheses.

Introduction

Copolymerization of a monovinyl monomer with a judicious amount of divinyl comonomer in the presence of a suitable alkanethiol is a convenient route to highly branched copolymers via conventional free radical copolymerization, as exemplified by Sherrington and coworkers.[1−7] Weaver and coworkers have recently shown that this Strathclyde route can be used to prepare highly functional branched copolymers for so-called "emulsion engineering".[8,9] We and others have extended this route to include living cationic polymerizations,[10] living anionic polymerizations,[11,12] and living radical polymerizations.[13−23] In principle, this approach should allow better control over the branching process because the primary chains are much less polydisperse. Moreover, the primary chain can be simply controlled by varying the comonomer/initiator molar ratio rather than the use of a malodorous alkanethiol. In the case of atom transfer radical polymerization (ATRP), detailed studies have revealed that near-ideal behavior can be observed under appropriate conditions.[15,18] Therefore, less than one fully reacted bifunctional branching comonomer per primary chain leads to soluble branched copolymers, whereas insoluble cross-linked gels are invariably obtained if this parameter exceeds unity. Such ideal behavior conforms with classical Flory−Stockmayer theory[24−26] and also is readily amenable to modeling by Monte Carlo simulation.[27] In contrast, in the case of branched copolymer syntheses using reversible addition−fragmentation chain transfer (RAFT), various research groups have reported strongly nonideal behavior: significantly more than one branching comonomer (up to 3.6) per primary chain can be tolerated without inducing gelation.[15,19,22,28] This is believed to be due to substantial degrees of intramolecular cyclization rather than intermolecular branching. In principle, this side reaction should be suppressed by conducting the RAFT branching copolymerization at a relatively high monomer concentration (which corresponds to the conditions under which most ATRP syntheses are conducted).[14,18,21] This hypothesis seems to be borne out by our studies of model systems, where near-monodisperse homopolymer chains are randomly coupled using bifunctional reagents in either dilute, semidilute, or concentrated solution.[28,29]

In the present work we have applied this new insight to develop the first RAFT formulation that allows near-ideal branching copolymerization. This is achieved by the one-pot RAFT copolymerization of methyl methacrylate (MMA) and a disulfide-based dimethacrylate (DSDMA) using cumyl dithiobenzoate (CDB) as a chain transfer agent (CTA) at a relative high monomer concentration (i.e., 50% w/w) in toluene at 90 °C using a 1,1′-azobiscyclohexanecarbonitrile (ACCN) initiator, see Scheme 1.

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. MMA (99%) and

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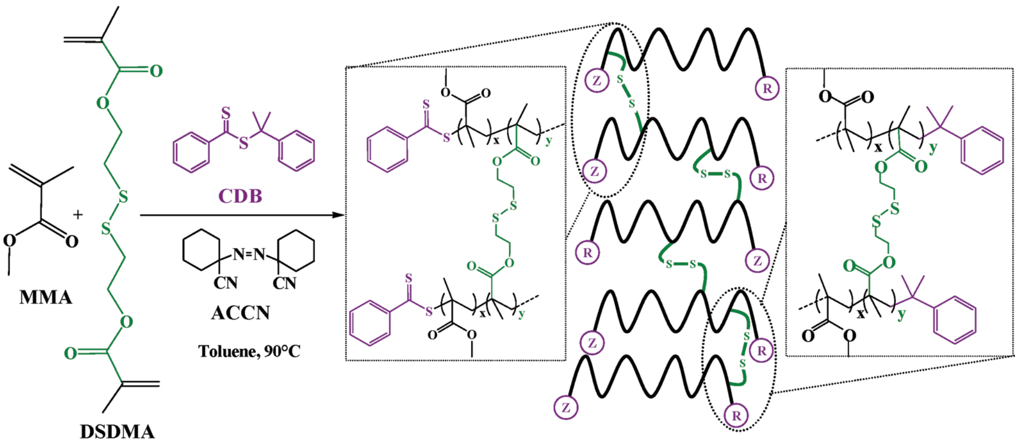
*To whom correspondence should be addressed. E-mail: S.P.Armes@sheffield.ac.uk.

Scheme 1. Synthesis of Branched Copolymers Obtained by Statistical Copolymerization of Methyl Methacrylate and a Disulfide-Based Dimethacrylate (DSDMA) Comonomer Using Cumyl Dithiobenzoate As a RAFT Chain Transfer Agent and ACCN as an Initiator at 90 °C in Toluene



α-methylstyrene (99%) were passed through an activated basic alumina column (Brockmann I) column to remove inhibitor before use. 1,1′-Azobis cyclohexanecarbonitrile (ACCN, 99%) was recrystallized from methanol. CDB was synthesized following a previously reported method.[30]

Synthesis of Disulfide-Based Dimethacrylate Branching Agent. Bis(2-hydroxyethyl)disulfide (BHEDS, 15.43 g, 0.10 mol, 1.0 equiv), triethylamine (22.1 mL, 0.30 mol, 3.0 equiv), and DMAP (1.22 g, 0.01 mol, 0.10 equiv) were dissolved in 150 mL of chloroform in a 250 mL two-necked round-bottomed flask under a nitrogen atmosphere. This flask was immersed in an ice bath for 15 min, and then methacrylic anhydride (46.25 g, 0.30 mol, 3.0 equiv) was added dropwise to the stirred solution via an addition funnel. The resulting solution was stirred at 20 °C for 24 h. This solution was washed twice with deionized water (200 mL each), three times with a saturated aqueous solution of sodium hydrogen carbonate (200 mL each), and finally twice with brine (200 mL each). The purified organic solution was dried using anhydrous $MgSO_4$, and chloroform was removed under reduced pressure. The resulting oil was then purified by column chromatography using neutral silica gel as the stationary phase and an eluent mixture comprising 1:20 ethyl acetate/petroleum ether (40−60 °C). The purest fractions were then mixed, and a radical inhibitor (MEHQ, 20 ppm) was added to prevent autopolymerization of the cross-linking agent during solvent evaporation. After drying under high vacuum in the absence of light, the light-yellow oil (25.9 g, 89% yield) was characterized by ^1H NMR spectroscopy ($CDCl_3$) δ 6.06 and 5.52 (4H, singlet, CH_2CCH_3COO), 4.36−4.31 (4H, triplet, $COOCH_2CH_2S-$), 2.93−2.88 (4H, triplet, $COOCH_2CH_2S-$), 1.87 (6H, singlet, CH_2CCH_3COO).

Synthesis of Linear Poly(methyl methacrylate) Homopolymer. The protocol used for the RAFT synthesis of a linear poly(methyl methacrylate) homopolymer with a target DP of 50 was as follows. CDB (0.654 g, 2.4 mmol) and MMA (12.01 g, 120.0 mmol) monomer were weighed into a 25 mL Schlenk flask, degassed using three freeze−pump−thaw cycles, and refilled with nitrogen. Anhydrous toluene (14.53 mL, 50% w/w) was added via a nitrogen-purged glass syringe, and the mixture was purged with nitrogen for 10 min. 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 were periodically extracted (typically 0.20 mL) for GPC analysis and ^1H NMR studies of the monomer conversion. In the latter case, spectra were recorded in $CDCl_3$ and the signals due to the residual vinyl protons of MMA monomer at δ 6.19 and 5.63 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. Toluene was removed under reduced pressure, and the crude polymer was dissolved in minimal THF before precipitating (twice) into excess *n*-hexane to remove any unreacted monomer. Finally, the polymer was dried for 24 h in a vacuum oven at 50 °C to produce a light-pink powder.

Synthesis of Branched Poly(methyl methacrylate) Copolymers. The experimental protocol for the synthesis of branched copolymers was very similar to that used for the linear polymer, except that various amounts of DSDMA branching comonomer were also added (N.B. the MEHQ inhibitor was removed from the DSDMA by passing through a short basic alumina column). Copolymerizations were conducted at 90 °C, and aliquots were periodically withdrawn for ^1H NMR and GPC characterization of monomer conversions and polymer molecular weights.

Cleavage of the Soluble Branched Copolymers by Reduction with Tributylphosphine. The $PMMA_{50}$-$DSDMA_{0.90}$ branched copolymer (0.200 g, 0.038 mmol disulfide bonds) was dissolved in 3.0 mL of THF containing an approximately 20-fold excess of tributylphosphine (Bu_3P; 15.3 mg, 0.757 mmol). This reaction solution was stirred at room temperature 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 colorless polymer was then analyzed by GPC.

Characterization of Branched Copolymers. ^1H NMR spectra were recorded in either $CDCl_3$ or CD_2Cl_2 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 triethylamine at a flow rate of 1.0 mL min^{-1}; two 5 μm (30 cm) mixed C columns; a WellChrom K-2301 refractive index detector operating at 950±30 nm, a Precision Detector 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 methacrylates) (M_p from 1280 to 330 000 g mol^{-1}) were purchased from Polymer Laboratories and employed as calibration standards with the above refractive index detector for the analysis of the linear $PMMA_{50}$ homopolymer and the Bu_3P-degraded branched copolymer. A mean refractive index increment (dn/dc) of 0.079 was taken from the literature for these branched copolymers.[20] For kinetic studies, aliquots (typically 0.20 mL) were extracted from the (co)polymerizing solutions, diluted with THF, and ultrafiltered using 0.22 μm Teflon PTFE filters prior to GPC analysis. The purified copolymer was analyzed in THF at a concentration of 5.0 g L^{-1}.

High-Performance Liquid Chromatography Studies of Comonomer Depletion. HPLC was used to monitor the depletion of the MMA monomer and DSDMA branching agent from the copolymerizing solution. The Waters 2695 Separations Module HPLC setup comprised a Waters Spherisorb S5 ODS2 analytical HPLC column (125 × 4.6 mm^2), 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 allowed good discrimination between the monomer MMA (eluted at 2.86 min) and the comonomer DSDMA (eluted at 7.19 min) but also good separation from the other species present in the copolymerizing solution (i.e., ACCN, toluene, and copolymer). Thus this UV HPLC protocol allowed convenient monitoring of the simultaneous depletion of both MMA and DSDMA branching comonomer from the reaction solution during copolymerization.

Cumyl Dithiobenzoate Efficiency Calculation. The CDB efficiency during the linear homopolymerization of PMMA$_{50}$ in toluene at 90 °C using ACCN initiator at a 5:1 CDB/ACCN molar ratio was estimated using both ^{1}H NMR and also GPC. An ^{1}H NMR spectrum of the purified linear PMMA$_{50}$ was recorded in CD$_2$Cl$_2$ (Figure 2) to compare the ten aromatic protons due to CDB with the three methyl ester protons of the PMMA. For a CTA efficiency of 100%, the methyl ester/CDB molar ratio should be 150:10, or 15: 1. Experimentally, a molar ratio of 16.1:1 was determined at a final monomer conversion of 96.1%, which indicates a CTA efficiency of 89.6%. The CDB efficiency can also been calculated by comparing the number-average molecular weight obtained for PMMA$_{50}$ by GPC (vs PMMA standards) with the theoretical value. This alternative approach yielded an efficiency of 90.6%, which is in very good agreement with the NMR value.

Results and Discussion

Initially, we conducted kinetic studies of the RAFT homopolymerization of MMA to confirm its living character and also to quantify the CTA efficiency. CDB was selected because this CTA is widely used for various methacrylic monomers in the literature, and it is known to afford good control over both the targeted molecular weight and the final polydispersity.[31,32] A relatively high polymerization temperature (90 °C) was chosen to increase the propagation rate[33] and hence obtain high final monomer conversions. This is a particularly important point because most of the branching in such syntheses was expected to occur in the final stages of the copolymerization.[18,22] ACCN was selected as a free-radical initiator because it has a half-life of approximately 10 h at 90 °C. Toluene was used as a high-boiling-point solvent. The target degree of polymerization of the primary chains was fixed at 50 because earlier RAFT[22] and ATRP[14,18,21] studies indicated that this was sufficient to obtain a high degree of branching within a reasonable time scale. We have recently demonstrated that intermolecular branching is favored over intramolecular cyclization when the initial monomer (or polymer) concentration is higher than the critical overlap concentration (c*).[29,34] Below c*, the divinyl comonomer is consumed via intramolecular cyclization, which can reduce the branching efficiency. Therefore, in the present work, we chose the initial monomer concentration to be 50% w/w. This is well above c*, which is estimated to be ~10% w/w for linear PMMA$_{50}$.[29,34] It is perhaps noteworthy that this monomer concentration is significantly higher than that employed in many RAFT syntheses.[15,19,22]

An M_n versus conversion plot proved to be linear for PMMA$_{50}$ homopolymer, as expected. (See Figure 1.) A relatively narrow polydispersity ($M_w/M_n < 1.25$) was indicated by GPC analysis after 20 h, see entry 1 in Table 1. The CDB efficiency was estimated to be approximately 90% on the basis of both GPC and ^{1}H NMR spectroscopy, see Figure 2. This means that a target degree of polymerization of 50 actually produces an experimental degree of polymerization of 55. Given that the relative molar ratio of DSDMA/CDB is fixed, this inevitably leads to a 10% higher DSDMA content per primary chain. This correction must be allowed for when calculating the critical target copolymer composition for the onset of gelation. Similar observations have been recently reported by Matyjaszewski's group for acrylic branched copolymers prepared by ATRP.[35] These workers show that reducing the initiator efficiency causes gelation to occur at lower comonomer conversions than that required for 100% initiator efficiency under otherwise identical conditions.

Our one-pot statistical copolymerization of MMA with DSDMA afforded a range of soluble, highly branched copolymers

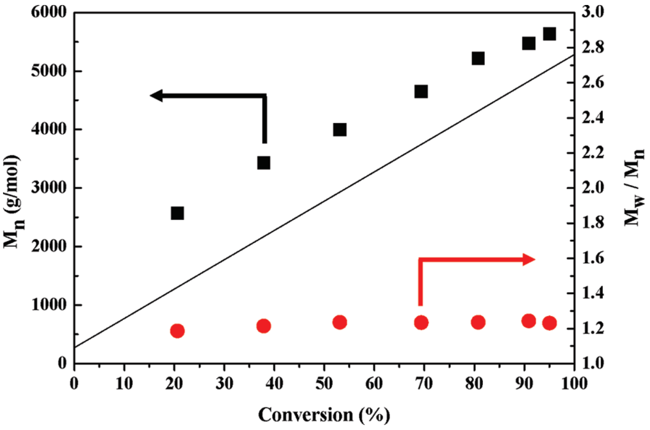


Figure 1. Evolution of number-average molecular weight and polydispersity with monomer conversion for the RAFT synthesis of linear PMMA$_{50}$ homopolymer (refractive index detector with PMMA calibration standards).

Table 1. Summary of Final Conversions, Molecular Weights and Polydispersities of PMMA Homopolymer and Branched Copolymers Prepared under RAFT Conditions in Toluene at 90°C

target copolymer composition	time (h)	conv (%)	M_n	M_w	M_w/M_n	corrected M_n[a]	n_b	$(M_n^b - M_n^l)/M_n^b$
PMMA$_{50}$ homopolymer	20	95.1	5 600	6 900	1.23	5 900	0	0
PMMA$_{50}$-DSDMA$_{0.60}$	35	96.2	8 800	41 400	4.70	9 100	0.55	0.35
PMMA$_{50}$-DSDMA$_{0.70}$	35	96.5	12 000	68 300	5.67	12 400	1.11	0.52
PMMA$_{50}$-DSDMA$_{0.80}$	35	97.3	13 900	331 500	23.92	14 300	1.42	0.59
PMMA$_{50}$-DSDMA$_{0.85}$	35	96.1	28 700	1 126 700	39.29	29 900	4.07	0.80
PMMA$_{50}$-DSDMA$_{0.90}$	35	96.6	92 000	3 324 900	36.14	95 200	15.2	0.94
PMMA$_{50}$-DSDMA$_{0.95}$	35	96.1	macroscopic gelation					

[a] Refractive index detector and poly(methyl methacrylate) calibration standards were used for GPC analysis of the linear PMMA$_{50}$ homopolymer (entry 1), whereas a light scattering detector was used for each branched copolymer, see entries 2–6. The corrected M_n is the extrapolation of the experimental M_n at 100% conversion. n_b is the average number of fully reacted branching comonomers per copolymer molecule, $M_n{}^b$ and $M_n{}^l$ are the number-average molecular weights of, respectively, the branched copolymer and the linear homopolymer. $(M_n{}^b - M_n{}^l)/M_n{}^l = 1$ is the condition for the formation of an infinite gel network.

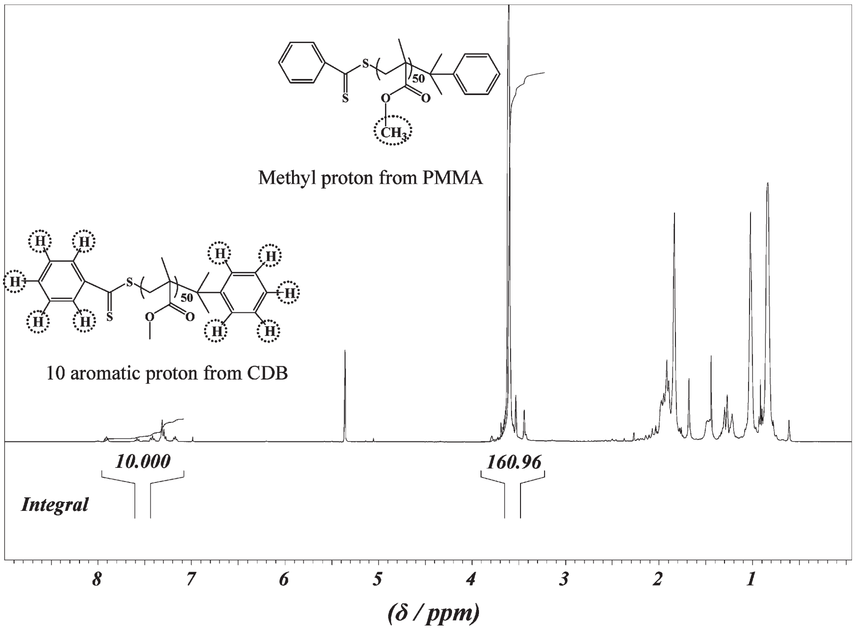


Figure 2. ^{1}H NMR spectrum (CD_2Cl_2) of a linear $PMMA_{50}$ homopolymer synthesized by RAFT using cumyl dithiobenzoate (CDB) chain transfer agent in toluene at 90 °C.

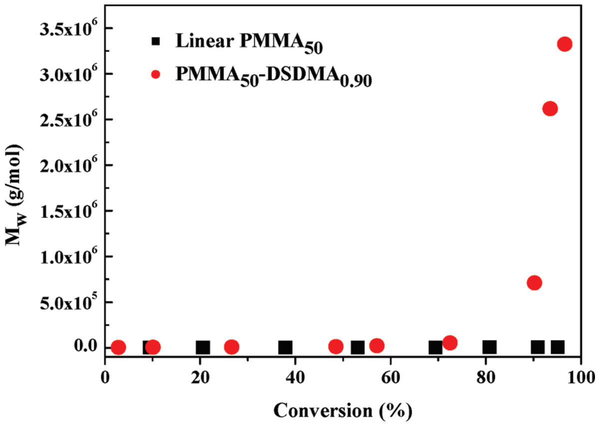


Figure 3. Evolution of weight-average molecular weight and polydispersity with monomer conversion for the RAFT synthesis of branched $PMMA_{50}$-$DSDMA_{0.90}$ copolymer (light scattering detector).

of varying molecular weights and polydispersities depending on the DSDMA/CDB relative molar ratio, see entries 2–6 in Table 1. A somewhat longer reaction time of 35 h was selected because of the highly viscous nature of the copolymerizing solution. The "corrected M_n" column refers to the molecular weight calculated at a theoretical 100% monomer conversion, taking into account the estimated RAFT CTA efficiency of 90%. Using the approach reported by Bannister and coworkers,[18] we calculate n_b and $(M_n^b - M_n^1)/M_n^1$ for all entries shown in Table 1. Here n_b is the average number of fully reacted branching comonomers per copolymer molecule, M_n^b is the number-average molecular weight of the branched copolymer, and M_n^1 is the number-average molecular weight of the linear homopolymer. Therefore the condition for the formation of an infinite gel network is when $(M_n^b - M_n^1)/M_n^1$ approaches unity. Inspecting Table 1, we find that this parameter increases with increasing DSDMA content, as expected, and is equal to 0.94 for the targeted composition of $PMMA_{50}$-$DSDMA_{0.90}$. This is comparable to the $(M_n^b - M_n^1)/M_n^1$ values calculated by Bannister et al. for the ATRP copolymerization of 2-hydroxypropyl methacrylate with ethylene glycol dimethacrylate just below the gel point.

Figure 3 compares the evolution of weight-average molecular weight (M_w) for the linear $PMMA_{50}$ and the $PMMA_{50}$-$DSDMA_{0.90}$ branched copolymer. There is relatively little deviation between the M_w values of the linear homopolymer and branched copolymer up to 70% conversion. Above this value, the M_w of the branched copolymer increases dramatically, which indicates the onset of branching. Similar observations were made by Bannister et al. for ATRP syntheses of methacrylic branched copolymers.[18] Clearly, the target $PMMA_{50}$-$DSDMA_{0.90}$ composition lies very close to the gel point because the final M_w achieved at 97% conversion is 3.3×10^6; this corresponds to a branched copolymer comprising 480 primary chains on average. This hypothesis is corroborated by the observation that the targeted composition of $PMMA_{50}$-$DSDMA_{0.95}$ produces a macroscopic gel rather than soluble branched copolymer.

Classical Flory–Stockmayer gelation theory assumes that copolymerization of a monovinyl and divinyl monomer is purely statistical. If this is correct, then no microgel fraction should be formed during the early stages of the copolymerization and no unreacted branching comonomer should remain at high conversion. If 100% conversion can be achieved, then no pendent vinyl groups should remain in the final copolymer structure. In the present work, we used ^{1}H NMR spectroscopy to determine monomer conversion during these living copolymerizations. This technique allows the calculation of the conversion of the overall vinyl groups due to both MMA and DSDMA comonomers. However, these vinyl signals are partially overlapping and are present at very different concentrations; this makes the assessment of the conversion of the individual comonomers rather problematic. In principle, UV HPLC can offer sufficient resolution between the two comonomers and also has superior sensitivity compared with ^{1}H NMR. Our HPLC protocol involved using an eluent gradient, which ensures good discrimination between the MMA and DSDMA comonomers, see Figure 4. Linear calibration curves were established to quantify the comonomer concentrations present in each aliquot extracted from the reaction mixture during the copolymerization. Figure 5a represents the evolution of the overall conversion of vinyl monomer with reaction time, as calculated by ^{1}H NMR, with the depletion of the individual MMA and DSDMA comonomers being determined by UV HPLC. At first sight, it appears that the rate of

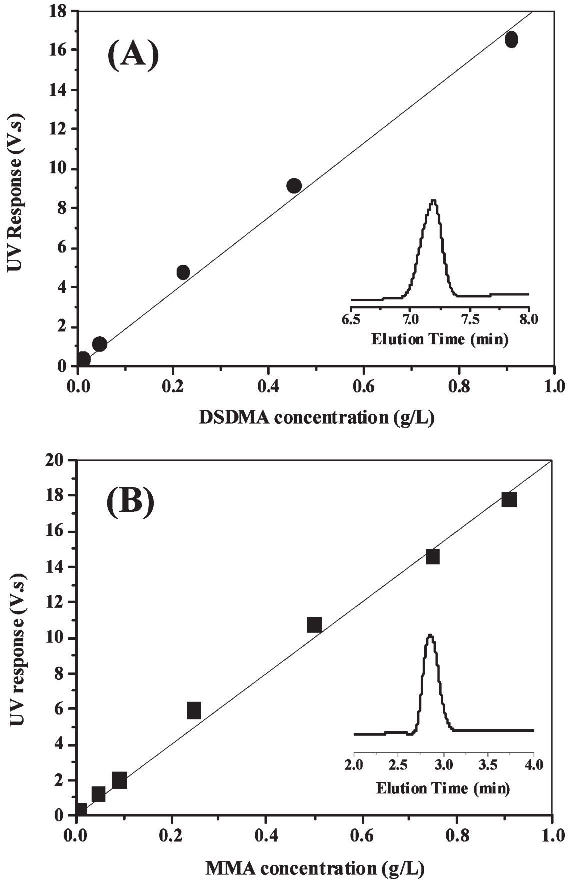


Figure 4. HPLC calibration curves obtained for (a) the disulfide-based dimethacrylate (DSDMA) branching comonomer and (b) the methyl methacrylate (MMA) monomer. These curves were used to determine the respective conversions of these two comonomers during the branching copolymerization of $PMMA_{50}$-$DSDMA_{0.90}$ under RAFT conditions in toluene at 90 °C, see entry 6 in Table 1.

consumption of DSDMA branching agent is significantly greater than that of MMA. However, the probability of incorporating the bifunctional DSDMA into the growing chains is twice that of the monofunctional MMA.[18,22] Moreover, if only one of the DSDMA vinyl bonds reacts, then this comonomer can no longer be detected by HPLC. Bannister et al. have recently shown that the remaining fraction of unreacted branching agent, p, in a statistical conversion of double bonds is related to the overall fractional conversion of all double bonds, F, by the following simple equation: $p = (1 - F)^2$. If this equation is used as a theoretical fit to the experimental data plotted in Figure 5b, then a reasonably good correlation is obtained. This provides convincing evidence of the statistical consumption of the DSDMA branching agent during these branching copolymerizations, which is consistent with the observed near-ideal behavior noted above.

The DSDMA branching agent was selected because it allows facile selective cleavage of the disulfide bonds using an appropriate reagent, for example, tributylphosphine.[14,17,22] All branch points are removed during this chemical degradation, and the branched copolymer is converted into its constituent primary chains. This "retro-synthesis" was conducted on the most highly branched $PMMA_{50}$-$DSDMA_{0.90}$ copolymer (M_w/M_n = 36.1). Subsequent GPC analysis (Figure 6) confirmed that the resulting primary chains were near-monodisperse (M_w/M_n = 1.24), with a number-average molecular weight close to that of the linear $PMMA_{50}$ homopolymer synthesized in the absence of any DSDMA branching agent (M_n = 6600 vs 5600, respectively).

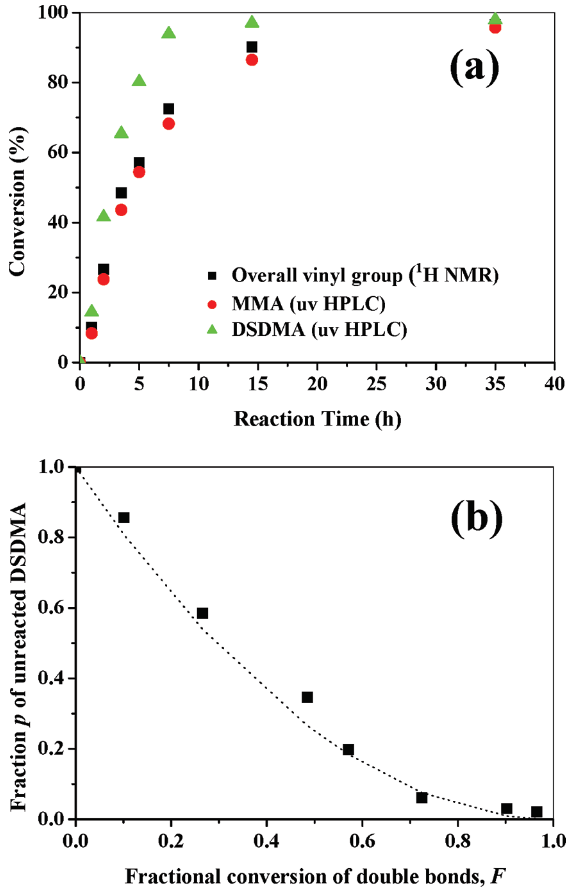


Figure 5. (a) Conversion versus time curves for disulfide-based dimethacrylate branching agent (DSDMA, ▲) and methyl methacrylate monomer (MMA, ●) during RAFT copolymerization mediated by cumyl dithiobenzoate (CDB) in toluene at 90 °C of $PMMA_{50}$-$DSDMA_{0.90}$ as determined using HPLC, with the overall vinyl bond conversion being determined by ^{1}H NMR (■). (b) Fraction of unreacted DSDMA, p, versus fractional conversion of double bonds, F, obtained for the data shown in part a. The dashed line is the theoretical fit to these data, assuming that $p = (1 - F)^2$.

Therefore, this "proof-of-structure" experiment confirms that the branched copolymers simply comprise statistically linked near-monodisperse primary chains, as expected. This also indicates that chain transfer to polymer must be negligible during these RAFT syntheses because this side reaction would otherwise introduce additional branch points comprising noncleavable carbon−carbon bonds, rather than disulfide bonds. It is perhaps also noteworthy that the largest signal in the refractive index detector trace obtained for the original branched copolymer (Figure 6) clearly corresponds to linear homopolymer chains. The presence of such nonbranched chains has been recently predicted by Monte Carlo simulation studies of ideal branching copolymerizations via living chemistry.[27]

Conclusions

In summary, we have devised an improved one-pot RAFT protocol for the synthesis of highly branched methacrylic copolymers that conforms quite closely to classical gelation theory. Increasing the branching comonomer/CTA molar ratio up to almost unity allows the degree of branching to be systematically varied in the final copolymers. Taking into account the CTA efficiency estimated from NMR and GPC, this represents a significantly more efficient protocol than that previously reported for RAFT syntheses of branched copolymers, in which a significant proportion of the bifunctional comonomer is consumed

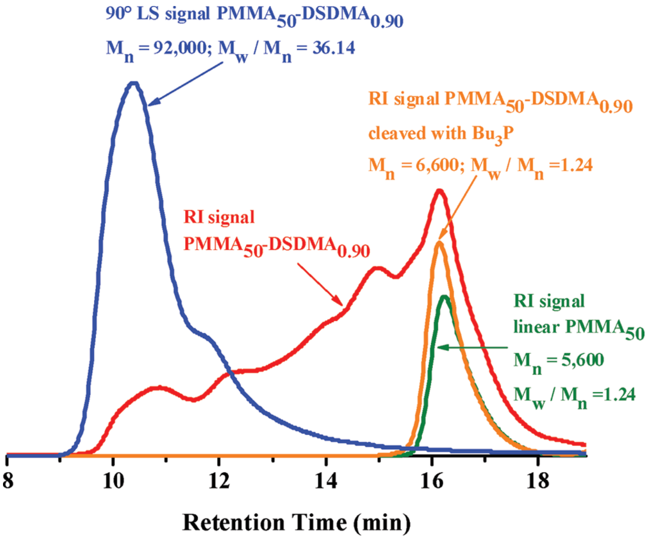


Figure 6. GPC traces recorded using the refractive index (RI) detector and the light scattering detector for the original $PMMA_{50}$-$DSDMA_{0.90}$ branched copolymer and also the RI trace of the degraded polymer chains obtained after the reduction of disulfide bonds of $PMMA_{50}$-$DSDMA_{0.90}$ branched copolymer using tributylphosphine (Bu_3P). The RI trace of the homopolymer prepared in the absence of any DSDMA branching comonomer is shown for comparison.

via intramolecular cyclization and thus does not lead to branching. Moreover, HPLC experiments confirm that the branching DSDMA comonomer is incorporated into the copolymer chains almost statistically. Therefore, provided that appropriate reaction conditions are selected, RAFT syntheses of branched copolymers are now amenable to Monte Carlo simulation. Disulfide cleavage experiments confirm that these highly branched copolymer chains simply comprise randomly coupled near-monodisperse primary chains with little or no evidence of any chain transfer to polymer. It appears that most, if not all, of our success can be attributed to our deliberate selection of a relatively high monomer concentration, which inevitably favors intermolecular branching over intramolecular cyclization. The effect of varying the monomer concentration on branching (non)ideality will be discussed in detail elsewhere in due course.

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