RAFT Synthesis of Branched Acrylic Copolymers

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ABSTRACT: We report the synthesis of branched acrylic copolymers based on 2-hydroxypropyl acrylate using reversible addition fragmentation chain transfer (RAFT) polymerization in *tert*-butanol at 80 °C. Three branching comonomers were investigated in this study: ethylene glycol diacrylate, bisphenol A ethoxylated diacrylate and a disulfide-based diacrylate. The latter comonomer allows chemical degradation of the branched acrylic copolymers to produce thiol-functionalized primary chains. Gel permeation chromatography analysis of these degraded copolymer chains indicated low polydispersities ($M_w/M_n < 1.22$), which confirmed that the living character of the RAFT chemistry was retained under branching conditions. RAFT allows significantly more than one branching agent per primary chain to be used in the copolymerization without causing gelation. This result was obtained with all three branching comonomers and differs from the near-ideal copolymerizations previously reported for the ATRP synthesis of branched methacrylic copolymers (*Macromolecules* **2006**, *39*, 7483−7492). Detailed HPLC analysis of the RAFT copolymerization of 2-hydroxypropyl acrylate with bisphenol A ethoxylated diacrylate indicates near-statistical incorporation of the latter comonomer. We suggest that intramolecular cyclization is the primary reason for the *apparent* violation of classical Flory−Stockmayer gelation theory. This hypothesis is supported by the observation that substantially more ethylene glycol diacrylate than bisphenol A ethoxylated diacrylate can be tolerated in such branching copolymerizations without causing gelation.

Introduction

It is well-known that free radical copolymerization of a monovinyl monomer with a small amount of a divinyl monomer usually leads to gelation, since it is only necessary to introduce an average of two branch points into each chain to obtain an insoluble gel network.[1] In a series of recent papers, Sherrington and co-workers[2−6] have reported a facile "Strathclyde" route to *soluble* branched copolymers. This approach is based on the addition of a thiol to a free radical copolymerization of a monovinyl and a divinyl monomer, typically methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA). In the presence of the chain transfer agent, the molecular weight of the primary chains is substantially reduced and gelation can be suppressed, even at high conversion, provided that less than one branching comonomer is incorporated per primary chain. The development of branching during such "Strathclyde" syntheses has been recently modeled by Steinke and co-workers.[7,8]

We[9−13] and others[14,15] have recently extended this "Strathclyde" approach to branched copolymers to include several types of (pseudo-)living polymerizations, including group transfer polymerization,[16] oxyanionic polymerization[17] and atom transfer radical polymerization (ATRP).[18] In principle, living polymerizations offer better control over the primary chain length and polydispersity and hence over the branching process. Moreover, no malodorous thiol is required, since the molecular weight is dictated solely by the monomer/initiator molar ratio. Two recent ATRP studies are of particular relevance to the present work. First, Li and Armes[12] reported the use of a disulfide-based dimethacrylate branching agent that allowed branched copolymers based on 2-hydroxypropyl methacrylate [HPMA] to be chemically degraded to their primary chains. This retro-synthesis confirmed that the living character of the ATRP chemistry was preserved under branching conditions, since the degraded primary chains were near-monodisperse ($M_w/M_n = 1.23$) and comparable to linear chains prepared under identical conditions in the absence of any branching comonomer. Second, Bannister et al.[13] examined the statistical copolymerization of HPMA with EGDMA using ATRP. In particular, the evolution of branching with conversion was investigated by periodic sampling of the reaction solution to gain a better understanding of the copolymerization mechanism. It was shown that significant branching only occurred relatively late in this copolymerization. Similar results were reported independently by Zhu and co-workers.[14,15] Moreover, in both studies the ATRP branching process conformed closely to classical gelation theory: soluble branched copolymers were obtained when the brancher/initiator molar ratio was less than unity, whereas insoluble copolymer gels were invariably obtained for brancher/initiator molar ratios exceeding unity.[19]

Perrier and co-workers[20] reported the use of reversible addition fragmentation chain transfer (RAFT) chemistry[21] to produce branched methacrylic copolymers via the one-pot copolymerization of MMA and EGDMA mediated by 2-(2-cyanopropyl)dithiobenzoate at 60 °C. In contrast to our ATRP syntheses of branched copolymers, these RAFT copolymerizations do not conform to classical gelation theory, since soluble branched copolymers were obtained at 97% conversion even at brancher/chain transfer agent molar ratios of 1.95. Similarly anomalous results were reported by Taton and co-workers[22] in their synthesis of "polymeric nanogels" when copolymerizing either acrylamide or acrylic acid with methylene bis(acrylamide) using RAFT-related chemistry. This discrepancy suggests that there is a fundamental difference between branching copolymerizations conducted under ATRP and RAFT conditions.

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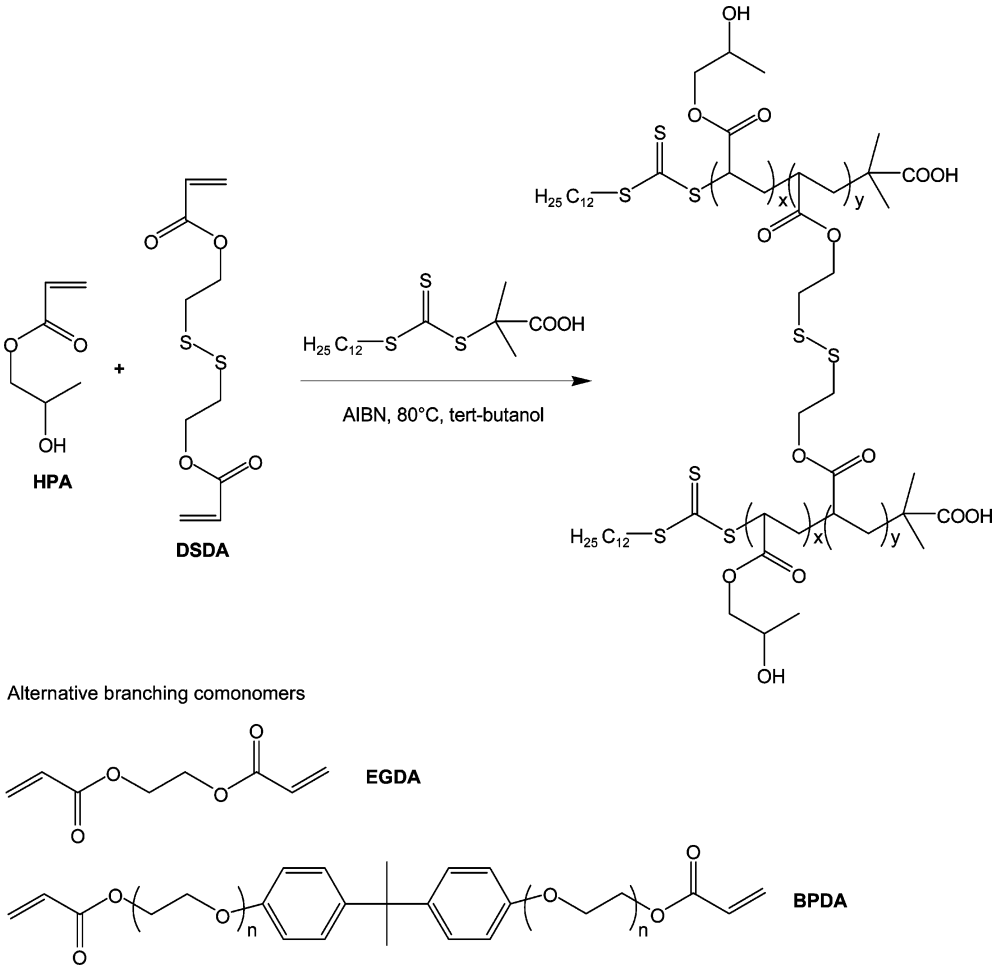
Scheme 1. Synthesis of Branched Copolymers Obtained by Statistical Copolymerization of 2-Hydroxypropyl Acrylate with Three Different Diacrylate Comonomers (DSDA, EGDA, and BPDA) Using a RAFT Chain Transfer Agent at 80 °C in *tert*-Butanol



Herein we investigate the synthesis of branched acrylic copolymers based on 2-hydroxpropyl acrylate (HPA) using RAFT polymerization (see Scheme 1). Three bifunctional branching comonomers were examined: ethylene glycol diacrylate (EGDA), bisphenol A ethoxylated diacrylate (BPDA), and a disulfide-based diacrylate (DSDA). Selective cleavage of the disulfide bonds in the DSDA branching units allowed chemical degradation of the branched copolymer and hence enabled us to assess the living character of the RAFT polymerization under branching conditions. A second fundamental question was whether gelation occurs at around one brancher per chain, as observed for ATRP syntheses of branched copolymers, or whether gelation is suppressed until higher proportions of brancher are utilized, as suggested by two previous studies of RAFT syntheses of branched copolymers.[20,22]

Experimental Section

Materials. HPA was kindly donated by Cognis Performance Chemicals (Hythe, U.K.) and was used as received. This monomer actually comprises an isomeric mixture of approximately 75% HPA and 25% 2-hydroxyisopropyl acrylate, as previously discussed for the closely related HPMA monomer.[17] For the sake of clarity, only the chemical structure of the major isomer is shown in Scheme 1. Anhydrous tetrahydrofuran, *tert*-butanol, tris(2-carboxyethyl)phosphine hydrochloride (TCEP), ethylene glycol diacrylate (90%), and bisphenol A ethoxylate diacrylate (>99%) were purchased from Aldrich and were used as received. 2,2′-Azobis(isobutyronitrile) (AIBN) was supplied by BDH and was used as received. Acryloyl chloride was purchased from Aldrich and was vacuum-distilled prior to use. The trithiocarbonate-based RAFT chain transfer agent (CTA) used in this study is shown in Scheme 1 and was a gift from Dr. John Lai of Noveon (Ohio). This CTA has already been reported to give good control in polymerizations of various acrylic monomers.[23]

Synthesis of Disulfide-Based Diacrylate (DSDA) Branching Comonomer. Bis(2-hydroxyethyl)disulfide (BHEDS, 7.7 g, 50 mmol, 1.0 equiv) and triethylamine (50 mL, 400 mmol, 8.0 equiv) were dissolved in 150 mL of anhydrous THF in a 250 mL flask. This flask was immersed in an ice bath for 15 min, and then acryloyl chloride (18.1 g, 200 mmol, 4 equiv) was added dropwise to the stirred solution. The resulting heterogeneous solution was stirred at 20 °C for 24 h. THF was removed by evaporation under reduced pressure and the crude product was dissolved in 150 mL of chloroform. This solution was washed three times with an aqueous 0.1 M K_2CO_3 solution followed by five washings with deionized water. The purified organic solution was dried using anhydrous $MgSO_4$, and the chloroform was removed under reduced pressure. The final disulfide-based diacrylate product was obtained as a brown oil (12.6 g, 96% yield) and was stored in a freezer under nitrogen in the absence of light prior to use. ^{1}H NMR spectroscopy ($CDCl_3$) indicated a mean degree of esterification of at least 98%: δ 6.40−6.50 and 5.80−5.90 ppm (4H, doublet, C**H**$_2$-CHCOO), 6.05−6.20 ppm (2 H, multiple, CH_2C**H**COO), 4.35−4.45 ppm (4H, triplet, COOC**H**$_2$$CH_2$), and 2.90−3.00 ppm (4H, triplet, $COOCH_2$C**H**$_2$S). An assigned ^{1}H NMR spectrum of this compound is shown in the Supporting Information (see Figure S1).

Synthesis of Linear Homopolymer. A linear homopolymer of 2-hydroxypropyl acrylate (HPA) was prepared using RAFT polymerization as follows. A mixture of CTA (0.1398 g, 0.384 mmol) and HPA monomer (2.50 g, 19.2 mmol, target Dp = 50) was placed in a flask and degassed using three vacuum/dry

nitrogen cycles. Nitrogen-degassed *tert*-butanol (3.75 mL) was then added via syringe. The AIBN initiator (3.0 mg, 0.0182 mmol) was added to this mixture under nitrogen and stirred at room temperature (20 °C) for 5 min. The flask containing this reaction mixture was then placed in an 80 °C oil bath to start the RAFT polymerization. After 2.5 h, monomer conversion had reached around 95%, as indicated by ^{1}H NMR analysis of an extracted aliquot diluted with CD_3OD. The light yellow reaction solution was cooled and the polymer was precipitated into excess 1:1 *n*-hexane/ethyl acetate to remove unreacted monomer. The crude solid was redissolved in a small amount of THF, reprecipitated into 1:1 *n*-hexane/ethyl acetate and dried under vacuum to yield a light yellow polymer.

Synthesis of Branched Copolymers. A mixture of DSDA branching comonomer (0.232 g, 0.884 mmol), CTA (0.280 g, 0.768 mmol), and HPA monomer (5.00 g, 38.41 mmol) was placed in a 25 mL flask and degassed using three vacuum/dry nitrogen cycles. Nitrogen-degassed *tert*-butanol (8.0 mL) was then added via syringe. AIBN initiator (6.0 mg, 0.0364 mmol) was added to this mixture under nitrogen and stirred at 20 °C for 5 min. The flask was then placed in an 80 °C oil bath to commence the polymerization. After the desired reaction times, aliquots were extracted for characterization and diluted with either CD_3OD (to assess monomer conversions by ^{1}H NMR) or THF for (GPC analysis). The final highly viscous copolymer solution was diluted with a two-fold excess of THF and then precipitated into a large excess of deionized water to remove unreacted monomer. This THF/water precipitation cleanup was repeated, followed by solvent removal under vacuum to yield a light yellow purified copolymer in each case. Essentially the same protocol was used for copolymerizations involving the EGDA and BPDA comonomers instead of DSDA. In the case of EGDA, due allowance was made for its 90% purity when calculating the brancher/CTA molar ratios.

Cleavage of the Disulfide-Containing Branched Copolymers by Reduction with Tris(2-carboxyethyl)phosphine Hydrochloride. The disulfide-containing $PHPA_{50}-DSDA_{1.15}$ branched copolymer (0.500 g, 0.080 mmol disulfide) was dissolved in 5.0 mL of deoxygenated methanol containing an approximate ten-fold excess of tris(2-carboxyethyl)phosphine hydrochloride (TCEP; 0.242 g, 0.844 mmol). The reaction mixture was stirred under nitrogen at 30 °C for up to 48 h. Aliquots were periodically withdrawn; methanol was removed under vacuum and the remaining product then redissolved in deoxygenated THF under nitrogen for immediate GPC analysis to determine the extent of cleavage of the disulfide branch sites in the copolymer.

Characterization of Branched Copolymers. ^{1}H NMR spectra were recorded in CD_3OD using a Bruker AC 250 MHz spectrometer. A Polymer Laboratories PL-GPC50 integrated GPC system was used to analyze the molecular weight distributions of the branched copolymers. Linear homopolymers 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 PD 2020 light scattering detector (at 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 near-monodisperse linear poly(methyl methacrylates) were purchased from Polymer Labs and employed as calibration standards with the above refractive index detector for the analysis of the linear PHPA homopolymer and the TCEP-degraded branched copolymer. The mean refractive index increment (d*n*/d*c*) of the branched copolymers was determined to be 0.0645 in THF using an Optilab differential refractometer operating at 633 nm. Aliquots (typically 1−2 mL) were extracted from the (co)polymerizing solutions, diluted with THF, and ultrafiltered using 0.22 μm Teflon PTFE filters prior to GPC analysis.

HPLC Studies. HPLC was used to monitor the depletion of the BPDA comonomer from the copolymerizing solution. The Waters 2695 Separations Module HPLC setup comprised a Gemini 5 μm C18 reverse phase HPLC column (150 mm × 46 mm), a Waters UV detector set at 254 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 5% acetonitrile and 95% of a 5 mM K_2CO_3 aqueous solution. The acetonitrile content was increased from 5% to 100% over 20 min and maintained at 100% acetonitrile for a further 10 min. This protocol increased discrimination between the hydrophilic HPA and the relatively hydrophobic BPDA. The latter comonomer is an oligomeric mixture of compounds, with a mean molecular weight of 464 g mol^{-1} (corresponding to an ethylene oxide/phenyl molar ratio of 1.5). This gave rise to a multiplet UV signal at a retention time of around 17.5 to 18.5 min. The strongest signal within the multiplet (at 18.4 min) was used to construct a linear calibration curve using Clarity 2.1 HPLC software (see Supporting Information). This UV HPLC protocol allowed convenient monitoring of the progressive depletion of the branching comonomer from the reaction solution during copolymerization.

Results and Discussion

2-Hydroxypropyl acrylate (HPA) was selected as the monomer for the present study primarily because our earlier (unpublished) experiments had confirmed that HPA homopolymer was THF-soluble and hence readily amenable to GPC analysis. A second reason is that HPA is isomeric with 2-hydroxyethyl methacrylate (HEMA), which forms water-soluble linear homopolymers but water-insoluble branched copolymers. Prior studies by Weaver et al. suggest that this subtle change in water solubility is essentially a molecular weight effect.[24] Thus, we wished to examine whether the same unusual solubility behavior was also observed with HPA-based homopolymers and copolymers. Our preliminary syntheses confirmed that linear PHPA was indeed water-soluble, as expected. Cloud points for aqueous solutions of PHPA varied between 37 and 63 °C at pH 6.5, depending on its mean degree of polymerization. The target degree of polymerization for the PHPA primary chains was fixed at 50, since earlier ATRP and RAFT studies indicated that this should be sufficient to obtain good-quality branched copolymers.[12,13,20] Moreover, we knew that such branched copolymerizations are typically significantly slower than the corresponding linear polymerizations[12,13,20] and such retardation should be minimized for lower target degrees of polymerization. Three types of bifunctional branching comonomer were investigated in this study: EGDA, BPDA, and DSDA, see Scheme 1. The high molecular weight branched copolymers obtained from such syntheses were invariably water-insoluble; thus, the aqueous solubility behavior of PHPA is quite similar to that of the isomeric poly(2-hydroxyethyl methacrylate) [PHEMA], as expected.

Initial branched copolymer syntheses were conducted using the DSDA comonomer in conjunction with the RAFT CTA. Although ^{1}H NMR studies confirmed that relatively high comonomer conversions (>95%) could be obtained within 4−5 h, these branching copolymerizations were invariably somewhat slower than the corresponding linear homopolymerizations; see Figure 1. This result was not unexpected; we have previously suggested that it may be due to the higher solution viscosity in the former syntheses.[13] This hypothesis seems less satisfactory in the present case, since GPC analyses (refractive index detection) of aliquots periodically extracted from a typical copolymerization suggested that significant branching did not occur in the early stages of the copolymerization; see Figure 2a. However, using a more sensitive light scattering detector confirmed the presence of a high molecular weight shoulder at 46% conversion; see Figure 2b. More importantly, it was immediately obvious that using DSDA/CTA molar ratios greater than unity did not necessarily lead to macrogelation, although

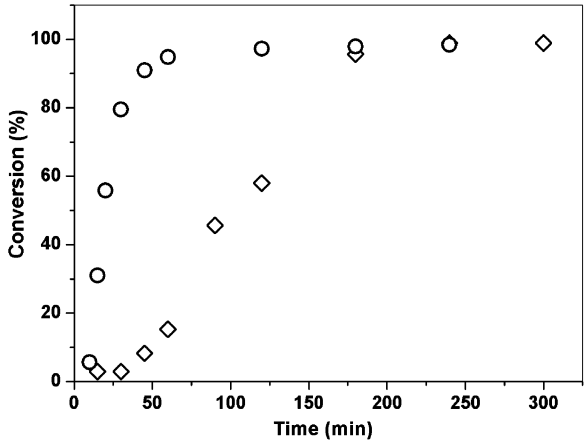


Figure 1. Kinetic data obtained at 80 °C in *tert*-butanol for (a) the RAFT homopolymerization of 2-hydroxypropyl acrylate (HPA) (circles) and (b) the statistical copolymerization of HPA with the DSDA branching comonomer (diamonds). The [HPA]:[CTA]:[AIBN] relative molar ratios were 50:1.0:0.05 for the homopolymerization, while the [HPA]:[DSDA]:[CTA]:[AIBN] molar ratios were 50:1.15:1.0:0.05 for the statistical copolymerization.

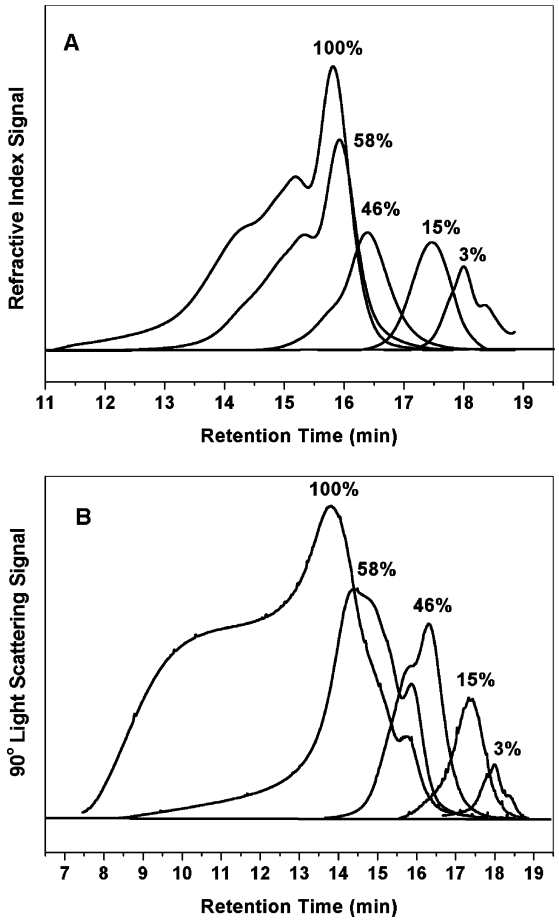


Figure 2. GPC traces recorded at various monomer conversions for the RAFT synthesis of a branched $PHPA_{50}$-$DSDA_{1.15}$ copolymer in *tert*-butanol at 80 °C using (a) a refractive index detector and (b) a 90° light scattering detector.

this was eventually observed at a DSDA/CTA molar ratio of 1.50; see entries 4−7 in Table 1. The evolution of molecular weight and polydispersity during monomer conversion is shown in Figure 3. Homopolymerization of HPA in the absence of any diacrylate brancher gave a linear relationship with a low final polydispersity, as expected. In contrast, significant departure from linearity (and increasing polydispersities) occurred

Table 1. Summary of Final Conversions, Molecular Weights, and Polydispersities of PHPA Homopolymer and Branched Copolymers Prepared under RAFT Conditions at 80 °C in *tert*-Butanol[a]

			mol wt data		
entry no.	target copolymer composition	convn (%)	M_n	M_w	M_w/M_n
1	$PHPA_{50}$ homopolymer	94.8	7950	8600	1.08
2	$PHPA_{50}$−$DSDA_{0.75}$	99.9	25 800	38 000	1.47
3	$PHPA_{50}$−$DSDA_{0.95}$	95.6	21 700	33 500	1.55
4	$PHPA_{50}$−$DSDA_{1.15}$	99.0	29 100	202 000	6.94
5	$PHPA_{50}$−$DSDA_{1.25}$	99.9	22 000	180 000	8.19
6	$PHPA_{50}$−$DSDA_{1.35}$	95.4	30 300	202 800	6.70
7	$PHPA_{50}$−$DSDA_{1.50}$	gel	gel	gel	gel
8	$PHPA_{50}$−$EGDA_{0.95}$	99.9	13 400	26 400	1.97
9	$PHPA_{50}$−$EGDA_{1.35}$	99.6	24 100	134 000	5.57
10	$PHPA_{50}$−$EGDA_{1.58}$	99.4	73 500	327 100	4.45
11	$PHPA_{50}$−$EGDA_{1.80}$	99.3	49 900	201 100	4.03
12	$PHPA_{50}$−$EGDA_{2.25}$	gel	gel	gel	gel
13	$PHPA_{50}$−$BPDA_{0.90}$	99.4	18 300	109 000	5.92
14	$PHPA_{50}$−$BPDA_{1.17}$	99.8	43 100	266 500	6.18
15	$PHPA_{50}$−$BPDA_{1.25}$	98.1	114 300	421 600	3.69
16	$PHPA_{50}$−$BPDA_{1.35}$	gel	gel	gel	gel

[a] A refractive index detector and poly(methyl methacrylate) calibration standards were used for GPC analysis of the linear $PHPA_{50}$ homopolymer (see entry 1), whereas a light scattering detector was used for each branched copolymer (see entries 2−16).

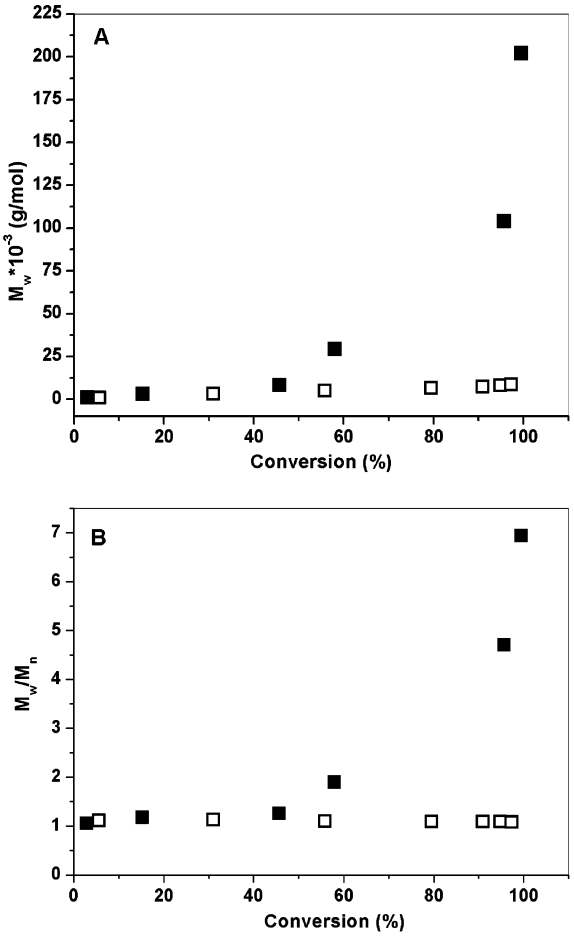


Figure 3. Evolution of weight-average molecular weight (A) and polydispersity (B) with monomer conversion for the RAFT synthesis of linear $PHPA_{50}$ homopolymer (open squares, refractive index detector using PMMA calibration standards) and branched $PHPA_{50}$−$DSDA_{1.15}$ copolymer (filled squares, light scattering detector, entry 4 in Table 1).

at around 50% conversion for the branching copolymerization conducted using the DSDA brancher (see entry 4 in Table 1 and Figure 3). This onset of branching occurs rather earlier than

that observed for the synthesis of branched methacrylic copolymers by ATRP, whereby macrogelation invariably occurred whenever more than one branching comonomer per primary chain was utilized.[12,13] Initially, we thought that perhaps the disulfide bond in the branching comonomer did not survive the RAFT polymerization conditions. However, this possibility was quickly discounted, because no macrogelation occurred when branching copolymerizations were conducted using the EGDA comonomer at EGDA/CTA molar ratios of up to 1.80 (see entry 11 in Table 1). Actually, similar observations were recently reported by both Perrier's group[20] and also by Taton and coworkers,[22] although no satisfactory explanation was offered in either case.

The statistical theory of gelation when copolymerizing monovinyl and divinyl monomers was developed by Flory[1,25−27] and Stockmayer.[28,29] Inherent assumptions are that all vinyl groups are equally reactive and that no double bonds are wasted in side-reactions such as intramolecular cyclization. However, subsequent experimental studies have suggested that neither of these assumptions are valid for many conventional free radical polymerizations. For example, Landin and Macosko[30a] showed that the copolymerization of MMA with small amounts of EGDMA leads to intramolecular cyclization of about 3−4% of the pendent vinyl groups under bulk polymerization conditions, and that this fraction increases rapidly with dilution. Other workers[30b,31−33] have suggested that both cyclization and also reduced reactivity of the pendent vinyl groups may occur. There are several possible explanations that would account for the *apparent* violation of the Flory−Stockmayer gelation theory suggested by the data shown in Table 1. First, the diacrylate branching comonomer may not be efficiently copolymerized with the HPA. Second, only one of the two vinyl groups in the diacrylate comonomer may react, leaving a pendent vinyl group. Third, the diacrylate comonomer may undergo intramolecular cyclization to a substantial extent, resulting in fewer intermolecular branch points than expected. Fourth, the diacrylate may be consumed relatively early in the copolymerization, leading to microgel formation:[34] such microgels may not pass through our guard column and hence would not be detectable by GPC analysis.

In order to shed further light on the nature of these branched copolymer syntheses, a third branching comonomer, BPDA, was investigated. This diacrylate was selected for two reasons: (i) its aromatic chromophores make it readily detectable at relatively low concentrations (see Figure S2); (ii) it is a much larger and less flexible molecule (the mean molecular weight of this oligomer is 464 g mol^{-1}) than the other two branching comonomers, which might be expected to reduce its propensity for intramolecular cyclization. Nevertheless, BPDA/CTA molar ratios of up to 1.25 could be employed in syntheses of PHPA−BPDA branched copolymers with no sign of macrogelation; see entry 15 in Table 1.

^{1}H NMR spectroscopy is often used to follow monomer conversions in living radical polymerizations. However, this technique lacks the sensitivity to accurately monitor the conversion of the branching comonomer, since this component is present at a relatively low concentration (in this case, around 2% of that of the HPA). Fortunately, UV HPLC offers much higher sensitivity and, under appropriate conditions, allows good discrimination between the HPA and BPDA comonomers. Linear calibration curves were obtained for both the HPA and BPDA comonomers (see Figure S2). Our HPLC protocol was validated by comparing the HPA conversion curve with the total comonomer conversion curve obtained by ^{1}H NMR (see Figure S3). Since the proportion of BPDA comonomer is relatively low, a reasonably good correlation was observed. The two HPLC conversion curves obtained for the HPA and BPDA comonomers are shown in Figure 4. It is noteworthy that a very high final conversion of BPDA is obtained. Thus, the possibility that not all of this comonomer participates in the branching copolymerization can be discounted. Cursory inspection of these HPLC data suggests that the initial rate of consumption of BPDA comonomer is significantly faster than that of the HPA. However, we would expect more rapid loss of the BPDA initially, since this brancher has two double bonds and reacting either of these bonds ensures that this species is no longer detectable by HPLC analysis. According to our earlier analysis[13] of the random consumption of double bonds, the fraction, p, of brancher that remains unreacted is related to the overall fractional conversion of all double bonds, F, by the simple equation: $p = (1 - F)^2$. The theoretical fit to this expression using the BPDA conversion data given in Figure 4a is shown in Figure 4b. The fit to the data is reasonable, which indicates that the consumption of BPDA is approximately statistical. This near-ideal copolymerization behavior is not unexpected and may indicate that microgel formation is less likely to occur during these RAFT syntheses.[34]

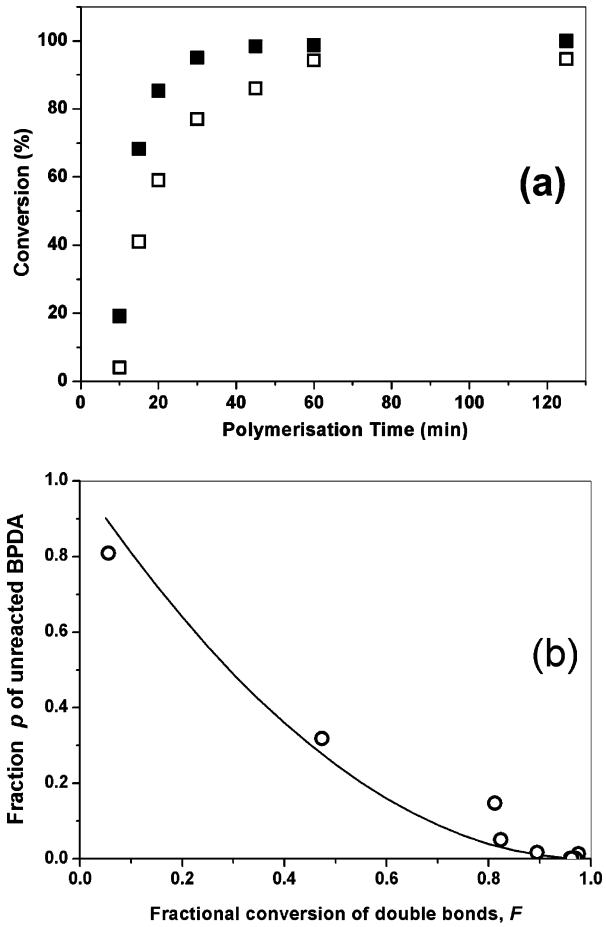


Figure 4. (a) Conversion vs time curves for BPDA branching comonomer (filled squares) and HPA monomer (open squares) during RAFT copolymerization in *tert*-butanol at 80 °C (entry 14 in Table 1) as determined using HPLC. (b) Fraction of unreacted BPDA, p, vs fractional conversion of double bonds, F, obtained for the BPDA data shown in Figure 4a. The solid line is the reasonable fit obtained for these data, assuming that $p = (1 - F)^2$.

Inspecting Table 1, it is clear that are significant differences between the three branchers investigated in this study. The EGDA, DSDA, and BPDA branchers could be used at up to a

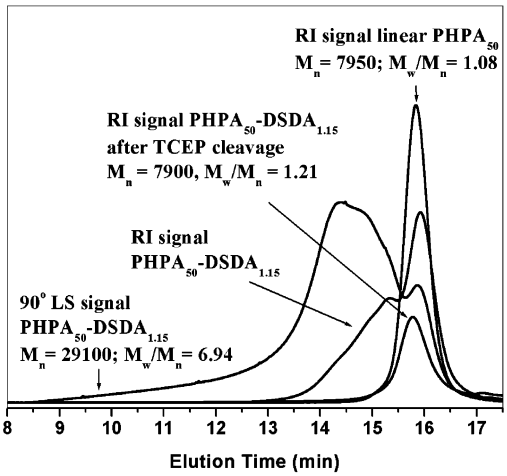


Figure 5. GPC traces recorded using the refractive index detector and the light scattering detector for the original $PHPA_{50}-DSDA_{1.15}$ branched copolymer (entry 4 in Table 1) and also the degraded polymer chains obtained after reduction of disulfide bonds in the $PHPA_{50}-DSDA_{1.15}$ branched copolymer using tris(carboxyethyl)phosphine (TCEP) for 48 h at 30 °C. For clarity, only selected light scattering curves are shown. The GPC curve obtained for linear, near-monodisperse $PHPA_{50}$ prepared by RAFT under the same conditions in the absence of any branching comonomer is included as a reference.

maximum of 1.80, 1.35, and 1.25 branchers per chain, respectively. This trend is in good qualitative agreement with that expected if intramolecular cyclization played a significant role in these branching copolymerizations. Thus, the shorter EGDA brancher should cyclize rather more easily than the much longer, relatively inflexible BPDA brancher, with the DSDA brancher showing intermediate behavior. In summary, the observed differences in brancher performance are consistent with intramolecular cyclization occurring during these branching copolymerizations, although as yet we have no direct evidence for this side reaction.

Using the disulfide-based DSDA comonomer allowed the final branched copolymer to be cleaved at every branch point under mild conditions.[12] This retro-synthesis is illustrated in Figure 5. Subsequent GPC analysis indicated the formation of near-monodisperse primary chains that were essentially indistinguishable from linear PHPA homopolymer synthesized in the absence of any diacrylate brancher (see entry 1 in Table 1). This confirms that these polydisperse branched copolymers simply comprise statistically linked near-monodisperse primary chains and that the pseudo-living character normally associated with RAFT is preserved under branching conditions. Chain branching to polymer is known to occur at around 1−2 mol % during the conventional free radical solution polymerization of acrylic monomers.[35] However, there is little or no evidence for such branching in the GPC curve obtained for the chemically degraded primary chains. Presumably, this is due to the relatively low degree of polymerization of the primary chains, which makes such light branching rather difficult to detect experimentally.

Conclusions

The RAFT synthesis of branched vinyl copolymers using the "Strathclyde" approach has a number of features in common with the corresponding ATRP syntheses. The branching copolymerization is significantly slower than the linear homopolymerization, the majority of the branching occurs at higher conversions and both the final copolymer molecular weight and the polydispersity increase with higher levels of branching comonomer. Moreover, our retro-synthesis of a RAFT-synthesized branched copolymer prepared using a disulfide-based diacrylate demonstrates for the first time that the polydisperse branched chains simply comprise statistically linked near-monodisperse primary chains. However, unlike ATRP, RAFT syntheses can be conducted using up to 1.8 branching comonomers per primary chain without observing macrogelation. This is not to say that the resulting copolymers are more highly branched, rather it simply indicates that these RAFT syntheses do not conform to classical gelation theory. HPLC analyses suggest that these copolymerizations are near-statistical and our ultrafiltration experiments have failed to isolate microgel fractions. Thus, the most likely explanation for our experimental observations seems to be that intramolecular cyclization occurs under RAFT synthesis conditions, which inevitably reduces the degree of actual branching achieved for a given level of branching comonomer. In this context, it is worth noting that the much lower synthesis temperature of 20 °C utilized in our earlier ATRP syntheses of branched methacrylic copolymers[13] may be a significant factor. It is also noteworthy that the amount of "excess" brancher that may be employed in these branching copolymerizations is in the order: EGDA > DSDA > BPDA. This observation is clearly consistent with some degree of intramolecular cyclization, because the bulkier (and less flexible) BPDA brancher is less likely to undergo cyclization.

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Supporting Information Available: Figures showing the assigned ^1H NMR spectrum for the disulfide-based diacrylate comonomer, HPLC calibration curves for 2-hydroxypropyl acrylate and bisphenol A ethoxylate diacrylate, and (co)monomer conversion curves obtained using both HPLC and ^1H NMR. This material is available free of charge via the Internet at http://pubs.acs.org.

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