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Controlled Synthesis of High Molecular Weight Polyacrylates Having a Dumbbell Topology

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ABSTRACT: Well-defined high molecular weight (MW) ($M_n \sim 500\,000$, $M_w/M_n < 1.2$) dumbbell-shaped copolymers based on butyl acrylates (BA) were synthesized by atom transfer radical polymerization (ATRP) in acetone. The synthesis was carried out by polymerization of BA initiated by a difunctional ATRP initiator. The resulting difunctional bromine end-functionalized PBA was used to initiate a small amount of hydroxyethyl acrylate (HEA). The resulting ABA type copolymer containing two short poly(hydroxyethyl acrylate) end blocks was reacted with α-bromoisobutyryl bromide. The resulting ABA polymer was used to reinitiate additional BA end arms to afford the desired dumbbell PBA. All polymer intermediates and the final polymer were characterized by NMR and multiangle laser light scattering size exclusion chromatography (SEC-MALLS). SEC analysis of the low-MW polymers obtained by base hydrolysis of the intended structure confirmed the successful BA polymerization at the A blocks. Hydrolysis gave the expected number and MWs of the grafted chains.

Introduction

Polymers of the so-called "dumbbell" architecture have a linear central block which connects two star branched ends. Such polymers have attracted attention because of their unique polymer topology and hence their potential to affect rheology properties.[1,2] Linear polymers are generally believed to change their configurations through reptation, leading to stress relaxation and viscosity scaling that is proportional to $M^{\sim 3.4}$. Molecular brushes or combs represent an interesting class that have been reported to behave as containing low molecular weight (MW) diluents that cannot be leached out of the sample.[2b,c] H-polymers or dumbbell polymers can be thought of as an extreme case where all the "comb" side arms are clustered at the two ends of a linear polymer. The presence of such arm clusters raise interesting questions with respect to their contribution toward modifying their viscoelastic properties that potentially arise from the frictional resistance borne at the branch points. Until relatively recently, most of these polymers were synthesized by living anionic polymerization, which requires stringent experimental conditions but gives excellent control with respect to the MW and polydispersity. For instance, super-H-shaped polymers having three polyisoprene branches at each end of a polystyrene middle block were prepared via living anionic polymerization followed by chlorosilane chemistry.[3] Later this approach was optimized to give dumbbell polymers with five and more arms at each chain end.[4,5] The synthesis and structural analysis of a H-shaped polybutadiene has also been reported.[5b] Dumbbell macromolecules having a soft polyisobutylene crossbar and 2, 4, or 8 rigid poly(methyl methacrylate) arms at both ends were recently synthesized by combination of living cationic and anionic polymerizations.[5c]

Controlled radical polymerization (CRP) techniques such as atom transfer radical polymerization (ATRP) and reversible addition−fragmentation chain transfer (RAFT) do not require special conditions or highly purified reagents and are used widely to obtain copolymers of relatively well-defined architecture such as block, graft, brush, star, and hyperbranched polymers.[6] Synthesis of a dumbbell-shaped dendritic triblock polymer was reported using RAFT.[7] Recently, dumbbell polymers based on *n*-butyl acrylate (*n*-BA) were prepared by copper-mediated ATRP polymerization of a poly(*n*-butyl acrylate) (P(*n*-BA)) macromonomer[8] onto difunctional P(*n*-BA) macroinitiator.[9] The molecular weights of the resulting dumbbells were below 100 000, and the crude product was contaminated by the macroinitiator and unreacted macromonomer. Dumbbell copolymers consisting of a soft middle block of poly(dodecyl methacrylate) and rigid poly(methyl methacrylate) grafts were prepared by ruthenium-mediated ATRP grafting of methyl methacrylate from a polyfunctional macroinitiator.[10a] The ATRP synthesis of a H-shaped poly(ethylene glycol) (PEG)−polystyrene (PS) polymer ($(PS)_2-PEG-(PS)_2$)) has also been reported.[10b] High molecular weight styrenic dumbbell macromolecules were prepared by combining living anionic polymerization, nitroxide-mediated radical polymerization, polymer−polymer coupling, and finally ATRP.[10c]

Here we report the controlled synthesis of high molecular weight (MW ≈ 500 000) poly(butyl acrylate) (PBA)-based dumbbell polymers by ATRP. We use a *n*-BA/*t*-BA 9/1 mixture in order to selectively hydrolyze *t*-BA in subsequent research but will refer to the mixture as "BA". Around 10 grafting sites were introduced at both ends of a central block by addition of hydroxyethyl acrylate (HEA), giving short PHEA blocks. The corresponding hydroxyl groups were then reacted with α-bromoisobutyryl bromide and used to initiate the ATRP of additional BA. This gave "dumbbell" polymers having predetermined molecular weights of the "crossbar". The numbers and MWs of grafted PBA chains were confirmed by SEC and SEC-MALLS measurements.

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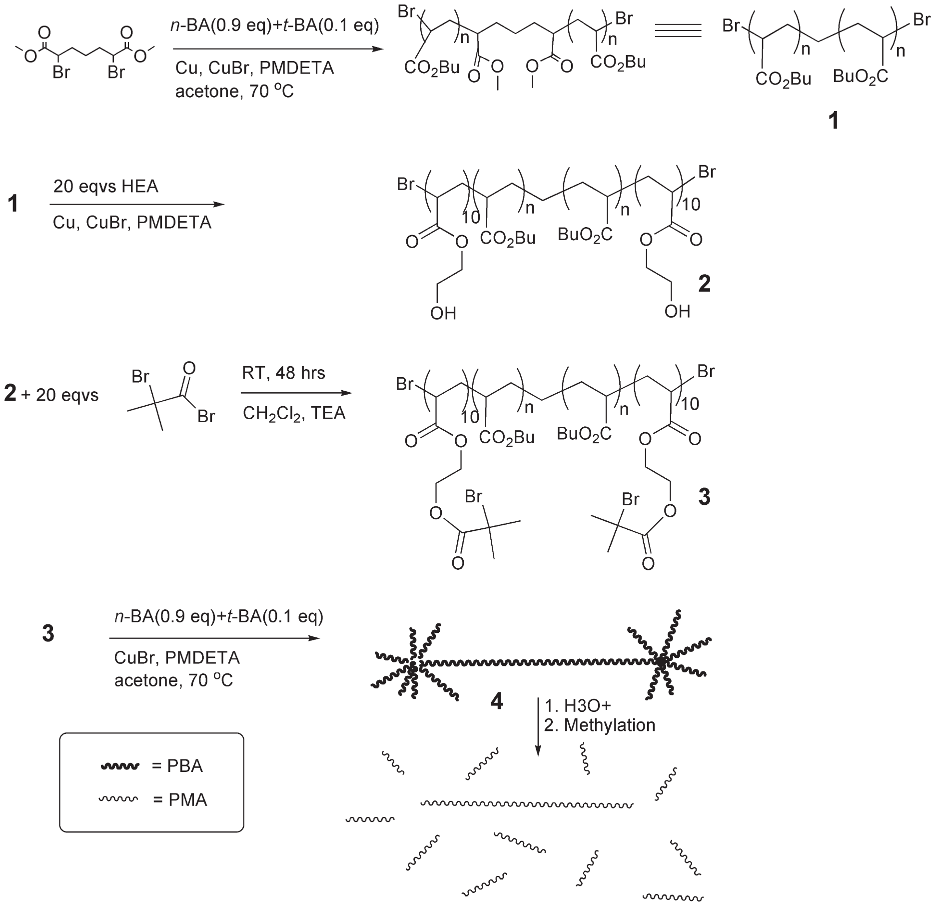
Scheme 1. Synthesis of Dumbbell PBA and Its Precursors



Experimental Section

Materials. Acetone (VWR ACS grade, 99.5%), dichloromethane (DCM, VWR HPLC grade), *n*-butyl acrylate (*n*-BA, 99.5%), *tert*-butyl acrylate (*t*-BA, 99.9%), 2-hydroxyethyl acrylate (HEA, 99.0%), dimethyl-2,6-dibromoheptanedioate (DMDBH, 97%), α-bromoisobutyryl bromide (99.8%), triethylamine (TEA, 98%), CuBr (99.99%), Cu nanopowder (99.8%), *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA, 99%), and trimethylsilyldiazomethane (2.0 M solution in diethyl ether) were all purchased from Aldrich and were used as received.

Synthesis and Characterization. *Difunctional Br−PBA−Br Macroinitiator*. To a round-bottom flask equipped with a Teflon stir bar were added 100 mL of acetone, 60 mL of *n*-BA (0.42 mol), 6.8 mL of *t*-BA (0.046 mol), 0.012 mL of PMDETA (6.0×10^{-5} mol), 0.065 mL of DMDBH (3.0×10^{-4} mol), 4.3×10^{-3} g of CuBr (3.0×10^{-5} mol), and 7.6×10^{-3} g of Cu nanopowder (< 100 nm, 1.2×10^{-4} mol). The flask was attached to a high-vacuum line, and the mixture was degassed at ambient conditions until a persistent high vacuum. Ultrahigh-purity argon (> 99.999%) was introduced, and the flask was sealed with a Suba-Seal rubber septum. The flask was then placed into an oil bath at 70 °C for about 24 h. The polymerization, terminated by opening the flask to the air, gave MWs that were 50−70% of the calculated values, assuming 100% conversion. The Cu compounds were removed by pouring ∼5 g of silica gel directly into the polymerization mixture followed by filtration. The resulting Br−PBA−Br macroinitiator was isolated by precipitation in methanol and drying under high vacuum. ^{1}H NMR ($CDCl_3$): δ 0.94 t (CH_3−$(CH_2)_3$−O); δ 1.32−1.42 m (CH_3−CH_2 + $(CH_3)_3C$; δ 1.6−1.9 m (CH_2−CH + CH_2−CH_2−O) δ 4.03 t (CH_2−CH_2−O).

Preparation of PHEA−PBA−PHEA Precursor. To a round-bottom flask equipped with a Teflon-coated stir bar were added 35 mL of acetone, 0.83 mL of HEA (5.8×10^{-3} mol), 34 g of Br−PBA−Br (2.9×10^{-3} mol), 4.1×10^{-3} g of CuBr (2.9×10^{-5} mol), 7.3×10^{-3} g of Cu nanopowder (1.1×10^{-4} mol), and 0.012 mL of PMDETA (5.8×10^{-5} mol). The flask was attached to a high-vacuum line, and the mixture was degassed by two freeze−thaw procedures. Ultrahigh-purity argon was introduced via the line, and a Suba-Seal rubber septum was attached to the flask's neck. The flask was placed into an oil bath at 75° −80 °C, and the polymerization was allowed to continue for about 24 h. After exposure to air, the polymer was worked up as described above: ^{1}H NMR ($CDCl_3$): δ 0.94 t (CH_3−$(CH_2)_3$−O); δ 1.32−1.42 m (CH_3−CH_2 + $(CH_3)_3C$; δ 1.6−1.9 m (CH_2−CH + CH_2−CH_2−O) δ 4.03 t (CH_2−CH_2−O).

Reaction of PHEA−PBA−PHEA with α*-Bromoisobutyryl Bromide*. The reaction was performed according to a procedure described by Jankova et al.[11] PHEA−PBA−PHEA copolymer (34 g having ∼5.8×10^{-3} mol of OH groups) were dissolved in 100 mL of dry DCM and under high-purity argon as described above. The solution was cooled down to 0 °C, and 2.4 mL of TEA (1.7×10^{-2} mol) was added and then 2.8 mL of α-bromoisobutyryl bromide (1.7×10^{-2} mol) was added dropwise. The reaction was allowed to continue at room temperature (RT) for 48 h. The product was initially precipitated in methanol, dissolved in acetone or THF, filtered, and repeatedly precipitated two to three times in methanol until no low-MW organic bromides that could initiate BA monomer could be observed by SEC. The resulting poly(2-(2′-bromo-2′-methylpropanoyloxy)ethyl acrylate)−PBA−poly(2-(2′-bromo-2′-methylpropanoyloxy)ethyl acrylate), ($P(HEABr)_n$−PBA−$P(HEABr)_n$) was dried under high vacuum until constant weight with a typical yield of around 80%. Proton NMR ($CDCl_3$): δ 0.94 t (CH_3−$(CH_2)_3$−O); δ 1.32−1.42 m (CH_3−CH_2 + $(CH_3)_3C$; δ 1.6−1.9 m (CH_2−CH + CH_2−CH_2−O) δ 4.03 t (CH_2−CH_2−O). δ 4.32 shoulder overlapping with previous peak (CH_2−CH_2−O−CO−$C(CH_3)_2Br$).

Table 1. Synthesis and Molecular Weight Characteristics of Br−PBA−Br (PBA*i*, Where $i = 1{-}3$) and $(PBA)_n$−PBA*i*−$(PBA)_n$[a]

no.	code	$100 \times M_n/M_{n(calc)}$[b] (%)	M_n[e] (SEC)	M_w/M_n[e] (SEC)	M_n (SEC-MALLS)	M_w/M_n (SEC-MALLS)	M[c]
1	PBA1	85	155 000	1.30	170 000	1.09	0.91
2	PBA2	65	125 000	1.30	129 000	1.16	0.97
3	PBA3	59	102 000	1.38	117 000	1.12	0.87
4	$(PBA)_n$−PBA1−$(PBA)_n$	63	356 000	1.24	486 000	1.11	0.73
5	$(PBA)_n$−PBA2−$(PBA)_n$	43	256 000	1.27	344 000	1.15	0.74
6	$(PBA')_n$−PBA3−$(PBA')_n$	69	350 000	1.23	460 000	1.17	0.76
7	$(PBA'')_n$−PBA3−$(PBA'')_n$	67	331 000	1.25	450 000	1.18	0.74
8[d]	$(PBA''')_n$−PBA3−$(PBA''')_n$	79	326 000	1.32	510 000	1.34	0.64

[a] M_n(calc) = 200 000 for entries 1−3; [CuBr]:[Cu(0)]:[PMDETA]:[DMDBH] = 1:4:2:10 for entries 1−3; M_n(calc) = 25 000 for each of the dumbbell's 20 theoretical arms for entries 4−8. [CuBr]:[PMDETA]:[P(HEABr)$_n$−PBA−P(HEABr)$_n$] = 1:2:5. [b] Corresponds to monomer conversion provided that initiating efficiency equals unity. [c] $M = M_{n(SEC)}/M_{n(SEC\text{-}MALLS)}$. [d] Polymerization temperature was 90 °C. [e] Calibrated with PS standards.

Synthesis of Dumbbell $(PBA)_n$−PBA−$(PBA)_n$ Copolymers. In a round-bottom flask 10 g of P(HEABr)$_n$−PBA−P(HEABr)$_n$ ($\sim 1.7 \times 10^{-3}$ mol of Br) was dissolved at room temperature in 40 mL of acetone, 42 mL of *n*-BA (0.30 mol), and 4.8 mL *t*-BA (0.033 mol). Then 0.05 g of CuBr (3.4×10^{-4} mol) and 0.14 mL of PMDETA (6.8×10^{-4} mol) were added, and the flask was attached to a high-vacuum line and the contents were degassed by two freeze−thaw cycles following the above procedures. The flask was refilled with argon and placed into an oil bath, and the polymerization was allowed to continue for about 48 h at 75−80 °C. After termination the $(PBA)_n$−PBA−$(PBA)_n$ polymer was worked up as described for Br−PBA−Br. ^{1}H NMR (CDCl$_3$): δ 0.94 t (CH_3−$(CH_2)_3$−O); δ 1.32−1.42 m (CH_3−CH_2 + $(CH_3)_3C$; δ 1.6−1.9 m (CH_2−CH + CH_2−CH_2−O) δ 4.03 t (CH_2−CH_2−O).

Hydrolysis of Dumbbell $(PBA)_n$−PBA−$(PBA)_n$ and Methylation. The hydrolysis of $(PBA)_n$−PBA−$(PBA)_n$ was carried out as described by Mueller et al.[12] To a glass vial equipped with a Teflon stir bar 0.2 g of dumbbell $(PBA)_n$−PBA−$(PBA)_n$ and 6 mL of saturated aqueous NaOH solution were added. The mixture was stirred for 5 days at 90 °C. After cooling the mixture it was neutralized with concentrated HCl and filtered through a 400 nm PTFE filter to remove NaCl. The final product was dried under high vacuum and redissolved in a small amount of DMF and filtered again. After evaporation of DMF 0.1 g of PAA's was dissolved at room temperature in a stirred solution of 6 mL of THF and 1 mL of deionized water. A trimethylsilyldiazomethane solution (2.0 M in diethyl ether) was added dropwise until the yellow color stayed longer than 24 h. A sample was taken and dried under high vacuum. After dissolution in THF a certain amount of insoluble material was observed (see below).

Characterization. Size exclusion chromatography (SEC) measurements of linear polymer precursors were performed in THF at 1 mL/min at 25 °C on a "Waters" 600 E system consisting of two "Polymer Laboratories" PL-Gel Mixed C 5 μm columns for 200 < MW < 2 000 000, a Waters 410 differential refractometer, and a Wyatt multiangle laser light scattering (MALLS) DAWN EOS detector. PS standards were used for SEC with RI detection. The specific refractive index increment for PBA in THF was taken as 0.069 mL/g.[7] The analysis was performed on Astra software (Wyatt). Proton NMR spectra were taken in CDCl$_3$ at 25 °C on a Bruker AMX 500 or on a Varian Mercury 400 spectrometer operating at 500 and 400 MHz, respectively.

Results and Discussion

The synthetic route to butyl acrylate dumbbell copolymers is presented in Scheme 1. The ATRP polymerization of BA has been reported to show first-order kinetics and to give polymers of predictable molecular weights and narrow dispersities.[13−15]

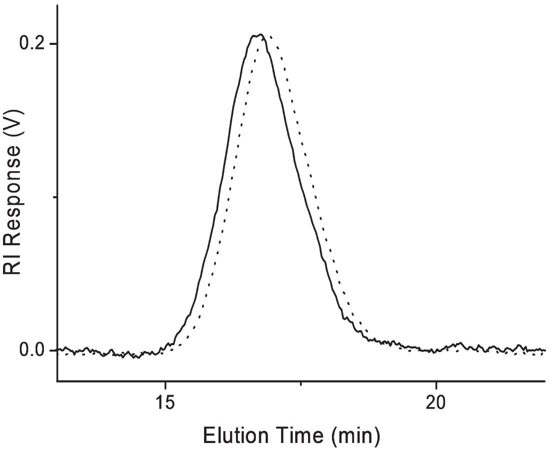


Figure 1. SEC RI overlay curves for PBA3 (dashed line) and HEA−PBA3−HEA (solid line).

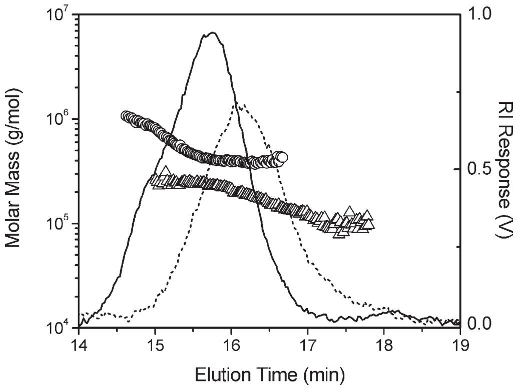


Figure 2. SEC-MALLS of samples 1 and 4. Dashed line and continuous line are the refractive index response vs elution time for samples 1 and 4, respectively. Triangles and circles represent the molar mass vs elution time dependence for samples 1 and 4, respectively.

For the synthesis of the high-molecular-weight Br-PBA-Br initiator (Scheme 1, **1**) small quantities of Cu nanoparticles (< 100 nm) were used in order to improve the kinetics and the control of the BA polymerization either by ARGET outer-sphere SET regeneration of the CuBr catalyst by Cu^{2+} oxidation of Cu(0) as described by Matyjaszewski[16a] or via a Percec et al.[16b] "inner-sphere" electron-transfer mechanism. This was, nevertheless, crucial with respect to achieving molecular weights well above 150 000. However, we found that acetone may be used instead of DMSO.[16b] This is particularly desirable as this solvent is more readily removed (and much less expensive) than DMSO or other high polarity solvents.

The polymerization of BA was followed by SEC and was typically stopped after achieving 50−75% (Table 1) of the calculated molecular weight in order to avoid MWD broadening due to radical coupling.[12] The SEC number-average molecular weights of the linear Br−PBA−Br (Table 1, nos. 1−3) are in good agreement with that obtained by SEC-MALLS. Furthermore, the calculated MWs are close to that expected when corrected for the partial monomer conversions.

Table 2. Molecular Weight Characteristics of the Dumbbell Arms after Hydrolysis and Methylation

no.	code	$M_n{}^a$ (calc)	$M_n{}^b$ (SEC-MALLS)	$M_{n(arms)}{}^c$ (SEC)	M_w/M_n (SEC)	N^e (calc)	N
4′	PMA1/(PMA)$_{2n}$	25 000	15 800	17 800	1.05	20	18
5′	PMA2/(PMA)$_{2n}$	25 000	10 750	19 300	1.20	20	11
6′	PMA3/(PMA′)$_{2n}$	25 000	17 150	15 800	1.08	20	22
7′	PMA3/(PMA″)$_{2n}$	25 000	16 650	15 300	*d*	20	22
8′	PMA3/(PMA‴)$_{2n}$	25 000	19 650	18 000	*d*	20	22

[a] Calculated from feed for the case of complete monomers conversions. [b] Calculated from SEC-MALLS ($M_{n(arm)} = [M_{n(dumbbell)} - M_{n(crossbar)}]/20$, where 20 is the calculated number of arms. [c] M_n was recalculated by multiplying the degree of polymerization of the PMA by the molecular weight of a BA unit. [d] Only sample 6′ was hydrolyzed, and methylated samples 6′, 7′, and 8′ are "twin" experiments performed with the same precursor and at similar conditions; therefore, the data for 7′ and 8′ were extrapolated from 3. [e] N = number of arms.

HEA readily polymerized when added to the acetone solution of Br−PBA−Br difunctional macroinitiator in the presence of Cu$^+$/Cu(0). It was previously reported that ATRP homopolymerization of HEA proceeds instantaneously and gives stable gels and a lack of MW control if carried out in bulk or at high monomer concentrations ($>$1.0 M).[17] Therefore, in our case HEA was polymerized at a lower concentration (0.16 M). The resulting PHEA−PBA−PHEA copolymers (Scheme 1, **2**) had the expected small M_n increases with the polydispersities (PDI's) remaining virtually the same (Figure 1). It was not possible to determine the quantitative molar content of HEA by proton NMR due to the extremely high weight fraction of the PBA relative to the HEA units. However, the reaction of PHEA−PBA−PHEA with 2-bromoisobutyryl bromide gave the intended multifunctional P(HEABr)$_n$−PBA−P(HEABr)$_n$ initiators (Scheme 1, **3**; Figure S7). For the case of primary OH groups this reaction is known to be quantitative, and this has been used to produce other ATRP initiators or macroinitiators.[11]

The ATRP polymerization of BA initiated by P(HEABr)$_n$−PBA−P(HEABr)$_n$ in the presence of only CuBr as the catalyst gave the final (PBA)$_n$−PBA−(PBA)$_n$ dumbbell copolymers (Scheme 1, **4**). The copolymers were all characterized by ^{1}H NMR, SEC, and SEC-MALLS (Table 1, Figures S1−S7). For the sake of clarity only data for Br−PBA−Br and the dumbbell (PBA)$_n$−PBA−(PBA)$_n$ are presented, as the molecular weights of PHEA−PBA−PHEA and P(HEABr)$_n$−PBA−P(HEABr)$_n$ differ only very slightly from Br−PBA−Br and the respective PDI's are virtually the same.

As expected, the apparent SEC molecular weights of the final dumbbell PBA's are lower than the respective values determined by SEC-MALLS. This is consistent with the presence of terminal branching in the dumbbell polymers as this branching should decrease hydrodynamic volumes.[18,19] Thus, the ratios $M = M_{n(SEC)}/M_{n(SEC\text{-}MALLS)}$ approach unity for linear polymers as seen in our case (Table 1, nos. 1−3) but are significantly lower than 1 and range from 0.64 to 0.76, consistent with a dumbbell architecture (Table 1, nos. 4−8). The MW distributions of the dumbbell polymers are relatively narrow and in the expected MW range, indicating that the polymerization of HEA and the subsequent functionalization and initiation of BA were occurring as expected. However, in all cases the SEC's of the dumbbell copolymers showed a small high-molecular-weight shoulder (Figure 2). The analysis performed on Astra software revealed that the molecular weight of the tail is ~2 times higher than the M_n of the main peak. This indicates an occurrence of radical recombination reactions especially at higher monomer conversions (Table 1, nos. 7 and 8) as also observed for the synthesis of star polymers using ATRP systems.[20,21] The coupling reactions can be controlled by varying the temperature, the concentrations of BA monomer, the ATRP catalyst, and especially the lower BA conversions.[15]

The dumbbell copolymers contain around 10 mol % of *t*-BA units both within the "crossbar" and the side arms. This was determined by ^{1}H NMR and was in good agreement with the composition calculated from the monomer feed (Figure S5). Provided that copolymerizations were stopped before full monomer conversion, the reactivity ratios of *t*-BA and *n*-BA are close to unity. The *t*-BA monomer units can be selectively hydrolyzed,[22] thus providing "random" carboxylic acid functionalities within the PBA dumbbell. In the present work we did not use this potential, but this is intended for future work with respect to rheology properties of the dumbbell macromolecules.

In order to further analyze the PBA dumbbell structures, the polymers were completely hydrolyzed to poly(acrylic acid)s (PAA's).[12] This detaches the dumbbell "arms" from the PHEA end blocks. The resulting mixture of poly(acrylic acid)s were methylated with trimethylsilyldiazomethane to obtain poly(methyl acrylate) (PMA) mixtures that were soluble in THF, thus allowing SEC analysis. The methylation of the middle PAA block is not a favorable process, plausibly due to its high molecular weight. Thus, after dissolution of the PMA in THF an insoluble fraction was typically observed, most likely corresponding to a high-MW partially methylated PAA (PBA) middle block (Figure S4). However, SEC analysis of the low-MW PMA "arms" provided M_n values in very good agreement with the calculated ones (Table 2). The only exception was sample 5′ from Table 2 where a discrepancy between $M_{n(SEC)}$ and $M_{n(SEC\text{-}MALLS)}$ of the arms was observed most likely due to a lower conversion of HEA (Scheme 1).

The above synthetic methods allow for the building of moderately high molecular dumbbell macromolecules, a task which would be certainly more difficult using the macromonomer approach. Future work is intended to elucidate the rheology of the dumbbell polymers in bulk or as additives.

Conclusions

High molecular weight ($M \leq 5 \times 10^5$) dumbbell-shaped poly(butyl acrylate)s (PBA's) having a predetermined average number of pendent arms at the ends of the crossbars were synthesized using Cu$^+$/Cu(0) ATRP methods in acetone using a "core first" approach via a triblock poly(hydroxyethyl acrylate)-*b*-poly(butyl acrylate)s-*b*-poly(hydroxyethyl acrylate) with controlled molecular weights. Reaction with α-bromoisobutyryl bromide gave the corresponding multifunctional macroinitiators that were used to giving the final dumbbell PBA polymers via ATRP initiation/polymerization of BA. Upon degradation of the PBA dumbbells by hydrolysis and methylation, the number of pendent PBA chains was proven to be in reasonably good agreement with calculated values.

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Supporting Information Available: SEC-MALLS curves of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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