

Synthesis of Amphiphilic Block Copolymers by Atom Transfer Radical Polymerization (ATRP)

Andreas Mühlebach,[†] Scott G. Gaynor,[‡] and Krzysztof Matyjaszewski^{*‡}

Additives Research, Ciba Specialty Chemicals Inc., CH-1723 Marly 1, Switzerland, and Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

Received March 25, 1998; Revised Manuscript Received July 6, 1998

ABSTRACT: The controlled/"living" radical polymerization of *n*-butyl acrylate (**n-BA**) and 2-trimethylsilyloxyethyl acrylate (**TMS-HEA**) by atom transfer radical polymerization (ATRP) is reported. Di- and triblock copolymers with predefined block lengths and low polydispersities were obtained, using methyl 2-bromopropionate as the initiator, Cu^IBr as catalyst and *N,N,N,N',N'*-pentamethyldiethylenetriamine as the ligand. Hydrolysis of the trimethylsilyl groups led to block copolymers with **n-BA** and 2-hydroxyethyl acrylate (**HEA**) units which were characterized by SEC, ¹H NMR, and DSC. Diblock copolymers of **n-BA** and **HEA** could also be obtained by successive addition of the two monomers, in that order. The amphiphilic di- and triblock copolymers formed dispersions in water.

1. Introduction

One of the most important goals in synthetic polymer chemistry is to gain control over not only the molecular weights and polydispersities of polymer chains but also their composition, architecture, and end group functionalities, thus getting closer to the world of natural polymers. Living polymerization appears to be the simplest technique to reach this goal.¹ Mainly performed by anionic,^{2,3} cationic,⁴ ring opening metathesis polymerization⁵ or group transfer polymerization,⁶ living polymerizations require specific experimental conditions and/or highly sophisticated catalysts, which often are air and/or moisture sensitive, thus making their industrial application difficult.

Free radical polymerization is generally much more tolerant to moisture and other impurities and is therefore of great commercial importance. However, the propagating radicals undergo nearly diffusion-controlled termination by bimolecular processes which limit control. This is in sharp contrast to ionic polymerization processes, in which bimolecular coupling does not occur. In recent years, however, significant advances have been made in the field of controlled free radical polymerizations by suppressing the contribution of termination and chain transfer reactions.^{7–13} One of the most versatile controlled/"living" radical polymerization methods developed so far is the Cu-catalyzed atom transfer radical polymerization (ATRP).^{13–21} Other transition metals that have also been successfully used include Fe,^{22,23} Ru,^{12,24} Ni,²⁵ Rh,²⁶ and Pd.²⁷ ATRP, which has its roots in organic chemistry's atom transfer radical addition (ATRA),²⁸ has proven to be effective for a wide range of monomers (styrenes, (meth)acrylates, acrylonitrile, etc.), either in bulk or in a variety of solvents (benzene, water, etc.). Furthermore, it is generally performed at moderate temperatures (80–120 °C). For these reasons, it emerges as a powerful tool for academic as well as industrial polymer chemists, allowing for the efficient synthesis of novel, tailor-made materials.²⁹

Although nature uses extensively the combination of hydrophobic and hydrophilic chain ends to form "walls"

and micelles, very few well-defined, synthetic, amphiphilic copolymers are commercially available. This is mainly due to the lack of clean, simple and reproducible syntheses. We report here on the synthesis (by ATRP) and characterization of amphiphilic di- and triblock copolymers between *n*-butyl acrylate (**n-BA**) and 2-hydroxyethyl acrylate (**HEA**), Scheme 1.

ATRP has been demonstrated to proceed via the establishment of an equilibrium between active (radical) species and dormant species (alkyl halide): Scheme 2.^{14,16} To have a controlled/"living" polymerization process with a negligible amount of termination, radical concentrations must be low during the polymerization, which means that the equilibrium has to be strongly on the side of the dormant species and M^n/L . In addition, the rate of deactivation of active species has to be very fast, on the order of the rate of propagation or faster. This is indeed the case for the monomers and catalysts used in this study (Cu(I)/PMDETA). In this work, we applied the use of *N,N,N,N',N'*-pentamethyldiethylenetriamine, PMDETA, an inexpensive and commercially available ligand, as the ligand for CuBr, instead of substituted bipyridines.³⁰

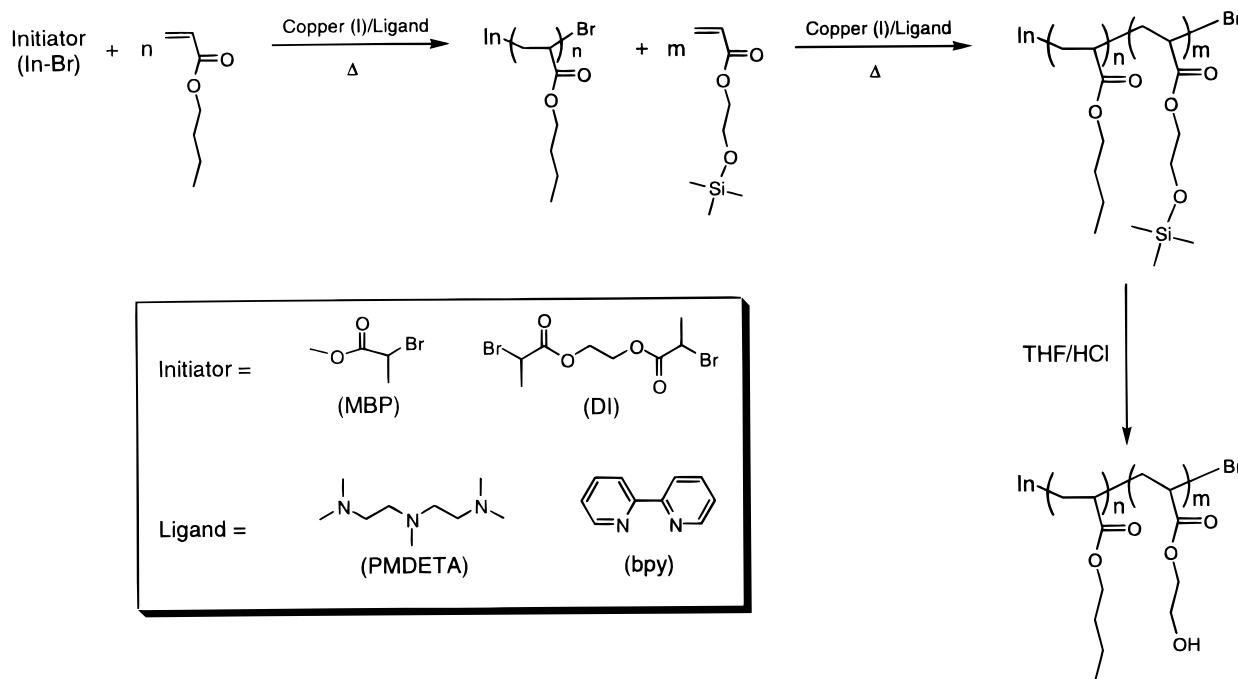
2. Experimental Section

2.1. Materials. *n*-Butyl acrylate (**n-BA**, Acros, 99+%) was distilled from CaH₂ under reduced pressure (150 mbar). 2-Hydroxyethyl acrylate (**HEA**, Aldrich, 96%) was purified by initially dissolving the monomer in water (25 vol %). Hydroquinone (0.1 wt %) was then added to the solution to inhibit polymerization. The solution was extracted 10 times with hexane to remove diacrylates and the aqueous solution was salted (200 g of NaCl/L). The monomer was then separated from the aqueous phase by ether extraction (4 times) to remove acrylic acid. Hydroquinone (0.05 wt %) and MgSO₄ (3 wt %) were added to the ether solution before the evaporation of the ether phase in the rotary evaporator. The purified monomer was distilled in vacuo (70 °C/3 mm Hg) immediately prior to use. Passing it through a column of basic alumina removed traces of acidic impurities and substantially improved conversions in ATRP. Methyl 2-bromopropionate (**MBP**, Aldrich, 99%) was distilled. *N,N,N,N',N'*-Pentamethyldiethylenetriamine (**PMDETA**, Aldrich, 99%) and 2,2'-bipyridine (**bpy**, Aldrich, 99+%) were used as received. Cu^IBr (Aldrich, 98%) was purified by stirring in acetic acid, washing with methanol,

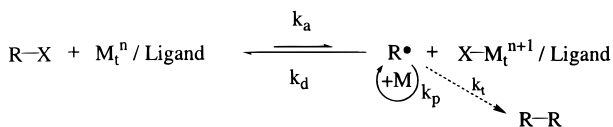
[†] Ciba Specialty Chemicals Inc.

[‡] Carnegie Mellon University.

Scheme 1



Scheme 2



and then drying in vacuo. All other reagents were used as received.

2-Trimethylsilyloxyethyl acrylate (**TMS-HEA**) was synthesized by silylation of 2-hydroxyethyl acrylate (50 mL, 435.3 mmol) with trimethylsilyl chloride (61 mL, 479 mmol) in $\text{CH}_2\text{Cl}_2/\text{NEt}_3$ (500 mL/73 mL) at 0 °C under Ar and then allowed to come to room temperature. The solution was filtered to remove $\text{NEt}_3\cdot\text{HCl}$, and the CH_2Cl_2 was removed by distillation. The product was filtered again, dissolved in EtOAc (300 mL), which was washed 3 times with water, the EtOAc solution was dried and EtOAc evaporated off, and the product was distilled in vacuo (103 °C/38 mmHg).

The difunctional initiator bis(2-bromopropionyloxy)ethane ($\rho = 1.66 \text{ g/cm}^3$) (**DI**; see Scheme 1) was prepared by esterification of ethylene glycol with 2-bromopropionyl bromide and NEt_3 .

2.2. Polymerization Procedures. The polymerizations were conducted in predried round-bottom flasks. Cu^IBr was added and the flask tightly closed with a rubber septum. After the air was removed by evacuation and purging with Ar (2 cycles), the monomer(s), solvent(s), internal standard(s) (for the conversion measurements by GC), and/or the ligand were added via syringe. The mixture was stirred and purged with Ar for 10 min and then, via syringe, the initiator was added and the flask placed in a preheated oil bath. After specified time intervals, samples (ca. 10 mg) were taken to determine conversions via ^1H NMR. After the specified conversion was reached, the flask was removed from the oil bath and the reaction mixture diluted (1:1 to 1:4) with THF or DMF. The solution was filtered through a column with neutral alumina (Fisher-Scientific, 80–200 mesh) to remove the catalyst and a sample taken for SEC analysis. The rest of the solution was concentrated by rotary evaporation, and the polymer was dried in vacuo at 60–80 °C ($p < 0.1 \text{ mmHg}$).

Block copolymerizations were conducted by two methods; i.e., the homopolymers were isolated as described above and then used as macroinitiators for the polymerization of the second monomer (addition of Cu^IBr , second monomer, ligand,

and macroinitiator in this order). Conversely, the first monomer was polymerized until the desired conversion was reached, the second monomer added, and polymerization continued as described above.

Example 1 (AM2-B, Homopolymerization of TMS-HEA, $[\text{M}]:[\text{I}]:[\text{Cu}] = 50:1:0.5$). A 38.0 mg (0.266 mmol) sample of Cu^IBr was weighed into a 10 mL round-bottom flask, which was tightly closed with a rubber septum, and the air was removed by evacuation and purging with Ar (2 cycles). Then 5.26 mL (5.0 g, 26.6 mmol) of the monomer **TMS-HEA** was added via syringe, followed by 55.4 μL (46 mg, 0.265 mmol) of the ligand **PMDETA**. The mixture was stirred and purged again with Ar for 10 min, and then, via syringe, 59 μL (88.5 mg, 0.53 mmol) of the initiator **MBP** was added and the flask placed in the preheated oil bath at 80 °C. After 20 min the conversion (determined by ^1H NMR) reached >95% and the flask was removed from the oil bath. The reaction mixture was diluted 1:2 with THF and the solution filtered through an Al_2O_3 column. A sample was taken for SEC analysis, while the rest of the solution was concentrated in the rotary evaporator and the polymer finally dried in vacuo at 60 °C overnight ($p < 0.1 \text{ mmHg}$). Yield: 3.40 g (68%). SEC: $M_n = 9390$, $M_w/M_n = 1.20$ ($M_n^{\text{calc}} = 9415$). ^1H NMR (CDCl_3), δ : 0.13 (s, SiMe_3), 1.7 and 1.9 (m, CH_2 in polymer main chain), 2.34 (m, CH in polymer main chain), 3.75 (m, $\text{CH}_2\text{-OSi}$), 4.10 (m, C(O)O-CH_2), 3.14 (s, OMe of end group) ppm. DSC: $T_g = -43$ °C.

Example 2 (AM4-B, 1:1 block copolymerization of n-BA and TMS-HEA, $[\text{M}_{\text{tot}}]:[\text{I}]:[\text{Cu}] = 100:1:0.5$). A 15.9 mg (0.111 mmol) sample of Cu^IBr was weighed into a 10 mL round-bottom flask, which was tightly closed with a rubber septum, and the air was removed by evacuation and purging with Ar (2 cycles). Then 1.61 mL (1.44 g, 11.2 mmol) of the first monomer **n-BA** was added via syringe, followed by 23.2 μL (19.2 mg, 0.111 mmol) of the ligand **PMDETA**. The mixture was stirred and purged again with Ar for 10 min, and then, via syringe, 24.9 μL (37.2 mg, 0.223 mmol) of the initiator **MBP** was added and the flask placed in the preheated oil bath at 80 °C. After 12 min reaction time, 2.22 mL (2.11 g, 11.2 mmol) of the second monomer (**TMS-HEA**) was added via a syringe. Polymerization was continued at 80 °C for 30 min, and then the reaction mixture cooled to room temperature and was diluted 1:2 with THF, and the resulting solution was filtered through a Al_2O_3 column. A sample was taken for SEC analysis, and the rest of the solution was concentrated in the

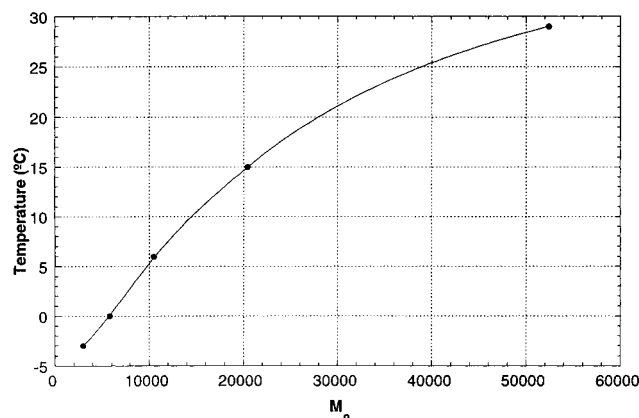


Figure 1. Dependence of the glass transition temperature (T_g) on the number average molecular weight (M_n) of poly(HEA).

rotary evaporator. The polymer was finally dried in vacuo at 60 °C overnight ($p < 0.1$ mmHg). Yield: 2.40 g (68%). SEC: $M_n = 12\,300$, $M_w/M_n = 1.19$ ($M_n^{\text{calc}}: 11\,870$). $^1\text{H NMR}$ (CDCl_3), δ : in addition to TMS-HEA peaks: 0.95 (t, CH_3), 1.36 and 1.60 (m, $2 \times \text{CH}_2$), 1.7, 1.9 and 2.3 (m, CH_2 and CH in polymer main chain), 4.0–4.1 (m, C(O)O-CH_2) ppm. Composition ($^1\text{H NMR}$): **n-BA/TMS-HEA** = 53/47 (theoretical: 50/50). DSC: $T_g = -46$ and -54 °C.

2.3. Deprotection of Polymers and Copolymers. Example (AM9-B): A sample of 0.956 g sample of poly(**n-BA-*b*-TMS-HEA**) 53/47 (AM4-B) was dissolved in 5 mL of THF and 1 mL of H_2O containing 3 drops of HCl_{conc} added dropwise with magnetic stirring. After 30 min, the homogeneous slightly yellow solution was added dropwise to 60 mL of H_2O , whereby a fine precipitate was formed. The mixture was neutralized with 5% NaOH_{aq} and the **nBA-HEA** block copolymer isolated by centrifugation (a substantial part of the precipitate was too small of a particle size for filtration). It was dried for 14 h at 90 °C in vacuo. Yield: 0.389 g. SEC (DMF): $M_n = 11\,200$, $M_w/M_n = 1.49$. $^1\text{H NMR}$ ($\text{DMSO-}d_6$), δ : 0.85 (CH_3 , **1**), 1.30 (CH_2 , **2**), 1.50 (CH_2 , **2**), 1.80–1.20 (CH_2 , **4**), 2.25 (CH, **5**), 3.54 (CH_2 , **7**), 3.95 (CH_2 , **3**, **6**) 4.70 (OH, **8**) ppm. Bold numbers correspond to assignments in Figure 2. Composition (according to $^1\text{H NMR}$): **n-BA/HEA** = 62/38. DSC: $T_g = -45$ and -2 °C.

2.4. Characterization of Materials. SEC measurements were carried out in THF or DMF on a Waters 510 LC pump

equipped with 4 Phenogel 5 μm columns in series (in THF; guard, 10^5 , 1000, and 100 Å; in DMF; guard, 5×10^6 , 5×10^4 , and 500 Å), with a Waters 410 RI detector and diphenyl ether as internal standard. Calibration was based on low polydispersity polystyrene standards (for the acrylates in THF) and poly(MMA) standards (for methacrylates in THF and all samples in DMF). A 300 MHz Bruker FT spectrometer was used for the $^1\text{H NMR}$ measurements with CDCl_3 or $\text{DMSO-}d_6$ as the solvent. GC measurements were performed on a Shimadzu GC-14A, equipped with a wide-bore capillary column (J&W Scientific, DB-WAX). The monomer conversion was determined either by GC using *p*-dimethoxybenzene as internal standard or by $^1\text{H NMR}$. DSC measurements were made on a Rheometric Scientific DSC Plus with RSI Orchestrator software. The samples were first heated at 150 °C for 5 min. (to remove thermal history and volatile solvents), cooled to -90 °C, and held there for 3 min. Then the sample was heated: -90 to $+150$ °C at 10 °C/min. MALDI-TOFMS data were collected using a PerSeptive Biosystems Voyager Elite MALDI mass spectrometer, equipped with a nitrogen laser ($\lambda = 337$ nm). The polymers were dissolved in DMF (ca. 20 mg/mL), and *trans*-3-indoleacrylic acid (IAA) (1:1 and 4:1 relative to polymer) was used as matrix material, doped with NaCl. Data collection was achieved in reflective mode using delayed extraction with a delay time of 150 ns. All spectra were averaged over 128 laser scans.

3. Results and Discussion

3.1. Homopolymerizations of n-BA and TMS-HEA. The polymerization of **n-BA** in bulk or in solution (benzene, ethylene carbonate and other solvents) has been studied in our group.³¹ 2,2'-Bipyridine (bpy) and 4,4'-di(5-nonyl)-2,2'-bipyridine (dNbpy) were used as ligands for Cu, leading to heterogeneous^{13,14,32} and homogeneous systems,^{15,16,33} respectively. When the commercially available PMDETA ligand was used (cf. Table 1), a very fast polymerization was observed,³⁰ for the three polymerizations of **n-BA** in Table 1, the conversions reached $>99\%$. The relatively broad molecular weight distributions suggested that either the deactivation of the growing radical chain ends was slow, or some side reactions, such as coupling of the polymer chains at very high conversion, were occurring. The polydispersities decreased with increasing chain length

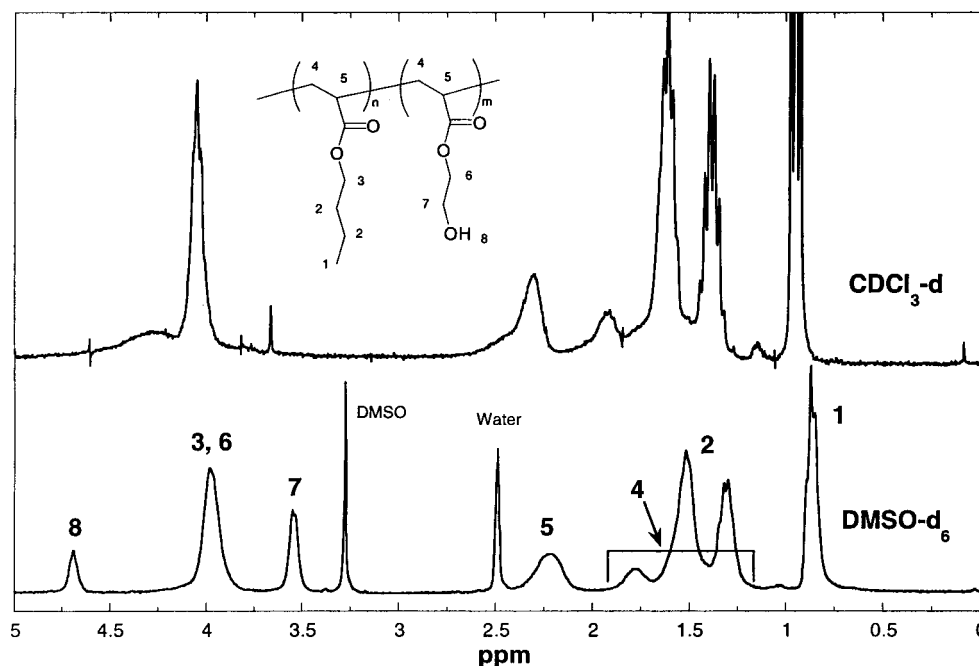


Figure 2. $^1\text{H NMR}$ of AM9-B in $\text{DMSO-}d_6$ (below) and in CDCl_3-d (above).

Table 1. Homopolymerization of n-BA and TMS-HEA at 80 °C in Bulk ([I]:[Cu]:[L] = 1:0.5:0.5)

sample	monomer	[M]:[I]	time (h)	M_n (calc)	M_n (^1H NMR)	M_n (SEC)	M_w/M_n
AM1-A	n-BA	25:1	0.8	3200	3500	3760	1.6
AM1-B	n-BA	50:1	2.8	6400	5500	5700	1.7
AM1-C	n-BA	100:1	3.8	12800	>12000	14400	1.3
AM2-A	TMS-HEA	25:1	0.3	4700	4700	4810	1.24
AM2-B	TMS-HEA	50:1	0.3	9400	9600	9390	1.20
AM2-C	TMS-HEA	100:1	0.7	18900	>12000	17030	1.26
AM2-A	TMS-HEA	200:1	2.75	37700	>12000	33000	1.24

Table 2. Synthesis of Poly(TMS-hea-*b*-n-BA) at 80 °C in bulk ([MI]:[Cu]:[L] = 1:0.5:0.5)

sample	[MI]:[n-BA]	time (h)	composition (^1H NMR)	M_n (calc)	M_n (SEC)	M_w/M_n
AM3-A	75:25	1.0	77:23	11600	12500	1.21
AM3-B	50:50	1.1	50:50	15800	16400	1.20
AM3-C	25:75	2.0	22:78	28700	31900	1.21

Table 3. Synthesis of Block Copolymers of n-BA and TMS-HEA by Successive Addition of Monomer at 80 °C in bulk^a ([M]_{tot}:[I]:[Cu]:[L] = 100:1:0.5:0.5)

sample	[n-BA]: [TMS-HEA]	time first monomer (h)	time second monomer (h)	composition (^1H NMR)	M_n (calc)	M_n (SEC)	M_w/M_n
AM4-A	70:30	0.3	0.25	73:27	12 580	11 960	1.20
AM4-B	50:50	0.2	0.4	53:47	11 870	12 300	1.19
AM4-C	30:70	0.15	0.5	31:69	14 810	14 000	1.24
AM5-A	70:30	0.5	1.3	70:30	13 100	11 800	1.26
AM5-B	50:50	0.9	0.8	48:52	14 300	13 100	1.32
AM5-C	30:70	0.95	0.8	29:71	16 200	14 700	1.34

^a AM4: first monomer = n-BA; second monomer = TMS-HEA. AM5: first monomer = TMS-HEA; second monomer = n-BA.

of poly(n-BA), as observed for systems with slow deactivation.³¹

In the homopolymerization of TMS-HEA (AM2-A to AM2-D), the polymerization time was shortened as compared to the n-BA polymerization and narrower molecular weight distributions were obtained (Table 1). Conversions were > 95% and the calculated molecular weight corresponded well to the M_n values obtained by ^1H NMR and SEC. The elution volumes of poly(n-BA) and poly(TMS-HEA) in THF were found to be comparable to those of PS standards in the same solvent.

3.2. Synthesis of Di- and Triblock Copolymers between TMS-HEA and n-BA. **3.2.1. Diblock Copolymers, Using Poly(TMS-HEA) as Macroinitiator.** Poly(TMS-HEA) with DP = 50 and M_w/M_n = 1.2 (AM2-B) was used as the macroinitiator (MI) for the polymerization of n-BA to obtain a block copolymer, Table 2. The compositions (found by ^1H NMR) of the block copolymers corresponded well with the feed ratio [MI]:[n-BA]. This was not surprising, since conversions measured by ^1H NMR exceeded 90% in all cases. Obtained and calculated molecular weights were in good agreement, and the molecular weight distributions were narrow and monomodal in all cases. The fast rate and control of this copolymerization prompted us to use the method of successive addition of monomers to obtain similar block copolymers.

3.2.2. Diblock Copolymers, Using Successive Addition of Monomers. Table 3 shows the results obtained polymerizing n-BA first and TMS-HEA second. Since the reaction times were rather short, yields were between 80 and 90%. As n-BA had a longer overall time to react, all copolymers were slightly "richer" in n-BA and the second block may not be completely "clean." Thus, the second block contained a small amount of n-BA in the TMS-HEA segment. However, the molecular weight distributions were narrow and monomodal and the obtained molecular weights corresponded very well to the calculated values, corrected for the amount of unconverted monomer.

To see if the order of monomer addition played an important role in the synthesis of the block copolymers, it was decided to change the order of addition, i.e., to polymerize TMS-HEA first and then add n-BA. Similar to the previous polymerizations, the yields were high, between 88 and 94%. In this case, however, the TMS-HEA segment was prepared first and the second block was primarily n-BA but also contained a small amount of TMS-HEA. The results displayed in Table 3 show a good agreement between calculated and obtained molecular weights and compositions, but the M_w/M_n values were slightly higher.

3.2.3. Triblock Copolymers of n-BA and TMS-HEA, Using a Difunctional Initiator. The difunctional initiator, 1, 2-bis(2-bromopropionyloxy)ethane (DI) (Scheme 1) allowed for the synthesis of triblock copolymers in two steps with either TMS-HEA (AM7-A) or n-BA (AM7-B) as the middle block. These copolymers were prepared by sequential addition of monomer with the center block being the monomer, which was added first. Although the compositions and molecular weights were in agreement with theoretical values, the polydispersities were broad, M_w/M_n = 1.5–1.8. Similar polymerizations were conducted with a higher concentration of catalyst, [DI]:[Cu] = 1:1, and these polymerizations had molecular weights M_n = 10 700 (M_w/M_n = 1.13) and M_n = 8900 (M_w/M_n = 1.14) for the n-BA and TMS-HEA central block, respectively, but the second monomer was added when conversion of the first was incomplete. The outer blocks more closely resembled random/statistical copolymers.

3.3. Hydrolysis of TMS-HEA (Co)polymers. **3.3.1. Hydrolysis of Poly(TMS-HEA).** The homopolymers of TMS-HEA were hydrolyzed using a catalytic amount of HCl in THF/H₂O. The degree of hydrolysis was >99% as determined by ^1H NMR. The byproduct, hexamethyldisiloxane, accumulated at the top of the reaction mixture and was easily separated. The polymers were water soluble and contained a small amount of NaCl (<5%) due to neutralization of HCl with

Table 4. Synthesis of the Triblock Copolymers Poly(TMS-HEA-*b*-n-BA-*b*-TMS-HEA) (AM7-A) and Poly(n-BA-*b*-TMS-hea-*b*-n-BA) (AM7-B) by Successive Addition of the Monomers at 80 °C in Bulk, Using DI as Initiator ([M]_{tot}:[DI]:[Cu]:[L] = 100:1:0.5:0.5)

sample	time first monomer (h)	time second monomer (h)	composition (found) ^a	<i>M</i> _n (calc)	<i>M</i> _n (SEC)	<i>M</i> _w / <i>M</i> _n
AM7-A	0.65	1.0	41:59	16 150	16 100	1.5
AM7-B	0.8	2.2	49:51	16 150	20 000	1.8

Table 5. Poly(HEA) Obtained by Hydrolysis of Poly(TMS-HEA)

starting material	product	<i>M</i> _n (calc)	<i>M</i> _n (¹ H NMR)	<i>M</i> _{n,SEC} (DMF)	<i>M</i> _w / <i>M</i> _n (SEC)	<i>T</i> _g (°C)
AM2-A	AM6-A'	3000	2600	9000	1.60	-3
AM2-B	AM6-B'	5800	4600	12500	1.45	0
AM2-C	AM6-C'	10500	10200	24000	2.29	6
AM2-D	AM6-D'	20400	>12000	53000	1.74	15

Table 6. Poly(n-BA-*b*-HEA) Obtained by Hydrolysis of Poly(n-BA-*b*-TMS-HEA)

starting material	product	composition [n-BA]:[HEA] (¹ H NMR)	<i>M</i> _{n,SEC} (DMF)	<i>M</i> _w / <i>M</i> _n (SEC)	<i>M</i> _n ; <i>M</i> _w / <i>M</i> _n (MALDI-TOFMS)	<i>T</i> _g (°C)
AM4-A	AM9-A	80:20	9250	1.41	8700; 1.32	-45; -3
AM4-B	AM9-B	62:38	11190	1.49	6500; 1.33	-45; -2
AM4-C	AM9-C	37:63	18450	2.02	4600; 1.36	-55; 0

NaOH. Their ¹H NMR spectra in DMSO-*d*₆ were consistent with earlier published data.³⁴ Table 5 lists compositions, calculated and obtained molecular weights, and *M*_w/*M*_n values.

The molecular weights of poly(HEA) measured by SEC in DMF, relative to poly(MMA) standards in the same solvent, were 2–3 times higher than the calculated values, obtained from earlier SEC data of the corresponding TMS-HEA homopolymers (Table 1). However, the calculated molecular weights corresponded well with those obtained by ¹H NMR (Table 5). This has already been observed previously³⁴ and may be attributed to different hydrodynamic volumes of poly(HEA) compared with poly(MMA). However, since *M*_w/*M*_n values were also substantially higher (as compared to the starting polymers), another explanation is that the poly(HEA) may form secondary structures, i.e., aggregates, in DMF.

The poly(HEA) had a substantially higher *T*_g than its silylated precursor. As expected, *T*_g values increased with increasing molecular weight until leveling off, Figure 1. The oligomers had a *T*_g ~ 0 °C, while the higher *M*_n materials had a *T*_g of ~ 30 °C.

3.3.2. Hydrolysis of Block Copolymers. The block copolymers of n-BA and TMS-HEA (AM4-A to AM4-C) were hydrolyzed in the same manner as the homopolymers, resulting in the formation of the poly(HEA) copolymers (AM9-A to AM9-C). By precipitation of the polymer solution (THF/H₂O 5:1) in 10-fold excess of water, white, soft, water-insoluble polymers were obtained as fine dispersions (similar to soap). The difference in polymer composition among the three polymers was clearly visible by observing the behavior of the precipitated solutions. AM9-A (n-BA content: 73%) consisted of rather large particles, which could be isolated by filtration, whereas the particles of AM9-B (n-BA content: 53%) were much smaller, passing partially through the filter paper. The particles of AM9-C (n-BA content: 31%) were so fine, that they could only be isolated by centrifugation. All three copolymers were soluble in DMSO-*d*₆, where their ¹H NMR spectra were measured to determine composition and degree of hydrolysis, which was >99% in all polymers. Interestingly, AM9-A and AM9-B were also soluble in CDCl₃, yielding clear solutions. However,

when “dissolved” in CHCl₃, the HEA block could not be observed in the ¹H NMR spectrum (broad lines with little resolution). This suggested that the HEA segments are not dissolved on a molecular level in CDCl₃ but formed micelles, thus resulting in broadening of the NMR lines due to much larger relaxation times. Figure 2 shows the ¹H NMR spectra of AM9-B in DMSO-*d*₆ and CDCl₃. All block copolymers displayed two *T*_gs in the DSC spectrum, one between -45 and -55 °C (n-BA block) and a second one between 0 and -3 °C (HEA block). Table 6 summarizes the data on molecular weights and molecular weight distributions obtained by SEC in DMF and MALDI-TOFMS.

All hydrolyzed block copolymers (AM9-A to AM9-C) had a substantially higher n-BA content when compared with their precursors. Since only the water-insoluble polymer particles were isolated and used for analysis, this could be explained by a partitioning effect in the water phase: The lower the n-BA content, the higher the water-solubility and therefore, the smaller particles will eventually become too tiny for efficient sedimentation and isolation. Indeed, the recovered polymer yields were only between 50 and 80%. Molecular weights obtained by SEC in DMF were again higher and *M*_w/*M*_n values were higher than expected, especially for block copolymers with longer HEA segments. It is interesting to note, that MALDI-TOFMS gave more reliable results for the block copolymers with higher n-BA content. HEA homopolymers and HEA-rich copolymers may not ionize very well in the MALDI-TOFMS with the matrix and conditions used.

3.4. Comparison of Different Block Copolymers between n-BA and HEA. To compare the physical properties of diblock, triblock, and random copolymers between n-BA and HEA of approximately the same composition and molecular weight, a statistical copolymer with 50:50 composition and DP_n of ca. 100 was synthesized (AM12) from n-BA and TMS-HEA and hydrolyzed as described above. Its apparent physical properties were compared with those of the triblock copolymers AM10-A and AM10-B (obtained by hydrolysis of AM7-A and AM7-B) and the diblock copolymer AM9-B, Table 7.

3.5. Homo- and Copolymerization of HEA. 3.5.1. Homopolymerization of HEA. The homopolymeri-

Table 7: Comparison of Different Random, Diblock and Triblock Copolymers between n-BA and HEA

sample	description	$M_{n,SEC}$ (DMF)	M_w/M_n (SEC)	M_n ; M_w/M_n (MALDI-TOFMS)	T_g (°C)	dispersion in water
AM9-B	[n-BA]/[HEA] = 62/38	11190	1.41	8700; 1.32	-45; -2	fine, goes partially through paper filter
AM10-A'	[n-BA]/[HEA]/[n-BA] = 19/62/19					very fine, could not be isolated by filtration or centrifugation
AM10-B'	[HEA]/[n-BA]/[HEA] = 15/70/15	6744	1.84	5900; 1.27	-47; -10	very fine suspension
AM12	statistical, [n-BA]/[HEA] = 50/50	17800; 10600 ^a	1.64; 1.22 ^a	8040; 1.29	-21	oil droplets

^a Measured in THF.**Table 8. Homopolymerization of Additionally Purified HEA in Bulk at 90 °C**

sample	[M]:[I]:[Cu]:[L]	time (h)	conversion (%)	M_n (calc)	M_n (¹ H NMR)	$M_{n,SEC}$ (DMF)	M_w/M_n
AM16-A	25:1:1:2	0.25	70	2030	1750	14500	4.67
AM16-B	50:1:1:2	0.50	60	3460	2900	14600	1.75
AM16-C	100:1:1:2	0.67	47	5420	5800	15300	1.48
AM16-D	400:1:1:2	5.50	44	20200	>15000	36500	1.53

zation of purified (washed with hexanes and distilled) **HEA** at 90 and 110 °C was conducted in bulk with bpy as the ligand. Conversions leveled off at around 50% and longer reaction times resulted in cross-linked polymers, but with little increase in conversion. When the monomer was additionally purified by passing it through a column of basic alumina, the reaction proceeded at a faster rate and higher conversions were obtained, Table 8. Acidic impurities, i.e., acrylic acid, may have played a role in reducing the rate of polymerization. Presumably this is by reaction with Cu(II)-X₂ to form copper acrylates. Since these copper(II) species cannot deactivate the polymerization by transfer of a halogen, the concentration of the deactivator (Scheme 2) decreases, resulting in termination.

Initially, the obtained polymers were darkly colored but water soluble (dark blue solutions) with the exception of AM16-D, which formed a gel, possibly due to partial cross-linking. Addition of Na₂S(aq) was used to remove all of the color by formation of insoluble copper salts, which could be removed by filtration, and resulted in the isolation of colorless polymer.

3.5.2. Block Copolymerization of n-BA with HEA. Using the above synthesized poly(HEA) as a macroinitiator for the **n-BA** polymerization failed due to the poor solubility of poly(HEA) in **n-BA**. Consequently, the sequential addition of **n-BA** to poly(HEA) failed because of the insolubility of the macroinitiator in butyl acrylate. However, when **n-BA** was polymerized first, and then **HEA** added, a block copolymer (AM18-A) was successfully obtained, which was purified by stirring in water followed by filtration; a white, creamy polymer was obtained: [n-BA]:[HEA] = 82/18. M_n (calc) = 9310; M_n (SEC, DMF) = 8630; M_w/M_n = 1.34.

4. Conclusions

The ATRP of **n-BA** and **TMS-HEA** with Cu^IBr/PMDETA as the catalyst was very fast and afforded well-defined homopolymers and di- and triblock copolymers with well-defined, predetermined block lengths and low polydispersities. Hydrolysis of the TMS groups with HCl in THF led to the formation of amphiphilic block copolymers with **n-BA** and 2-hydroxyethyl acrylate (**HEA**) units. Similarly, diblock copolymers were also obtained by successive addition of first **n-BA** and second **HEA**. Although the ¹H NMR spectra in CDCl₃ displayed well-defined lines for the **n-BA** block, the **HEA** segments were not observed, suggesting that the later block was not dissolved on a molecular level in chloroform. DSC measurements displayed two T_g s, -45

to -55 °C for the **n-BA** block and -10 to 0 °C for the **HEA** block, whereas the statistical copolymer had just one T_g at -21 °C. The amphiphilic di- and triblock copolymers formed dispersions in water of variable size, depending on the block length of the hydrophobic (**n-BA**) vs the hydrophilic (**HEA**) units, whereas the random copolymer gave only an oil.

Acknowledgment. The authors wish to thank Ciba Specialty Chemicals Co. for financial support, Peter J. Miller for the synthesis of the difunctional initiator (DI) and Dr. Christina B. Jasieczek for assistance with the MALDI-TOFMS spectra.

References and Notes

- Webster, O. *Science* **1991**, 251, 887.
- Szwarc, M. *Carbanions, Living Polymers and Electron-Transfer Process*; Interscience: New York, 1968.
- Hsieh, H. L.; Quirk, R. P., *Anionic Polymerization: Principles and Practical Applications*, Marcel Dekker: New York, 1996.
- Matyjaszewski, K. *Cationic Polymerizations: Mechanisms, Synthesis and Applications*; Marcel Dekker: New York, 1996.
- Ivin, K. J.; Mol, G. S. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: London, 1996.
- Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1983**, 105, 5706.
- Matyjaszewski, K., *Controlled Radical Polymerization*; ACS Symposium Series 865; American Chemical Society: Washington, DC, 1998.
- Greszta, D.; Mardare, D.; Matyjaszewski, K. *Macromolecules* **1994**, 27, 638.
- Solomon, D. H.; Rizzardo, E.; Cacioli, P. US 4,581,429, 1985.
- Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, 26, 2987.
- Wayland, B. B.; Basicckes, L.; Mukerjee, S.; Wei, M.; Fryd, M. *Macromolecules* **1997**, 30, 8109.
- Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, 28, 1721.
- Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, 117, 5614.
- Matyjaszewski, K.; Wang, J.-S. *Macromolecules* **1995**, 28, 7901.
- Matyjaszewski, K.; Patten, T.; Xia, J.; Abernathy, T. *Science* **1996**, 272, 866.
- Matyjaszewski, K.; Patten, T. E.; Xia, J. *J. Am. Chem. Soc.* **1997**, 119, 674.
- Grimaud, T.; Matyjaszewski, K. *Macromolecules* **1997**, 30, 2216.
- Gaynor, S. G.; Matyjaszewski, K.; Muller, A. H. E. *Macromolecules* **1997**, 30, 7034.
- Matyjaszewski, K.; Coca, S.; Gaynor, S. G.; Wei, M.; Woodworth, B. E. *Macromolecules* **1997**, 30, 7348.
- Matyjaszewski, K.; Jo, S. M.; Paik, H.; Gaynor, S. G. *Macromolecules* **1997**, 30, 6398.
- Percec, V.; Kim, H.-J.; Barboiu, B. *Macromolecules* **1997**, 30, 8526.

- (22) Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30*, 4507.
- (23) Matyjaszewski, K.; Wei, M.; Xia, J.; McDermott, N. E. *Macromolecules* **1997**, *30*, 8161.
- (24) Ando, T.; Kato, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1996**, *29*, 1070.
- (25) Granel, C.; Dubois, P.; Jerome, R.; Teyssie, P. *Macromolecules* **1996**, *29*, 8576.
- (26) Moineau, G.; Granel, C.; Dubois, P.; Jerome, R.; Teyssie, P. *Macromolecules* **1998**, *31*, 542.
- (27) Lecomte, P.; Drapier, J.; Dubois, P.; Teyssie, P.; Jerome, R. *Macromolecules* **1997**, *30*, 7631.
- (28) Curran, D. P. *Synthesis* **1988** 489.
- (29) Gaynor, S. G.; Matyjaszewski, K. *ACS Symp. Ser.* **1998**, *685*, 396.
- (30) Matyjaszewski, K.; Xia, J. H. *Macromolecules* **1997**, *30*, 7697.
- (31) Matyjaszewski, K.; Nakagawa, Y.; Jasieczek, C. *Macromolecules* **1998**, *31*, 1535.
- (32) Percec, V.; Barboiu, B. *Macromolecules* **1995**, *28*, 7970.
- (33) Percec, V.; Barboiu, B.; Newmann, A.; Ronda, J. C.; Zhao, H. *Macromolecules* **1996**, *29*, 3665.
- (34) Coca, S.; Jasieczek, C.; Beers, K. L.; Matyjaszewski, K. *J. Polym. Sci., Polym. Chem. Ed.* **1998**, *36*, 1417.

MA9804747