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Synthesis of Molecular Bottlebrushes by Atom Transfer Radical Polymerization with ppm Amounts of Cu Catalyst

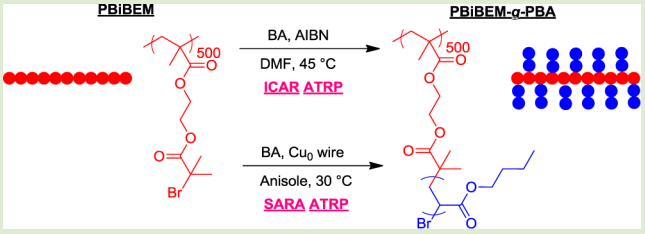
Alper Nese,[†,‡] Yuanchao Li,[§] Sergei S. Sheiko,*[,§] and Krzysztof Matyjaszewski*[,†]

[†]Department of Chemistry, Center for Macromolecular Engineering, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213, United States

[§]Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, United States

Supporting Information

ABSTRACT: Molecular bottlebrushes were prepared by ICAR (initiators for continuous activator regeneration) atom transfer radical polymerization (ATRP) and supplemental activator and reducing agent (SARA) ATRP in the presence of 50 ppm Cu-based catalyst. Poly(*n*-butyl acrylate) (PBA) side chains were grafted from a polymethacrylate backbone resulting in well-defined molecular bottlebrushes. Imaging of individual bottlebrush macromolecules by atomic force microscopy corroborated the targeted degrees of polymerization of the backbone and side chains. Initiation efficiency was determined by cleaving the side chains to be around 50%.



Densely grafted copolymers, also called molecular bottlebrushes,[1−6] demonstrate a characteristic conformation of an extended backbone decorated with bristles of side chains. The rod-like shape of individual macromolecules leads to several potential applications including high aspect ratio nanowires,[7−9] supersoft elastomers,[10] nanotubes and hollowed nanoparticles,[11−13] photonic crystals,[14−16] molecular tensile machines,[17,18] and nanoporous materials.[19,20] There are three methods used for the synthesis of bottlebrush macromolecules: grafting-onto,[21] grafting-through,[22,23] and grafting-from.[1,24,25] The grafting-from method using controlled radical polymerization techniques allows the preparation of bottlebrushes with relatively high degrees of polymerization of the side chains[3] and high grafting density.[26] Reversible addition−fragmentation chain transfer (RAFT) polymerization[15,25,27−29] and atom transfer radical polymerization (ATRP)[17,30−37] are the most extensively used controlled radical polymerization methods for preparation of molecular bottlebrushes. However, using ATRP, it is essential to remove the residual Cu catalyst to prevent covalent cross-linking through Br-terminated side chains.[38] This purification requires several precipitation cycles that could be avoided by using ATRP techniques that utilize low Cu catalyst concentration.

Recently, several new methods were introduced to carry out ATRP with very low catalyst concentrations.[32,36,39−42] One of these methods is ICAR (initiators for continuous activator regeneration) ATRP.[39,43,44] ICAR ATRP enables controlled polymerization with catalyst concentrations below 100 ppm copper. In an ICAR ATRP, the Cu(I) species lost by termination reactions are regenerated from the resulting Cu(II) species using an organic radical initiator such as AIBN. Another method to realize ATRP under low catalyst concentration conditions is achieved by using solid Cu^0 as a supplemental activator and reducing agent (SARA) ATRP.[45−51] Cu^0 species participate in the supplemental activation process and also function in a role similar to that of AIBN in an ICAR ATRP by regenerating the Cu(I) species from Cu(II). The benefit of low copper catalyst concentration employed in these two methods makes SARA ATRP and ICAR ATRP potentially attractive processes for molecular bottlebrush synthesis. Concurrently, low concentrations of copper could reduce initiation efficiency and control of brush architecture. This paper describes the first molecular bottlebrushes prepared by grafting from polymethacrylate backbone using ICAR and SARA ATRP in the presence of ppm amounts of Cu catalyst.

Synthesis: Poly(*n*-butyl acrylate) (PBA) bottlebrushes were chosen as model compounds that can be easily imaged by AFM due to spontaneous spreading of PBA side chains on conventional substrates.[52] PBA bottlebrushes were prepared by the following synthetic routes shown in Scheme 1. Two different polymerization techniques, ICAR ATRP and SARA ATRP, were used for side-chain polymerization at low catalyst concentrations. Poly((2-(2-bromoisobutyryloxy)ethyl methacrylate) (PBiBEM) was selected as the backbone macroinitiator for side chain grafting as it provides a cleavable link between the backbone and side chains required for characterization of the initiation efficiency. A [monomer]/[initiator] ratio of 400:1 was used to synthesize three bottlebrushes at partial monomer conversion, Brush-1, Brush-2, and Brush-3. Reaction conditions are listed in Table 1 and GPC traces of the backbone and the molecular bottlebrushes are provided in Figure 1. PBA side chains were grafted from the PBiBEM backbone using ICAR-

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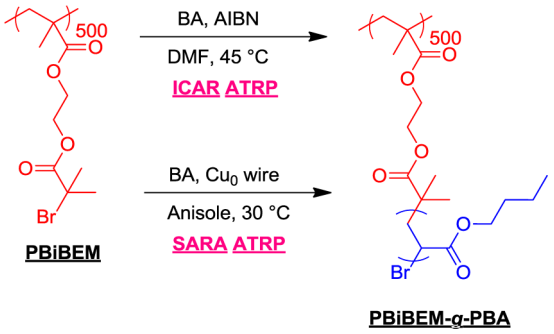
Scheme 1. Synthesis of Molecular Bottlebrushes with PBA Side Chains Grown from a Polymethacrylate Backbone



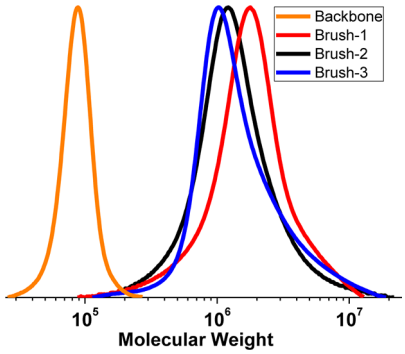


Figure 1. GPC traces of the backbone and the corresponding molecular bottlebrushes.

ATRP to yield Brush-1 with [2-bromoisobutyrate]/[AIBN] ratio of 1:0.5. A reaction temperature of 45 °C was selected to provide slow decomposition of AIBN and maintain a low radical concentration. It is essential to have low radical concentration during side chain growth to avoid brush−brush intermolecular coupling reactions and to decrease the amount of polymer chains initiated by AIBN. DMF was used as a solvent to dissolve the AIBN. The reaction was stopped after 18 h. Molecular weight distributions (MWD) were analyzed by GPC (Table 1, Figure 1) and AFM (Table 2, Figure 2). Only a very small amount of low molecular weight linear polymer (~4%) was observed by GPC showing most of the decomposed AIBN was used to reduce Cu(II) to Cu(I) species dominating over free polymer initiation and radical transfer reactions to monomer.[43] Broader polydispersity of brushes versus backbone could be due to either small contributions of transfer reactions or inherent broadening of the GPC elution curves. As shown in Table 2, the polydispersity index (PDI) of individual macromolecules imaged by AFM is consistent with the PDI of the backbone measured by GPC (Table 1).

For comparison, Table 1 provides molecular weight data of Brush-2 and Brush-3 prepared by the SARA-ATRP technique. Even though both reactions were started using only 50 ppm $CuBr_2$/TPMA, copper halides concentration gradually increased due to the reduction with Cu wire, and therefore, an excess of ligand was used for synthesis of Brush-3. The copper wire for Brush-3 synthesis was twice longer and, thus, has doubled surface area than one used for the synthesis of Brush-2. Due to a combination of these two different variables, the reaction proceeded faster and a similar conversion value was reached after 4.25 h in Brush-3 synthesis and after 141 h for Brush-2. Both bottlebrush copolymers displayed similar apparent molecular weights and polydispersities (Table 1).

AFM characterization: Dense films of the bottlebrush molecules were prepared using a Langmuir−Blodgett (LB) trough (KSV-5000 instrument equipped with a Wilhelmy plate balance, Milli-Q double-distilled water ρ = 18.2 MΩ). LB monolayers were transferred to freshly cleaved mica at a controlled low pressure of 0.5 mN/m. The films were imaged using multimode atomic force microscopy (Bruker Scientific Instruments) in tapping mode.[53] Silicon cantilevers were used with a resonance frequency of about 160 kHz and a spring constant of about 5 N/m. The analysis of molecular dimensions from digital images was performed using a custom software program developed in-house.

Figure 2 shows individual bottlebrush molecules (Brush-1, -2, and -3) that exhibit worm-like conformation, suggesting extension of the backbone in the densely grafted molecular bottlebrushes. The number-average contour length (L_n) of all three bottlebrushes was about L_n = 125 ± 2 nm. This corresponds to the backbone with DP = L_n/l_0 = 500, assuming the fully extended conformation with the length of the C−C−C monomeric unit in the tetrahedral configuration of l_0 = 0.25 nm. The combination of the AFM and LB techniques allowed measurement of the absolute molecular weight, including the number average molecular weight M_n and the polydispersity index L_w/L_n, of the bottlebrush molecules.[54] The results are summarized in Table 2. As expected, the molecular weights obtained by AFM-LB are significantly higher than the relative GPC numbers in Table 1 obtained relative to PMMA standards and considered to be more accurate. Note also that the polydispersity indices obtained by AFM are consistent with the PDI values of the corresponding backbones (Table 1). The distance between Brush-1 macromolecules is significantly larger than the distance between the Brush-2 and Brush-3 counterparts. This is consistent with the large degree of polymerization of the Brush-1 side chains. Table 2 depicts the number average MW of side chains, which was calculated for each bottlebrush assuming 100% initiation efficiency. These data were used to determine the actual initiation efficiencies through solvolysis

Initiation efficiency: The side chains of the bottlebrushes were cleaved by solvolysis prior to injecting to GPC to measure the

Table 1. Experimental Conditions for the Synthesis of PBA Molecular Bottlebrushes by ICAR-ATRP and SARA-ATRP[a]

entry	M	I	TPMA	$CuBr_2$	AIBN	Cu0 wire	solvent	time	conv.[b]	DP_{sc}[b]	$M_{n,exp}$[c]	PDI[c]
backbone											92500	1.2
Brush-1	400	1	0.02	0.02	0.5		33 vol%	18 h	30%	120	1330000	1.6
Brush-2	400	1	0.02	0.02		2.5 cm	10 vol%	141 h	20%	80	1130000	1.7
Brush-3	400	1	0.04	0.02		5.0 cm	10 vol%	4.25 h	18%	72	1050000	1.6

[a] M, I, and L stand for relative ratios of initial monomer, initiator, and ligand concentrations, respectively; Brush-1 synthesis was carried out at 45 °C; Brush-2 and Brush-3 syntheses were carried out at 30 °C. [b] Based on NMR (B1) and gravimetry (B2−B3). [c] Polydispersity index (PDI = M_w/M_n) obtained by GPC using linear PMMA standards.

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Table 2. Characterization of the Molecular Bottlebrushes by the AFM-LB Approach

	$M_{n,AFM-LB}$[a]	$DP_{backbone}/DP_{side\ chain}$	L_w/L_n[b]	L_n[c] (nm)	D[d] (nm)	$M_{n,side\ chains,AFM-LB}$	$M_{n,side\ chains,solvolysis}$[e]	M_w/M_n (side chains, solvolysis)[e]	initiation efficiency[f] (%)
Brush-1	7470000	500/115	1.09	126 ± 2	106 ± 3	14940	27100	1.12	55
Brush-2	3950000	500/60	1.12	125 ± 2	56 ± 2	7900	16300	1.20	48
Brush-3	3820000	500/55	1.12	124 ± 2	55 ± 2	7640	13800	1.21	55

[a]Determined by AFM-LB method. [b]Polydispersity index of the molecular lengths obtained from AFM images. [c]Number average contour length measured for an ensemble of more than 500 molecules. [d]The width of molecular bottlebrushes. [e]Calculated by cleaving the side chains measuring by GPC with PS standards. [f]Calculated by comparing MW of the cleaved side chains by GPC with the MW of the side chains measured by AFM-LB assuming 100% initiation efficiency.

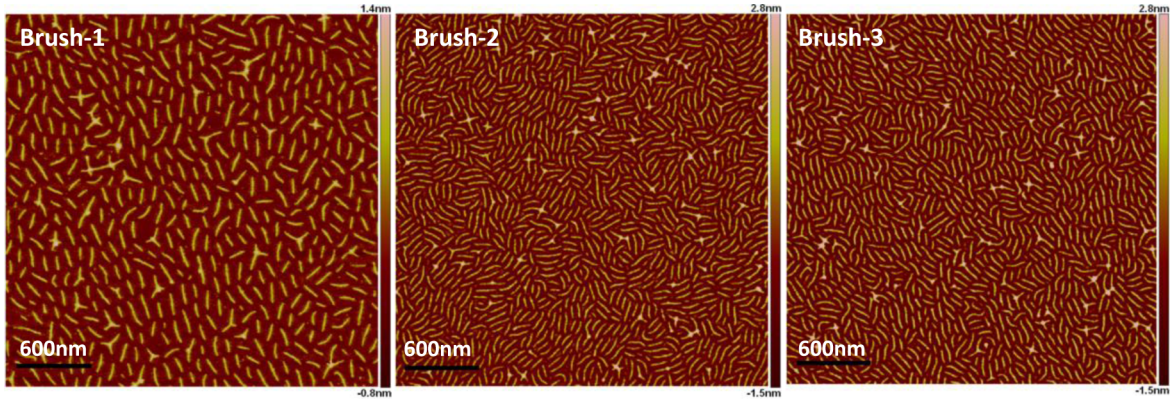

Figure 2. AFM height images of the molecular bottlebrushes.

molecular weight by using polystyrene standards and initiation efficiencies were determined by comparing these values with values of MW of the side chains calculated by AFM-LB approach.[26,54] Initiation efficiencies were estimated as 55, 48, and 55% for Brush-1, Brush-2, and Brush-3 samples, respectively. Also, the bottlebrush sample prepared by ICAR ATRP, Brush-1, had more narrow MWD, M_w/M_n = 1.12, whereas bottlebrushes prepared by SARA ATRP had M_w/M_n values of the side chain of about 1.20 (Table 2). Initiation efficiencies were lower than when normal ATRP was used, which exceeded 60% initiation efficiency already at 6% monomer conversion.[26,55] This is due to a relatively lower concentration of Cu^{II} deactivators and more monomer units added during each activation step. Nevertheless, chain extended worm-like conformations were observed by AFM for all the bottlebrush copolymers (Figure 2) proving successful synthesis of molecular bottlebrushes.

ICAR ATRP and SARA ATRP were used to prepare poly(butyl acrylate) based molecular bottlebrushes. Both systems allowed the use of reduced concentrations of ligand (soluble ATRP catalyst), 50 ppm, providing a more environmentally friendly synthesis compared to conventional ATRP. Initiation efficiency values were lower than when normal ATRP was used, but grafting density was sufficiently high to generate an extended backbone conformation. Successful molecular bottlebrush synthesis was confirmed by AFM imaging of individual macromolecules.

■ ASSOCIATED CONTENT

Supporting Information

Materials, characterization, and experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: km3b@andrew.cmu.edu; sergei@email.unc.edu.

Present Address

‡Department of Chemical Engineering and Materials Science, University of Southern California, Los Angeles, CA 90089.

Notes

The authors declare no competing financial interest.

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