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Synthesis of Amphiphilic Poly(*N*-vinylpyrrolidone)-*b*-poly(vinyl acetate) Molecular Bottlebrushes

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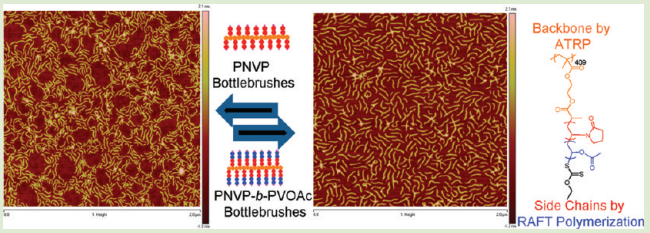
Supporting Information

ABSTRACT: Well-defined molecular bottlebrushes with poly(*N*-vinylpyrrolidone) and poly(*N*-vinylpyrrolidone)-*b*-poly(vinyl acetate) (PNVP-*b*-PVOAc) side chains were prepared via a combination of atom transfer radical polymerization (ATRP) and reversible addition−fragmentation chain transfer (RAFT). A macro chain transfer agent poly(2-((2-ethylxanthatepropanoyl)oxy)ethyl methacrylate) (PXPEM) was prepared by attaching xanthate chain transfer agents onto each monomeric unit of poly(2-hydroxyethyl methacrylate). Subsequently, a RAFT polymerization procedure was used to synthesize molecular bottlebrushes with PNVP side chains with controlled molecular weight and low polydispersity by grafting from the PXPEM backbone. The side chains were then chain extended with PVOAc, yielding a bottlebrush macromolecule with PNVP-*b*-PVOAc side chains. The comb-like shape of the chain extended bottlebrushes was confirmed by atomic force microscopy (AFM).



Molecular bottlebrushes are a special class of graft copolymers in which their extended comb-like conformation is due to the high grafting density.[1−7] The densely grafted side chains sterically repel each other and push the polymer backbone into an extended rod like topology. The fact that molecular bottlebrushes have several potential applications such as supersoft elastomers,[8] precursors to nanoparticles or nanowires[9−12] or nanotubes,[13] photonic crystals,[14,15] and molecular tensile machines[16] has increased the level of attention focused on their synthesis. Molecular bottlebrushes have been prepared by ring-opening polymerization,[17] ring-opening metathesis polymerization,[15,18] ionic polymerization,[19] alkyne−azide click coupling reactions,[20] reversible addition−fragmentation chain transfer (RAFT) polymerization,[13,21−24] and grafting-from methods using atom transfer radical polymerization (ATRP).[25−29]

Previously, we have described the design and use of a macro chain transfer agent (macroCTA) for the preparation of bottlebrush macromolecules.[22] Xanthate groups were attached to the PHEMA backbone using a DCC coupling reaction to form the macroCTA, poly(2-((2-ethylxanthatepropanoyl)oxy)-ethyl methacrylate) (PXPEM). This macroCTA was used to prepare molecular bottlebrushes with poly(vinyl acetate) (PVOAc) side chains. In this paper, we expand this concept by preparing molecular bottlebrushes with side chains formed by sequential copolymerization of *N*-vinylpyrrolidone (NVP) followed by VOAc, forming block copolymer arms. Because PNVP displays good biocompatibility and low toxicity, it has been used in pharmaceutical, medical, and cosmetic applications.[30,31] Thus, molecular bottlebrushes having PNVP segments in their side chains can find some new applications. This paper describes the first molecular bottlebrush with block copolymer side chains having PNVP as one of the blocks prepared by RAFT polymerization.

Synthesis: The synthetic route, shown in Scheme 1, was used for the preparation of PNVP-*b*-PVOAc bottlebrushes. PXPEM (prepared by attaching ethyl xanthate groups onto each hydroxyl group of the PHEMA, as previously reported)[22] was used as a macroCTA for the preparation of molecular bottlebrushes. The presence of the ethyl xanthate groups make the PXPEM a suitable macroCTA for the synthesis of both PNVP and PVOAc blocks.

PNVP side chains were grown from PXPEM multifunctional macroCTA by RAFT polymerization to obtain PXPEM-*g*-PNVP bottlebrush polymers. The molar ratios used for the side chain synthesis were NVP/PXPEM/AIBN = 400:1:0.2 (B1 and B2 in Table 1) and 400:1:0.5 (B3 and B4 in Table 1). The reaction temperature was 45 °C for both systems, allowing very slow decomposition of AIBN. This targeted slow decomposition of AIBN was selected to minimize radical concentration in the system, which is an essential requirement that minimizes radical termination reactions (both intramolecular and intermolecular) and also to decrease the amount of initiated new chains. To study the effect of AIBN

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Scheme 1. Synthesis of Molecular Bottlebrushes with PNVP and PNVP-*b*-PVOAc Side Chains Grown from a PHEMA Backbone

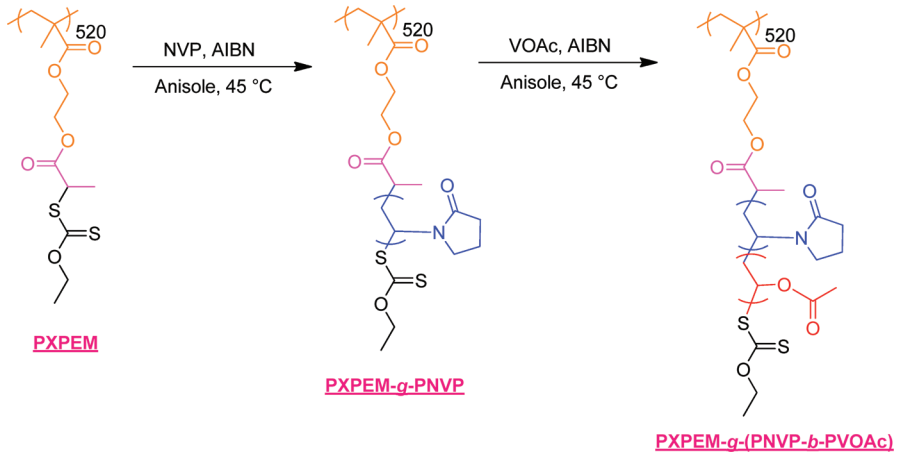

Table 1. Conditions for the Synthesis of PNVP and PNVP-*b*-PVOAc Side Chains from a PXPEM Backbone[a]

entry	label side chains	*M*	CTA	AIBN	anisole	time	conv[b] (%)	$M_{n,abs}$[b]	$M_{n,exp}$[d]	M_w/M_n[d]	% linear pol.[e]
B0	PXPEM (backbone)							125000[c]	92500	1.17	
B1	NVP30	400	1	0.5	10 vol%	4.5 h	7.5	1490000	251000	1.27	13
B2	NVP50	400	1	0.5	10 vol%	6.75 h	12.5	2390000	364000	1.25	15
B3	NVP15	400	1	0.2	10 vol%	11 h	3.8	806000	218000	1.25	9
B4	NVP130	400	1	0.2	10 vol%	48 h	33	6030000	673000	1.19	40
B5	NVP40	400	1	0.5	10 vol%	4.25 h	10	1940000	327000	1.25	9
B6	NVP40VOAC20	400	1	0.1	10 vol%	13 h	5	2640000	432000	1.37	11
B7	NVP40VOAC50	400	1	0.1	10 vol%	20 h	13	3700000	714000	2.12	18
B8	NVP40VOAC60	800	1	0.1		2 h	7.5	4050000	547000	1.45	13
B9	NVP40VOAC80	800	1	0.1		3 h	10	4750000	691000	1.51	15
B10	NVPc40VOAc200	800	1	0.1		18 h	25	8980000	1110000	2.27	27

[a]M, I, and CTA stand for NVP (for B1−B5) and VOAc (B6−B10), AIBN, and PXPEM, respectively; All reactions were carried out at 45 °C. [b]Based on gravimetry (for B1−B6) and NMR (B6−B10). [c]Theoretical molecular weight calculated by using the DP of the backbone multiplied by the MW of each monomeric unit;[22] [d]Based on GPC using PMMA standards. [e]Calculated by using GPC comparing the peak areas of linear polymers with the ones of bottlebrushes.

Table 2. Characterization of Molecular Bottlebrushes with PNVP-*b*-PVOAc Side Chains

	GPC					AFM-LB		
	DP[a]	M_{abs}[b]	M_n[c]	PDI[d]	M_n[e,f]	L_w/L_n[g]	L_n[h]	*D*[i]
B5	520/40	1940000	327000	1.25	3410000	1.09	128 ± 2	28 ± 3
B6	520/40−20	2640000	432000	1.37	3770000	1.08	128 ± 2	35 ± 3
B7	520/40−50	3700000	714000	2.12	4400000	1.07	128 ± 2	43 ± 5
B8	520/40−60	4050000	547000	1.45	4900000	1.10	129 ± 2	50 ± 5
B9	520/40−80	4750000	691000	1.51	5080000	1.09	133 ± 2	61 ± 3
B10	520/40−200	8980000	1110000	2.27	6050000	1.09	134 ± 2	104 ± 10

[a]DP of backbone measured by AFM and side chains measured by gravimetry. [b]Absolute molecular weight determined by gravimetry. [c]Number average molecular weight determined by GPC. [d]Polydispersity index of the molecular weight measured by GPC. [e]DP of backbone and side chains determined by AFM-LB approach. [f]Number average molecular weight determined by AFM-LB approach. [g]Polydispersity index of the molecular length obtained from AFM images. [h]Number average contour length measured for an ensemble of more than 500 molecules. [i]The width of molecular bottlebrush.

concentration, two different ratios of PXPEM/AIBN were selected: 1:0.2 and 1:0.5. The only difference observed for systems with 1:0.2 and 1:0.5 PXPEM/AIBN ratios were polymerization rates. Due to the higher radical concentration in the later system, the polymerization proceeded faster. Dispersity values of the polymers were similar: around 1.2−1.3 for all the samples. After these control experiments, the 1:0.5 PXPEM/AIBN ratio was selected to prepare bottlebrushes on a larger scale to provide sufficient amount of polymer for subsequent chain extension with PVOAc. The resulting polymer had side chains with DP ∼ 40, which is a typical side chain length required to obtain a comb like shape with a backbone DP ∼ 500 and visualize by AFM.[1] MW and PDI values of the synthesized PNVP bottlebrush polymers are listed in Table 1.

At the next step, PNVP side chains were chain extended with PVOAc. [M]/[PXPEM] ratios of 400:1 and 800:1 were used to study the effect of targeted DP on polymerization behavior. The PXPEM/AIBN ratio was 1:0.1 and reaction temperature was also 45 °C, to provide a low concentration of radicals,

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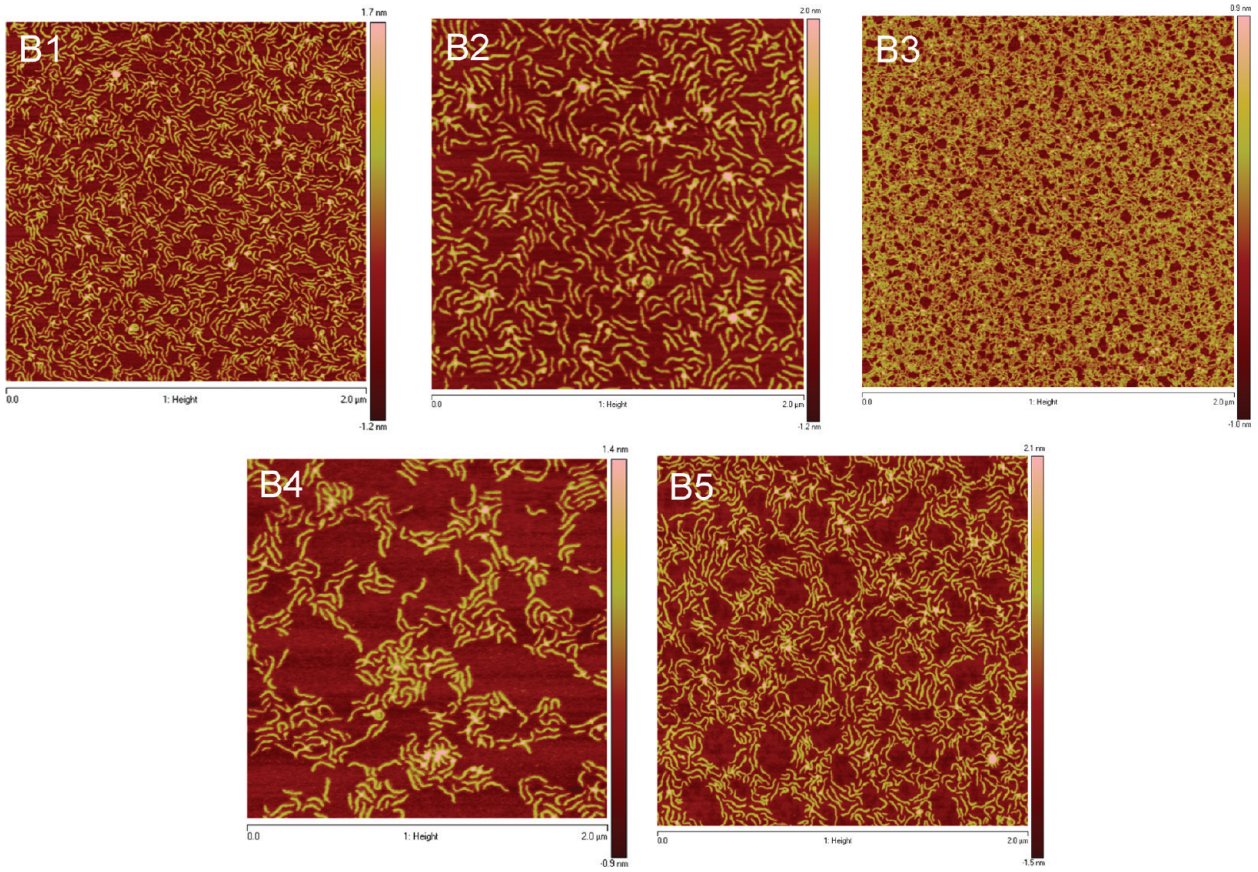

Figure 1. AFM height images of the PXPEM-*g*-PNVP bottlebrushes (B1−B5 in Table 1).

allowing uniform and controlled growth of the PVOAc side chains.[22] Polymerization proceeded faster when the ratio of M/PXPEM was 800:1. It was necessary to add 10% solvent to the 400:1 system to completely dissolve the polymers (B6 and B7 in Table 1). Thus, a series of PNVP-*b*-PVOAc bottlebrushes (B6−B10 in Table 1) were prepared and characterized using GPC. For the polymerizations that were stopped at low conversion (up to 10% for samples B6, B8, and B9), controlled MW and low dispersities were observed. However, when the polymerization was allowed to proceed to higher conversion (13 and 25% for samples B7 and B10, respectively), poorly defined molecular bottlebrushes were obtained. Intermolecular coupling reactions start to occur at high monomer conversion which was first manifested by a high molecular weight shoulder at the brush peak which subsequently formed another higher molecular weight peak, if optionally continued to higher conversion (Figures S3−S10). However, it was possible to reach monomer conversion as high as 33% while maintaining low dispersity for the bottlebrushes during NVP grafting (B4 in Table 1). The $M_{n,exp}$. values given in Table 1 represent apparent values calculated using linear PMMA standards. Theoretical MW values were calculated by gravimetry ($M_{n,abs}$ in Table 1) and by AFM (Table 2) to better estimate the molecular dimensions. Linear polymers were present in the samples due to the radical transfer reactions to monomers, VOAc and NVP.[32,33] These linear polymers can be seen as the low molecular weight peaks in all GPC traces (Figures S1−S10, Table 1). Side chain DP values of the bottlebrushes were calculated by excluding these unattached polymer chains. These DP values are lower than the real values because the number of the growing chains increase and consequently decrease the molar ratio of consumed monomer to growing chains. This should lead to lower DP at a certain monomer conversion compared to a system without unattached polymer chains.

AFM analysis: Individual bottlebrush molecules (B1−B10) were visualized by AFM (Figures 1 and 2). The imaged molecules exhibit wormlike conformation, suggesting extension of densely grafted molecular bottlebrushes. The "holes" in the molecular bottlebrush films can be ascribed to the presence of linear polymers.

The combination of the AFM and Langmuir−Blodgett (LB) techniques was used to characterize the molecular weight distribution (MWD; including M_n and L_w/L_n) of the bottlebrush molecules with PNVP-*b*-PVOAc side chains (B5−B10).[34] The results are summarized in Table 2. The dispersity of the molecular bottlebrush contour length agrees with the dispersity of PXPEM backbone (1.17). Assuming the backbone is fully extended, one can estimate the backbone DP of ∼520 from L_n. DP of backbone calculated by using GPC with linear PMMA standards for lower (409) than the value calculated by AFM-LB approach (520). This difference may be due to the difference of hydrodynamic volumes of the backbone compared to GPC standards and the value calculated by AFM-LB approach should be more precise. Molecular weights measured by AFM-LB approach are in good agreement with the values calculated by gravimetry. Also, molecular weights of the bottlebrushes increase with bottlebrush width (Figure 3).

Well-defined PNVP and PNVP-*b*-PVOAc bottlebrush macromolecules were prepared using a combination of ATRP and RAFT. The polymer backbone was prepared by ATRP of HEMA and then converted into a mCTA by attaching xanthate groups onto each monomeric unit. These xanthate groups were

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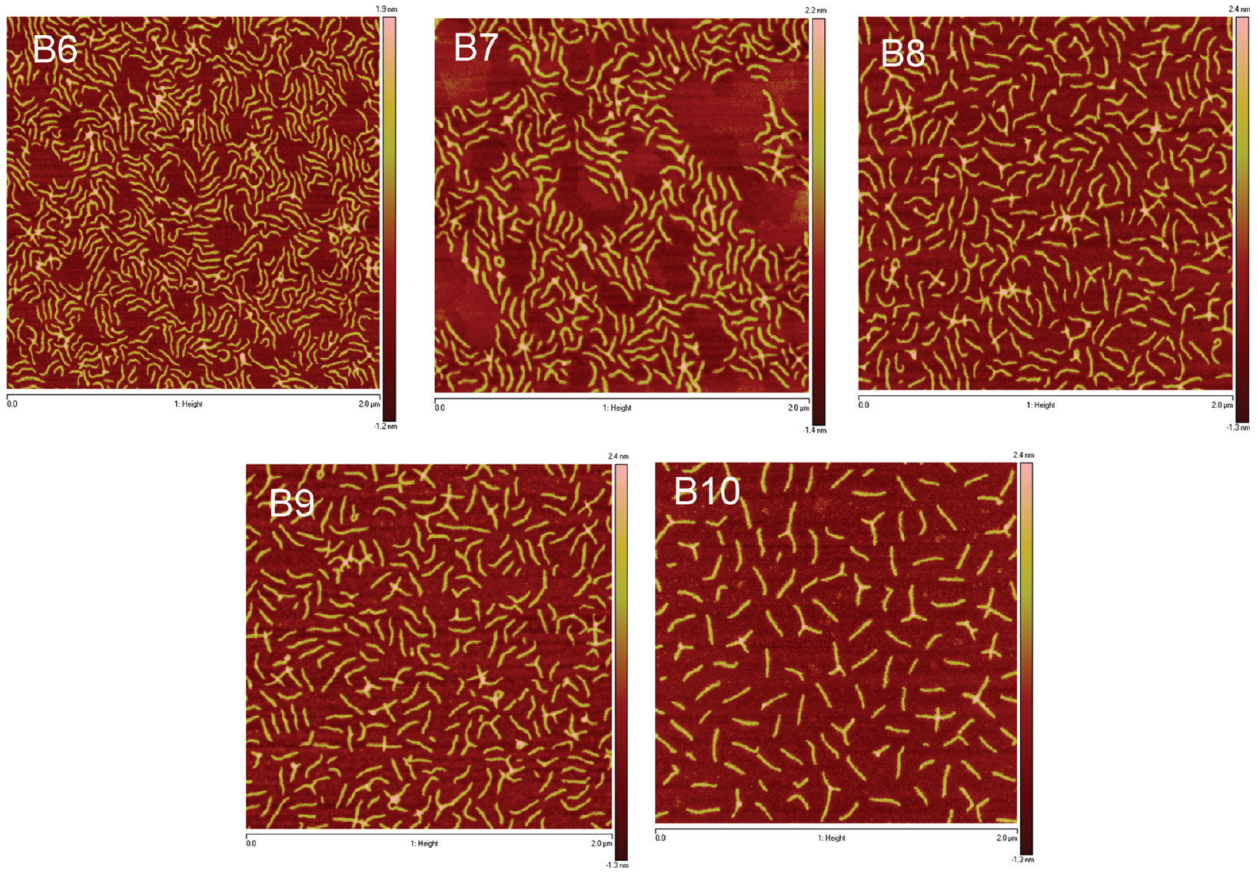

Figure 2. AFM height images of the PXPEM-*g*-(PNV-*b*-PVOAc) bottlebrushes (B6–B10 in Table 1).

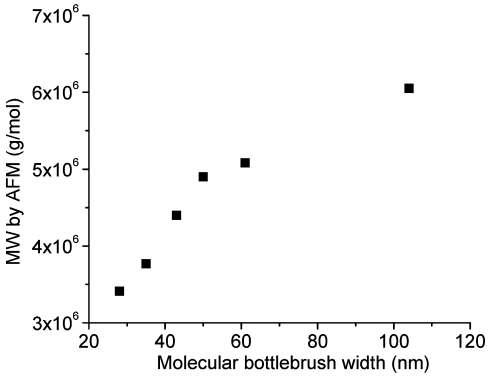

Figure 3. Correlation of molecular weight with molecular bottlebrush width.

used to grow block copolymer side chains with PNVP and PVOAc segments, respectively. Molecular bottlebrushes with different side chain lengths were prepared and thoroughly characterized by AFM. Relatively large amounts of linear polymer chains were formed due to transfer reactions and new chains generated by AIBN during the side chain growth. These free polymer chains caused void formation at AFM-LB film images. It is essential to stop polymerization at low monomer conversion to avoid intermolecular coupling reactions.

■ ASSOCIATED CONTENT

Supporting Information

Materials, analytical methods, experimental procedures, GPC traces, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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