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Macromolecules
COMMUNICATION TO THE EDITOR

Synthesis of Poly(vinyl acetate) Molecular Brushes by a Combination of Atom Transfer Radical Polymerization (ATRP) and Reversible Addition−Fragmentation Chain Transfer (RAFT) Polymerization

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Introduction. Densely grafted copolymers are also termed molecular brushes or bottle-brush copolymers due to their chain extended brushlike shape.[1−7] The increasing attention focused on molecular brushes could be related to their potential applications such as supersoft elastomers,[8] precursors to nanoparticles or nanowires[9−12] or nanotubes,[13] photonic crystals,[14] and molecular tensile machines.[15] Although there are several reports on the successful preparation of molecular brushes using ring-opening metathesis polymerization,[16] ionic polymerization,[17] alkyne−azide click coupling reactions,[18] and reversible addition−fragmentation chain transfer (RAFT) polymerization,[13,19] most well-defined molecular brushes have been prepared by the grafting-from method using atom transfer radical polymerization (ATRP).[20−24] Backbones containing ATRP initiators were used as macroinitiators for the subsequent polymerization of substituted acrylates, methacrylates, acrylonitrile, and styrene as monomers yielding molecular brushes with controlled molecular weight, grafting density, and narrow molecular weight distribution of the side chains. It is appealing to expand range of polymerizable monomers and include also less reactive ones such as vinyl acetate (VOAc). However, because of the very low ATRP equilibrium constant, polymerization of VOAc is very challenging.[25−27] On the other hand, VOAc can be polymerized by degenerative transfer processes,[28] such as RAFT.[29−34] Xanthates have been reported to be efficient chain transfer agents (CTAs) for the controlled polymerization of VOAc.[35−37] The intermolecular exchange between growing radicals and CTA (i.e., alkyl xanthate) is required in RAFT. This process could be accompanied by significant steric hindrance when applied to the synthesis of molecular brushes, resulting in low grafting efficiencies, high dispersity of side chains, and poorly defined architectures. Indeed, when poly(vinyl alcohol) (PVA) was functionalized with xanthate moieties to form a macro-CTA for the subsequent growth of PVOAc side chains by RAFT, a limited control was observed.[38] In fact, the obtained polymers should be regarded more as starlike (rather than comblike),[39] since the side chains were longer than the backbone. The molecular weight distribution of the obtained molecular brushes was multimodal, and control of molecular architecture was relatively limited. This could be due to the intrinsic difficulty for using RAFT for synthesis of molecular brushes or more plausibly due to very congested structure of the used backbone xanthate moieties. The R group of the CTA was directly connected to the backbone and separated from the backbone by only three atoms (Figure S3b).

In order to test this possibility, we prepared another macro-CTA in which xanthate moiety was linked by the 2-acetoxyethyl isobutyrate group and separated from the backbone by seven atoms (Figure S3a). Also, the backbone has a much higher degree of polymerization, as required for a true molecular brush. To overcome the steric hindrance in the immediate xanthate vicinity, poly(2-hydroxyethyl methacrylate) (PHEMA) with high molecular weight (degree of polymerization, DP = 409) was prepared by ATRP with narrow molecular weight distribution (M_w/M_n = 1.11) as a precursor of the brush backbone. Hydroxyethyl acetate side groups of PHEMA act as spacers and should facilitate the RAFT exchange process. In the next step, −OH groups of PHEMA were esterified with the xanthate containing 2-propionic acid to form a macromolecular multifunctional CTA (PPXEM). PVOAc side chains were then grown from this macro-CTA to generate molecular brushes. The molecular brushes were characterized by atomic force microscopy (AFM), confirming the successful controlled radical polymerization synthesis.

Synthesis. PVOAc brushes were prepared by following the synthetic route shown in Scheme 1. Ethyl xanthate was selected as CTA, since it is an efficient chain transfer agent for VOAc polymerization. 2-Bromopropionic acid was reacted with potassium xanthate to form a secondary xanthate species with acid functionality (XA) as a yellow liquid. Structure and purity (97%) of XA were confirmed by ^{1}H NMR analysis (Figure S1).

The XA transfer agent was incorporated to every repeating unit in a PHEMA backbone to form the desired multifunctional macro-CTA. PHEMA-TMS, which was used as the precursor of PHEMA, was prepared by ATRP of HEMA-TMS in anisole at 90 °C, using the CuBr/dNbpy catalyst system.[15] 40% monomer conversion was reached in 9 h, and PHEMA-TMS with $M_{n,GPC}$ = 82 800 (DP = 409) and M_w/M_n = 1.11 (Table 1) was obtained. This PHEMA-TMS was then converted to PHEMA by stirring in slightly acidic methanol. The −OH groups of PHEMA were subsequently functionalized with XA using dicyclohexylcarbodiimide as a coupling agent. Successful functionalization of PHEMA to PPXEM was confirmed by ^{1}H NMR analysis (Figure S2). No side reactions with the xanthate moiety were observed under mild reaction conditions (1 h at 0 °C and overnight at room temperature (RT) in dimethylformamide). The GPC traces of the brush backbone shown in Figure 1 indicate that the apparent molecular weight did not change during transformation from PHEMA-TMS to PHEMA and then to PPXEM. This implies that the hydrodynamic volume of PPXEM is similar to that of PHEMA-TMS and PHEMA.

To obtain PPXEM-*g*-PVOAc brush copolymers, PVOAc side chains were grown from PPXEM multifunctional macro-CTA by RAFT in the presence of AIBN. The following reaction conditions were used for the side chain synthesis: VOAc:PPXEM:AIBN = 400:1:0.2 and 400:1:0.1 for the synthesis of $PPXEM_{409}$-*g*-$PVOAc_{50}$ and $PPXEM_{409}$-*g*-$PVOAc_{60}$, respectively. The effect of AIBN concentration was studied by selecting PPXEM:AIBN ratios of 1:0.1 and

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Scheme 1. Synthesis of Molecular Brushes with PVOAc Side Chains Grown from a PHEMA Backbone

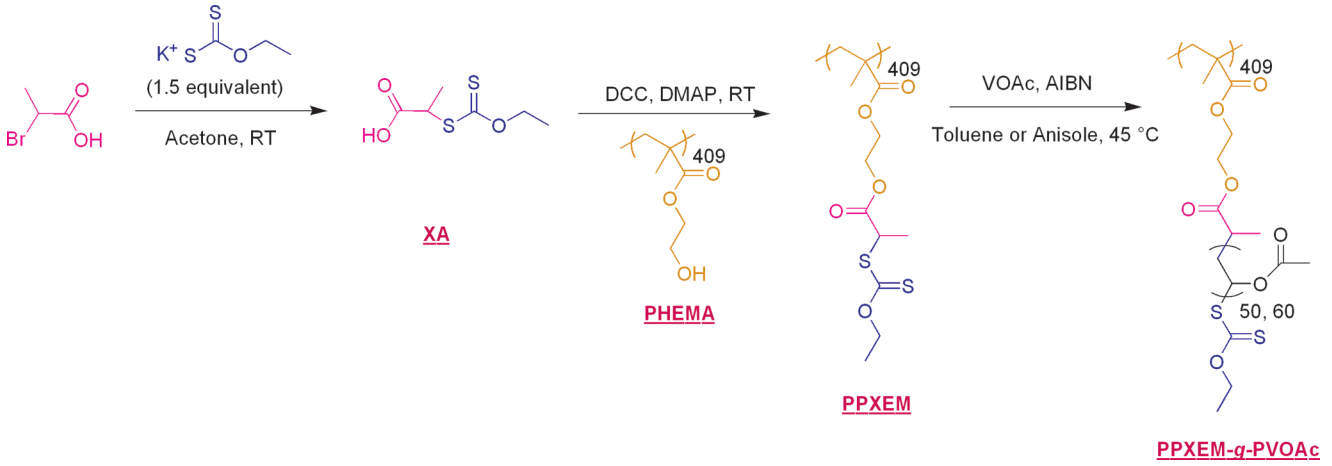

Table 1. Molecular Weight and PDI Data for the Backbone and the Brushes

name	DP	$M_{n,NMR}$	$M_{n,AFM}$	$M_{n,GPC}$	M_w/M_n
PHEMA-TMS$_{409}$	409[a]	81 000[b]		82 800[a]	1.11[a]
PHEMA$_{409}$	409	52 100		85 700[c]	1.13[c]
PPXEM$_{409}$	409	123 000		92 500[a]	1.17[a]
PPXEM$_{409}$-*g*-PVOAc$_{50}$	409−50[d]	1 880 000[d]	1 800 000	315 000[a]	1.21[a]
PPXEM$_{409}$-*g*-PVOAc$_{60}$	409−60[d]	2 240 000[d]	2 200 000	396 000[a]	1.26[a]

[a] Calculated by GPC in THF with PMMA calibration. [b] Calculated from monomer conversion measured by ^{1}H NMR. [c] Calculated by GPC in DMF with PMMA calibration. [d] Calculated from ^{1}H NMR by comparing the areas of the −CH− of the PVOAc next to the ethyl xanthate chain end (D in Figure S4, 6.60 ppm) to total PVOAc (D + H in Figure S4, 6.60 ppm + 4.90 ppm), assuming that polymer chains grow in the same fashion from each backbone unit.

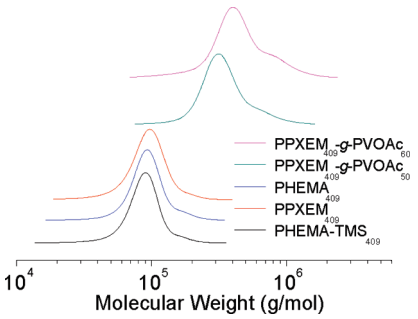

Figure 1. GPC traces of PHEMA-TMS$_{409}$, PHEMA$_{409}$, PPXEM$_{409}$, PPXEM$_{409}$-*g*-PVOAc$_{50}$, and PPXEM$_{409}$-*g*-PVOAc$_{60}$ (measured by using linear PMMA standards). *X*-axis shows the apparent molecular weight, and *y*-axis shows the RI-detector signal.

1:0.2. The reaction temperature was only 45 °C for both systems in order to decompose AIBN very slowly. This reduced the amount of growing radicals and also the amount of new chains generated from the initiator. This also reduced probability of intermolecular radical−radical coupling reactions, critical during the growth of molecular brushes side chains. Samples, periodically taken from the reaction mixture, were analyzed by GPC to follow the progress of the polymerization. Polymerization started after a 30 min inhibition period in both systems, and then the polymer peak gradually shifted to higher molecular weights. This inhibition period could result from the trace amount of impurities in the reaction mixture system and high sensitivity of growing PVOAc radicals.[35,38] The reaction was stopped by opening the flask to ambient atmosphere (air) after 9 h in the synthesis of PPXEM$_{409}$-*g*-PVOAc$_{50}$ and after 20 h in the synthesis of PPXEM$_{409}$-*g*-PVOAc$_{60}$. As expected, the polymerization was faster in the system with the higher AIBN concentration (PPXEM$_{409}$-*g*-PVOAc$_{50}$ synthesis). The GPC traces of the final brush copolymers indicated an apparent molecular weight (based on linear polystyrene standards) of $M_{n,GPC}$ = 315 000 and M_w/M_n = 1.21 for the PPXEM$_{409}$-*g*-PVOAc$_{50}$ and $M_{n,GPC}$ = 396 000 and M_w/M_n = 1.26 for the PPXEM$_{409}$-*g*-PVOAc$_{60}$. M_w/M_n values were low for both systems, showing controlled growth of the side chains from the PPXEM macro-CTA (Figure 1 and Table 1). The small shoulder at high molecular weight region can be due to small amount of intermolecular coupling (this can be also visible in AFM images, cf. Figure 2). The GPC results only provide apparent molecular weight, and NMR as well as AFM analyses were conducted to generate more precise information about the molecular weight and size distribution of the brush copolymers (discussed below).

AFM Analysis. Individual molecules of PPXEM$_{409}$-*g*-PVOAc$_{50}$ and PPXEM$_{409}$-*g*-PVOAc$_{60}$ molecular brushes adsorbed on a mica substrate were imaged by AFM (Figure 2a,b). The imaged molecules exhibit a wormlike conformation, suggesting extension of the brush backbone. Contour length distributions of the imaged molecules are depicted in Figure 2c,d. The polydispersity indexes L_w/L_n = 1.16 and 1.18 are consistent with the corresponding values measured by GPC and confirms the well-defined architecture of the synthesized molecules. With a backbone DP = 409 and a number-average contour length (L_n) of 96 ± 5 nm for both brushes, the calculated length per monomeric unit for the backbone $l = L_n/DP = 0.23 \pm 0.01$ nm is close to the length l_0 = 0.25 nm of the C−C−C monomeric unit in the tetrahedral configuration.[40] This indicates a fully stretched all-trans backbone of the brushlike macromolecules on the mica substrate.

Molecular imaging of Langmuir−Blodgett films (method described elsewhere[41]) was used to measure the number-average molecular weights of the brushes as 1 800 000 and 2 200 000 for the PPXEM$_{409}$-*g*-PVAc$_{50}$ and PPXEM$_{409}$-*g*-PVOAc$_{60}$ molecules, respectively. These measured molecular weights allow more accurate determination of the degrees of polymerization of the PVOAc side chains as $DP_{AFM} \cong M_n/(DP \times M_0)$, where M_0 = 86 g/mol is the molar mass of vinyl acetate. The determined values DP_{AFM} = 51 ± 3 and 62 ± 3 are very similar to the DP values calculated by NMR. This indicates

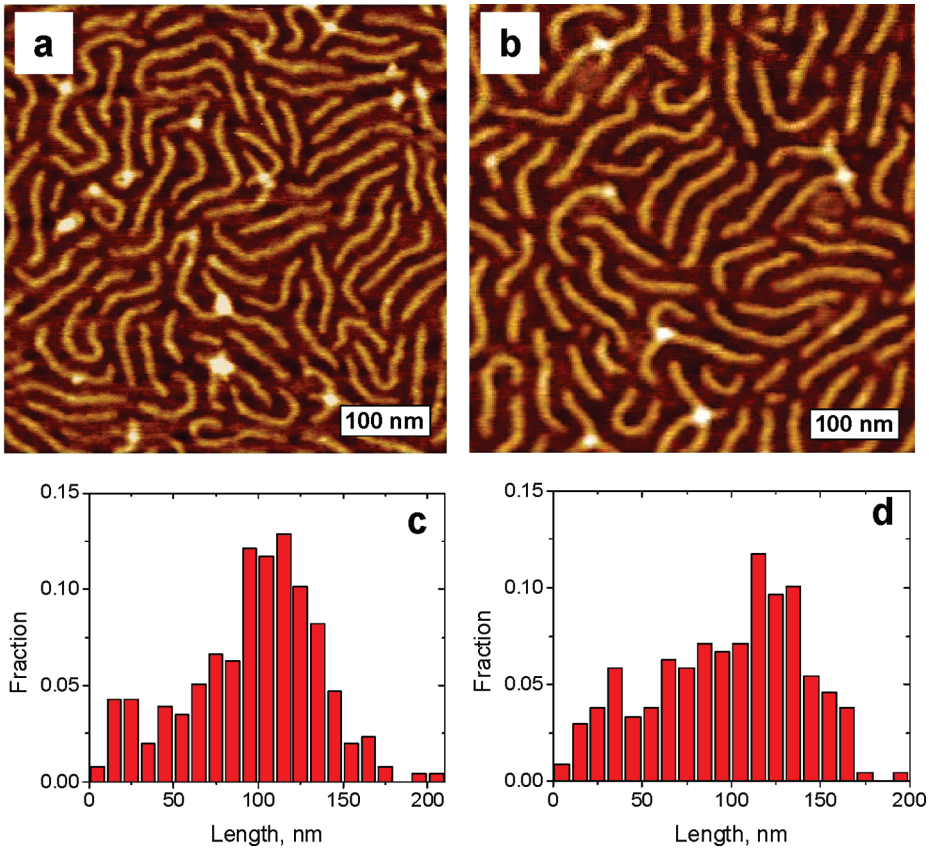

Figure 2. Height images and the corresponding length distributions of (a, c) $PPXEM_{409}$-*g*-$PVOAc_{50}$ and (b, d) $PPXEM_{409}$-*g*-$PVOAc_{60}$ brushes were measured by AFM on a mica substrate.

nearly quantitative initiation efficiency from the $PPXEM_{409}$. Such high initiation efficiency can be explained by the relatively small volume of the VOAc monomer and also the uniform growth of the side chains by intramolecular exchange reactions of the CTA groups. The values determined by the AFM-LB method are consistent with the average distance between the adsorbed $PPXEM_{409}$-*g*-$PVAc_{50}$ and $PPXEM_{409}$-*g*-$PVOAc_{60}$ brushes as $D = 26 \pm 2$ and 32 ± 2 nm, respectively. From the ratio $D/2DP_{AFM}$, one obtains the average distances per monomeric unit of the side chain as 0.25 ± 0.02 and 0.26 ± 0.02 nm, which indicate a fully extended conformation of the PVOAc side chains.

Conclusions. Well-defined PVOAc molecular brushes were prepared using a combination of ATRP and RAFT polymerization techniques. The longer spacer separating the xanthate moiety from the backbone (7 vs 3 atoms) was essential for the synthesis of the well-defined PVOAc side chains, via the "grafting from" approach. Imaging of individual brush macromolecules by AFM confirmed the well-defined architecture of the molecular brushes, with a characteristic chain extended conformation.

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Supporting Information Available: Materials, analytical methods, and experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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