Radical Polymerization

A Covalent-Chemistry Approach to Giant Macromolecules and Their Wetting Behavior on Solid Substrates**

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Synthetic polymers commonly lack any sizable extension into the second dimension (thickness) and are best described as more or less flexible threads. Recently there have been two synthetic approaches to address the problem of how to make macromolecules "thick": one is referred to as molecular brushes,[1,2] the other as dendromized polymers.[3] Dendromized polymers (denpols) differ from molecular brushes in that their side chains are not linear but highly and regularly branched (dendrons), which results in a considerable density of molecular segments in the direct neighborhood of the central backbone. Denpols, especially those of higher generation, have the built-in character of a cylindrical object, a feature which found application in basic experiments in nanoscience in which the bottom-up approach was investigated.[4] These objects can reach lengths of several hundred nanometers and widths of 5–7 nm depending on their chemical structure and generation number and, in this regard, are amongst the largest molecules ever prepared. It seems difficult, for both synthetic and space reasons, to extend the denpol concept to a degree such that the dimensions of biologically relevant cylindrical objects such as the tobacco mosaic virus (TMV envelope: diameter 18 nm, length ca. 300 nm) can be mimicked. Therefore, we set out to merge the brush and denpol concepts. Herein, we report a joint synthetic and scanning force microscopy (SFM) inves-

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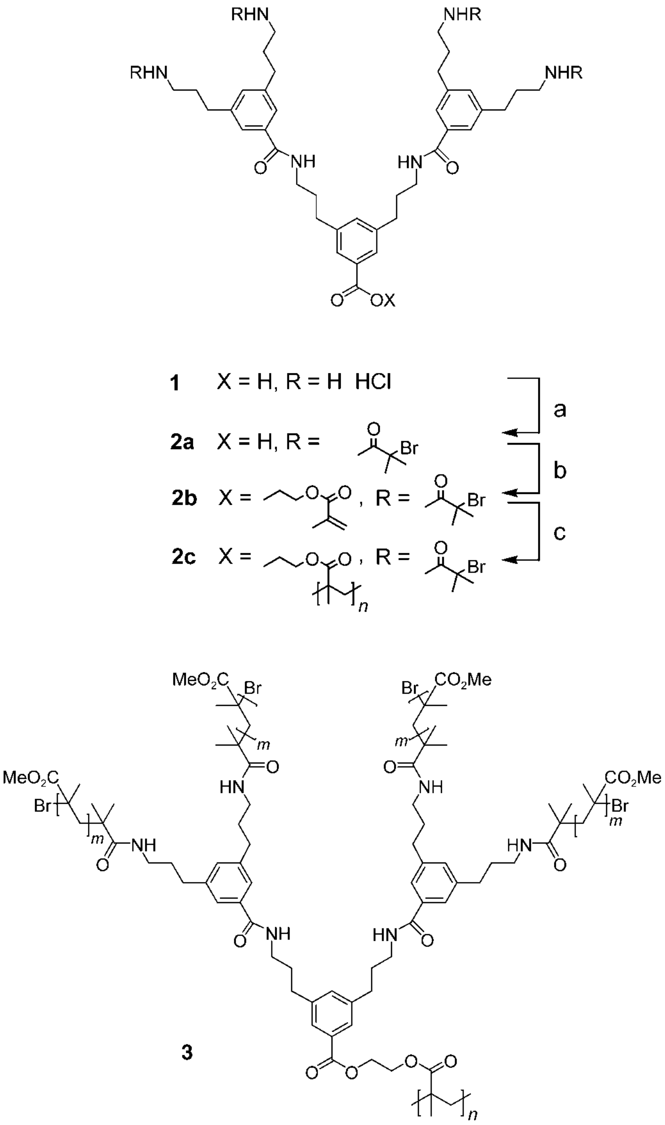
tigation of our attempts to further increase the diameter of denpols. The synthetic issues comprise: a) synthesis of a denpol macroinitiator whose number of initiator sites per repeat unit (four) is inherently fixed; b) growth of poly(methyl methacrylate) (PMMA) chains off this denpol's "surface"[5] by using atom-transfer radical polymerization (ATRP);[2a,6] c) determination of polymer hair length; and d) estimation of the initiation efficiency. Since the starting material already has a molar mass easily in the range of 1 × 10^6 Daltons, it was clear that a complete characterization of the product according to organic chemistry standards would not be feasible. We therefore carried out a detailed characterization of the starting material, restricted ourselves at this initial stage to second-generation (G2) denpols, and performed model reactions for the growing process. SFM was used to investigate the interaction of the hairy denpols with solid substrate surfaces and served not only to further characterize these huge molecules but also, and more importantly, to study the response of hairy denpols to the nature of the surface on which they are adsorbed. These investigations specifically included: a) the imaging of spin-coated samples on three different substrates, namely mica, MoS_2, and highly oriented pyrolytic graphite (HOPG); b) characterization of the denpol backbone contour as well as the structure of the hairy shell; and c) observation of whether there is a systematic tendency of the hairs to fold back as their interaction with the substrate becomes increasingly less favorable. This latter aspect is considered important for a distant goal of this research, which is to force the hairs to completely fold back and produce cylindrical molecular entities with unprecedented dimensions, for example, by subsequent photochemical cross-linking.

The present study was carried out with the G2 denpol **2c**, which has four terminal 2-bromoisobutyramide groups in each repeat unit. They serve as initiator sites for the ATRP of methyl methacrylate. The synthesis starts from the known G2 dendron **1**, whose amine functions are completely converted by reaction with the succinidyl active ester of 2-bromoisobutyrate, and then the resultant **2a** is converted into the methacrylate G2 macromonomer **2b** (Scheme 1). Compounds **2a** and **2b** were fully characterized (see Supporting Information). As has already been discovered for similar dendronized macromonomers, simple heating of **2b** to 55 °C for a few hours in an extremely highly concentrated solution (0.6 g of **2b** in 0.4 mL of benzene) resulted in its polymerization to the high-molecular weight polymer **2c**. Notably, polymer **2c** automatically has four initiator sites per repeat unit in this mode of synthesis.[7] Standard workup and lyophilization from dioxane[8] afforded a colorless foam (yields: 82–86%) which, despite its hygroscopic character, gave correct data from combustion analysis (see Supporting Information). Additionally, the ^1H (500 MHz) and ^{13}C NMR spectra could be fully assigned, although the signals were relatively broad as a result of the high molecular weight. Gel permeation chromatography (GPC) in DMF calibrated with G1 denpol standards[9] furnished number-average molar masses between 900000 and 1500000 $g\,mol^{-1}$ and polydispersity indices (PDI) of 3.4–4.0. The GPC elution curves were basically monomodal (see Supporting Information). For the following experiments the highest molecular weight sample with PDI = 3.4 was used.



Scheme 1. Reagents and conditions: a) **1**, 2,5-dioxopyrrolidin-1-yl 2-bromoisobutyrate, TEA, CH_2Cl_2, MeOH, −30 °C, 15 h (86%); b) **2a**, DCC, HEMA, DMAP, CH_2Cl_2, RT, 15 h (68%); c) **2b**, DCM, 55 °C, 8 h (85%). TEA = triethylamine, DCC = *N*,*N*′-dicyclohexylcarbodiimide, HEMA = hydroxyethylmethacrylic acid, DMAP = 4-dimethylaminopyridine.

Molecular brushes were prepared by grafting polymeric chains from the backbone,[1e,f,2a] in which the most critical aspect is cross-linking. ATRP is a so-called controlled radical polymerization (CRP) procedure, which means that the lifetime of a free radical chain end is reduced by the action of a transition metal (Cu^I in the case of ATRP). Thus, chain termination by radical recombination (and disproportionation), which would lead to intra- and intermolecular cross-linking, is reduced. A rough estimation of the number of initiator sites shows that polymer **2c** can initiate 6000 PMMA chains per individual **2c** chain in the optimum case.[10] Although not many of the chain ends will be active at the same time, from this simple estimation it suggests that the experimental conditions should be better designed such that cross-linking is reduced as far as possible. Approximately 30 independent experiments to grow hairs off the denpols were performed, each using 58 mg of **2c** and 5 g of methyl methacrylate (MMA). Cu^{I}Br and pentamethyldiethylenetriamine (PMDETA) were always employed in a constant molar ratio to **2c**; the reaction time, however, was varied from 0.5 to 2 hours to change the lengths of the hairs (for a detailed synthetic procedure, see the Supporting Information). The volume of the solvent DMF was critical.[11] In a number of cases where 58 mg of polyinitiator **2c** and 5 g of monomer were dissolved in 5 mL of DMF cross-linking could instantaneously be visually recognized and no soluble product could be isolated. Cross-linking still occurred if 10 mL of DMF was used but some hairy denpols, specifically those with "short hair" at low conversion and short reaction times (10 min), could be isolated. The optimum results were finally obtained with 20 mL of DMF, where only small amounts of insoluble product were obtained (ca. 5 mass %). For both reaction times all other material was fully soluble and was purified by passing it through a short column of silica gel (100–200 mesh, eluent: dichloromethane), which left the Cu salts behind as a blue layer on the top of the column. This process was associated with a considerable loss of material, which stayed on the column and could not be eluted despite the fact that it was fully soluble before.[12] Removal of solvent furnished 1 g (0.5 h) and 1.2 g (2 h) of a colorless, transparent film (20 and 25 % conversion, respectively, based on MMA). The apparent number-average molar masses of **3** obtained by GPC were 2000000 (0.5 h) and 3500000 (2 h) (apparent PDIs: 2.5 and 1.4, respectively). These values need to be considered with care because there is no appropriate standard available for such complex molecular structures. The actual molar masses will most probably be higher.[9] The hair lengths were roughly estimated by hydrolyzation experiments with denpol **3** and a model compound to be on the order of 20000–25000 g mol^{-1} (PDIs ca. 1.3; see Supporting Information). These figures were used to derive the number of initiator sites per repeat unit of **2c** that had actually been active. Assuming the above hair molecular weights are correct and doing a simple mass consideration, an initiator efficiency of roughly 50 % (two out of four) was obtained (see Supporting Information).

Denpol **3**, which had been purified from nonbound PMMA chains,[13] was spin-coated from diluted chloroform solution onto mica, MoS$_2$, and highly oriented pyrolytic graphite (HOPG) and investigated by SFM in the tapping mode (Figure 1 a–c). In all cases the adsorbed denpol molecules exhibit a backbone conformation in quasi two dimensions.[14] Single denpol molecules are found on mica and MoS$_2$ on atomically flat terraces, whereas on HOPG they are predominantly in islands and at step edges because of a high mobility on the HOPG terraces. The image on mica (Figure 1 a) reveals single denpol molecules with a central backbone and a frayed-out corona, with a total width of about 122 nm (average value from 64 cross-sectional profiles) and a thickness between 0.5 and 1 nm, which decreases gradually from the backbone toward the edge. In addition, there are small islands with the same apparent thickness as the corona and no backbone. We attribute the corona to extended flat-lying PMMA chains covalently linked to the denpol backbone and the islands to free PMMA chains, which obviously had not been removed during purification. Given a number-average molar mass of $M_n = 20000$ g mol^{-1}, a fully extended chain (hair) would on average be 50 nm long, which is in good agreement with half of the corona width (61 nm). The backbone conformation was analyzed by plotting $\langle \cos \Theta \rangle$ versus ℓ, where Θ is the change in orientation between two segments at a distance ℓ apart along the backbone contour. A fit to the wormlike chain model in 2D[15] would result in a persistence length of 65 nm (see Supporting Information). The corona exhibits holes and a sharp edge on MoS$_2$. Moreover, it is narrower (90 nm, average value from 114 cross-sectional profiles) and thicker (between 1 and 2 nm), and the apparent persistence length of the backbone amounts to 164 nm. The corona width is not so well defined on HOPG since, because of their high mobility, free PMMA molecules diffuse across the surface and into the corona of the denpol,

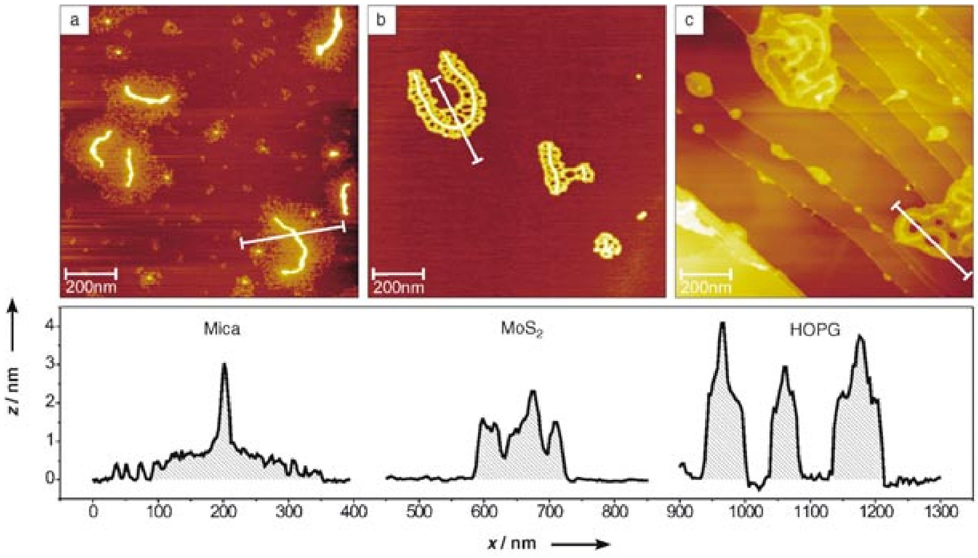


Figure 1. SFM images and cross-sectional profiles of **3** with PMMA hairs of $M_n = 20000–25000$ g mol^{-1} on a) mica, b) MoS$_2$, and c) HOPG.

thereby increasing its thickness. A typical distance between the backbones on the order of 50 nm is observed in the islands, which is attributed to a corona width. The height profile indicates a homogeneous layer of roughly constant height of about 2 nm, which decreases sharply at the edge.

The determined hair lengths of approximately 50 nm correspond well with half of the corona width on mica, which indicates that the PMMA chains are more or less stretched out perpendicular to the backbone direction. The fraying reflects the polydispersity of the hairs. The narrower corona on MoS_2 shows that the hairs now deviate from an all-stretched conformation by bending back. They dewet into bundles that form a sharp corona edge, thus indicating a less favorable interaction of the PMMA chains with MoS_2 as compared to mica. The relatively small distance of 50 nm between the backbones on HOPG indicates that the PMMA chains also bend back on this substrate. There is no indication of the above kind of dewetting. The continuous increase in apparent corona height on going from mica to MoS_2 and HOPG (Figure 1, bottom) suggests that the hair/substrate interaction on HOPG is the least favorable.

The results show that the hair/substrate interaction has a considerable effect on hair conformation. The hairs behave quite differently on MoS_2 and HOPG, but in either case the all-stretched conformation perpendicular to the backbone direction is avoided, which results in a much narrower corona than on mica. The hairy denpols, with their sensitive response to solid substrates, open the possibility of controlling the persistence of a single polymer at a surface. This could potentially be exploited for polymers having hairs of different natures and lengths on the same substrate or, alternatively, for the same polymer on different substrates. SFM studies of hairy denpols clearly also allows the independent investigation of hairs and backbone. This can lead to a better understanding of the mutual hair/backbone interaction.

The next steps include increasing the interaction of the hairs with the denpol backbone and decreasing their interaction with the substrate. Also, it seems likely that the use of a "thicker" backbone (e.g., G4), where the hairs near to the backbone "see" only other hairs, may also have a positive effect.

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[1] a) Y. Tsukahara, K. Mizuno, A. Segawa, Y. Yamashita, *Macromolecules* **1989**, *22*, 1546–1550; b) M. Wintermantel, M. Schmidt, Y. Tsukahara, K. Kajiwara, S. Kohjiya, *Macromol. Rapid Commun.* **1994**, *15*, 279–284; c) P. Dziezok, S. S. Sheiko, K. Fischer, M. Schmidt, M. Möller, *Angew. Chem.* **1997**, *109*, 2894–2897; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2812–2815; d) S. Qin, K. Matyjaszewski, H. Xu, S. S. Sheiko, *Macromolecules* **2003**, *36*, 605–612; e) M. Zhang, T. Breiner, H. Mori, A. H. E. Müller, *Polymer* **2003**, *44*, 1449–1458; f) C. Li, N. Gunari, K. Fischer, A. Janshoff, M. Schmidt, *Angew. Chem.* **2004**, *116*, 1121–1124; *Angew. Chem. Int. Ed.* **2004**, *43*, 1101–1104.

[2] For recent reviews, see: a) K. Matyjaszewski, J. Xia, *Chem. Rev.* **2001**, *101*, 2921–2990; b) N. Hadjichristidis, M. Pitsikalis, H. Iatrou, S. Pispas, *Macromol. Rapid Commun.* **2003**, *24*, 979–1013.

[3] A. D. Schlüter, J. P. Rabe, *Angew. Chem.* **2000**, *112*, 860–880; *Angew. Chem. Int. Ed.* **2000**, *39*, 864–883; A. Zhang, L. Shu, Z. Bo, A. D. Schlüter, *Macromol. Chem. Phys.* **2003** *204*, 328–339; A. D. Schlüter, *Top. Curr. Chem.* **2004**, in press.

[4] L. Shu, A. D. Schlüter, C. Ecker, N. Severin, J. P. Rabe, *Angew. Chem.* **2001**, *113*, 4802–4805; *Angew. Chem. Int. Ed.* **2001**, *40*, 4666–4669; J. Barner, F. Mallwitz, L. Shu, A. D. Schlüter, J. P. Rabe, *Angew. Chem.* **2003**, *115*, 1976–1979; *Angew. Chem. Int. Ed.* **2003**, *42*, 1932–1935.

[5] A. Zhang, A. D. Schlüter, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **2003**, *44*, 524–525.

[6] M. Kamigaito, T. Ando, M. Sawamoto, *Chem. Rev.* **2001**, *101*, 3689–3746.

[7] In brush synthesis the polymeric initiators are normally prepared by attaching initiator sites to a precursor polymer in an independent synthesis step, which may lead to complications and incompleteness. Structural proof of the resulting macroinitiators does not always meet accepted standards.

[8] If the lyophilization was done in DMF or benzene, the polymer was obtained in a morphology which did not dissolve or molecularly disperse in DMF, the medium for the following ATRP step, but instead formed a gel.

[9] A. Zhang, B. Zhang, E. Wächtersbach, M. Schmidt, A. D. Schlüter, *Chem. Eur. J.* **2003**, *9*, 6083–6092; A Zhang, L. Okrasa, T. Pakula, A. D. Schlüter, *J. Am. Chem. Soc.* **2004**, 126, 6658–6666.

[10] Given an average molecular weight of 1500000 and 1000 for polymer **2c** and its repeat unit, respectively, an individual chain has $1500 \times 4 = 6000$ initiator sites. Of course, one has to consider that not all the initiator sites will actually act as such for steric reasons.

[11] Several experiments were also tried in toluene but cross-linking could not be prevented. Presumably toluene does not dissolve or disperse **2c**. In a recent report on cross-linking reactions in ATRP, Cu^{II} salts were proposed to deactivate the reactivity of the chain end: K. Matyjaszewski, S. Qin, J. R. Boyce, D. Shiravanyants, S. S. Sheiko, *Macromolecules* **2003**, *36*, 1843–1849.

[12] In three independent experiments these losses amounted to 59% (100 mesh), 50% (100 mesh), and 76% (300–400 mesh). It is assumed that it is the high-molecular weight hairy denpols which strongly adhere to the silica surface. Tests confirmed that nonconnected PMMA easily passed through the column.

[13] The denpols were purified by preparative GPC such that no PMMA was detectable. Nevertheless, all samples still contained some nonbound PMMA hairs, as observed in the SFM images.

[14] There must have been a process which converts the 3D structures into the 2D structures in solution.

[15] C. Rivetti, M. Guthold, C. Bustamante, *J. Mol. Biol.* **1996**, *264*, 919–932.