

Superhelices of Poly[2-(acetoacetoxy)ethyl methacrylate]

Helmut Schlaad,* Theodora Krasia,[†] and Markus Antonietti*Contribution from the Max Planck Institute of Colloids and Interfaces, Colloid Department, Am Mühlenberg 1, 14476 Potsdam-Golm, Germany*

Received April 14, 2004; E-mail: schlaad@mpikg-golm.mpg.de

Abstract: Poly[2-(acetoacetoxy)ethyl methacrylate] (PAEMA) homopolymers were found to self-assemble into hierarchical superstructures, that is, double-stranded helical tubes of either screw sense (scanning force microscopy). Both the diameter and the pitch of the superhelices are ~ 12 nm, and their length is 200–500 nm. It is proposed that PAEMA chains first organize into ribbons, the width of which determines the pitch of the helix, and then coil up into the helical superstructure. The formation of these structures is driven by the establishment of hydrogen-bridging interactions between adjacent acetoacetoxy groups (NMR and dielectric relaxation spectroscopy) and compensation of dipole moments.

Introduction

Biopolymers, such as peptides or proteins, are well known for their ability to produce highly ordered hierarchical structures scaling from a few nanometers to several microns. On the lowest level, hydrogen-bridging interactions between amino acid sequences (primary structure) produce a distinct conformation or secondary structure of segments, the most important being the α helix and β sheet. Folding and aggregation of the protein molecules, driven by noncovalent interactions (apart from hydrogen bridging these are electrostatic, dipole–dipole, π -stacking, hydrophobic interactions, etc.),¹ then lead to complex tertiary and quaternary structures such as keratin, collagen, or silk fibroins, which exhibit ultimate functionality, materials properties, and so forth.²

Undoubtedly, there is quite a gap between the performance of most synthetic polymers and biological polymers. This gap might be closed by employing a biomimetic approach, that is, the implementation of the basic secondary structure and folding motifs into synthetic polymers for the production of high-performance materials and structures with multilevel ordering.^{3–7} Nylons, for instance, owe their superb mechanical strength to the establishment of a β -sheet-like network between amide bonds (cf. spider silk). Regarding synthetic helical polymers, numerous work has been devoted to polymethacrylates, polyaldehydes, polysilanes, polyisocyanides, polyisocyanates, polyarylenes, and polyacetylenes.^{8,9} The helical conformation of

polymer chains results from some steric restrictions because of the presence of bulky substituents in the side chain and/or a hindered rotation around single bonds in the backbone. Most polymers were made from optically active monomers, often employing chiral initiators or catalysts (asymmetric polymerization) to produce an excess of helices with one screw sense.

Only a few tertiary structures of synthetic polymers have been reported so far, for instance, a double-stranded helical stereo-complex of isotactic and syndiotactic poly(methyl methacrylate)¹⁰ and a 3:1 helix of enantiomeric poly(lactic acid)s.¹¹ Hierarchical structures, however, have been observed for a number of amphiphilic rod–coil block copolymers containing polysilane (superhelices),¹² polypeptide (hexagonal-in-lamellar morphology),^{13–16} polyisocyanate (zigzag morphology),^{17,18} polyester (mushroom-shaped supramolecular structures),¹⁹ and poly(isocyanodipeptide) segments (fibrils and helical superstructures).^{20,21} Also worth mentioning are the “helical cables” of amphiphilic poly(phenylacetylene) bearing L-valine pendants²² and the 3D fibrous networks of organogelators.²³ As a

[†] Present address: University of Cyprus, Chemistry Department, P.O. Box 20537, 1678 Nicosia, Cyprus.

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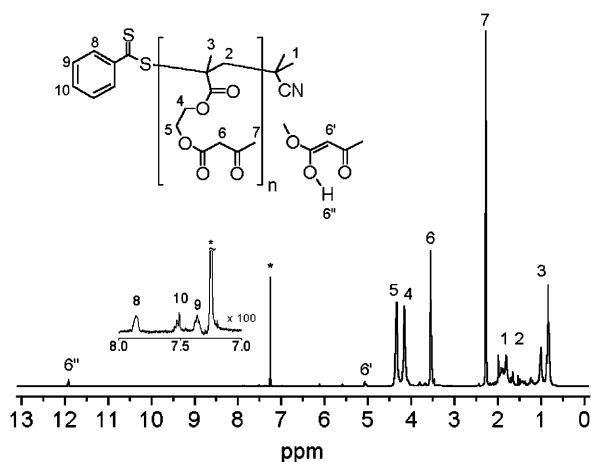


Figure 1. ^1H NMR spectrum (400.1 MHz) of PAEMA-30 in CDCl_3 at 25 $^\circ\text{C}$ (* = CHCl_3).

general rule, however, diversity and complexity of superstructures should go with the number of simultaneous noncovalent interactions.¹

Here, we report on the formation of very large, supposedly hollow, double-stranded superhelices by linear poly[2-(acetoacetoxy)ethyl methacrylate] (PAEMA, see the structure in Figure 1). The observation of such a kind of hierarchical superstructure is amazing because the building polymer chains exhibit neither high stereoregularity nor chirality nor amphiphilicity. The formation of the superstructures is solely driven by the establishment of hydrogen bridges between adjacent acetoacetoxy groups and compensation of dipole moments. Scanning force microscopy (SFM) was applied to visualize the superstructures; ^1H NMR and dielectric relaxation spectroscopy (DRS) provided evidence for the existence of hydrogen-bridging interactions.

Experimental Section

Descriptions of the synthesis of PAEMA- n samples (average number of repeating units, $n = 30, 44,$ and 176 ; polydispersity index, $\text{PDI} \approx 1.15$) and of characterization methods are provided as Supporting Information.

Results and Discussion

Figure 1 shows the chemical structure and a typical ^1H NMR spectrum of PAEMA-30 made by RAFT radical polymerization.²⁴ It is evident by looking at the assignment of signals in Figure 1 that adjacent acetoacetoxy groups of PAEMA preferentially exist in the form of the keto tautomer ($\sim 92\%$).²⁵ The triad tacticity of the polymer is $mm \approx 0.1$, $mr \approx 0.3$, and $rr \approx 0.6$ (m : meso, r : racemic) as determined from the signals of α -methyl protons of the backbone (3, $\delta = 0.8$ – 1.2 ppm). Note that such tacticity is very typical for poly(alkyl methacrylate) made by a radical polymerization process.²⁶

The signals of acetoacetoxy units show at $\delta = 2.28$ (7) and 3.55 ppm (6), that is, at lower field as compared to the ones of the model compound *tert*-butyl acetoacetate (*t*BAA; $\delta = 2.23$

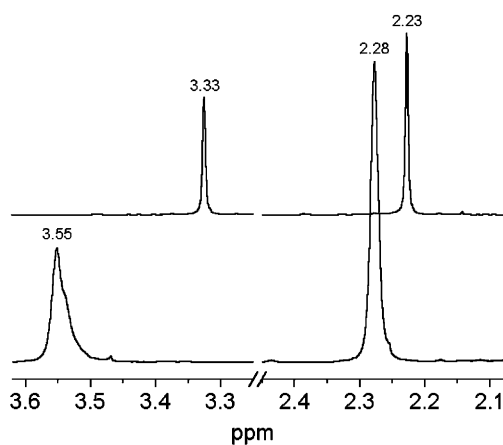


Figure 2. ^1H NMR spectra (400.1 MHz) of *t*BAA (top) and PAEMA-30 (bottom) in CDCl_3 ; region of methylene (6, $\delta = 3.3$ – 3.6) and methyl (7, $\delta = 2.2$ – 2.3) proton signals of the acetoacetoxy unit, cf. Figure 1.

and 3.33 ppm, respectively) (Figure 2). The downfield shift, particularly of the methylene proton signals, might be attributed to the presence of a carbonyl group in the proximity and thus hydrogen-bonding interactions between PAEMA acetoacetoxy units. Note that this situation is promoted by the fact that acetoacetoxy units in PAEMA are covalently linked together. However, regarding tacticity of the PAEMA chain, it seems important that acetoacetoxy groups are attached via a flexible ethylene glycol spacer to the backbone to achieve proper spatial arrangement for the establishment of hydrogen bridges. Hydrogen-bridging interactions along the PAEMA main axis might well explain the large effective dipole moment per monomer unit of $\mu \approx 2.4$ D, obtained by DRS analysis of a solid film of PAEMA-30. This value ranges between the ones reported for poly(vinyl acetate) (1.0 D)²⁷ and polypeptides (3.5 D).²⁸

Notwithstanding the not-so-high stereoregularity of chains, PAEMA can form very large assemblies at higher polymer concentrations, for example, when drying ~ 0.3 wt % solutions of PAEMA in THF on a hydrophobic substrate. However, no aggregates could be observed in dilute solution by dynamic light scattering. Figure 3 shows typical SFM images of the solid rodlike superstructures formed by PAEMA-44 (top) and PAEMA-176 (bottom) on graphite (PAEMA-30 not investigated). Rods are ~ 12 nm in diameter and about 200–500-nm long, the longer ones being formed by PAEMA-176. The persistence length (l_p) of PAEMA rods appears to be in the order of hundreds of nanometers (cf. DNA in 0.2 N aqueous saline solution: $l_p \approx 60$ nm, and poly(γ -benzyl-L-glutamate) in *N,N*-dimethylformamide: $l_p \approx 150$ nm).²⁹

SFM amplitude imaging with a sufficiently high resolution (Figure 3, right) revealed a helical makeup of these rods. As can be expected for a nonchiral system, both types of helices with opposite screw sense are observed. The pitch of PAEMA-176 superhelices is ~ 12 nm and the turning angle is about 20° (cf. Figure 3 (bottom)), thus by far larger, as expected for any kind of single-stranded helix. Note that even a DNA double helix of type A is no wider than 2.55 nm.² It is therefore believed that the PAEMA superhelices are hollow rather than solid. Pitch

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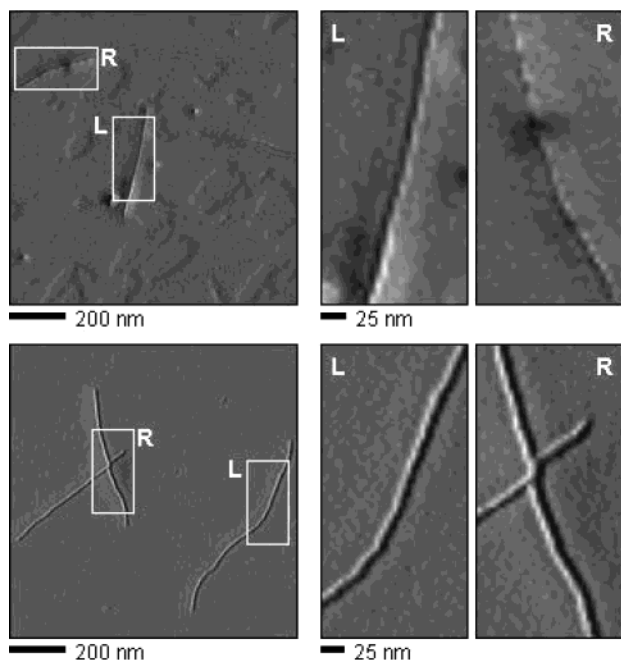


Figure 3. Tapping-mode SFM amplitude images of the rodlike superstructures formed by PAEMA-44 (top) and PAEMA-176 (bottom) upon evaporation of a drop of a ~ 0.3 wt % polymer solution in THF on graphite. L: Superhelices with left-handed screw sense, R: Superhelices with right-handed screw sense.

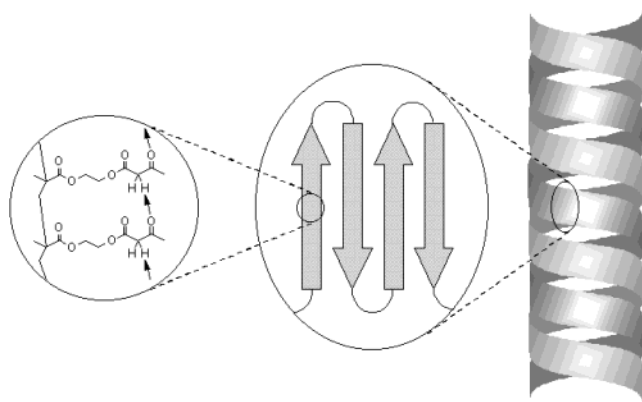


Figure 4. Tentative model of the hierarchical structure of PAEMA superhelices.

and turning angle values, however, point to the existence of a helical tube made of two strands.

As a working hypothesis, we propose that PAEMA chains first assemble into ribbons of ~ 12 nm in width and then coil up into double-stranded hollow superhelices (Figure 4). A similar hierarchical structure has recently been described for the complexes of an H-shaped oligopeptide with lipids or surfactants.³⁰ The structure of the ribbons, the formation of which is supposedly being driven by the compensation of local dipole moments, should be a kind of antiparallel β -pleated sheet made of PAEMA chains folded x times. Taking into account the contour length of PAEMA chains, $l_c = 11$ (PAEMA-44) and 44 nm (PAEMA-176), PAEMA-44 should be in a fully stretched, nonfolded conformation ($x = 0$), whereas PAEMA-176 should be folded three times ($x = 3$) to fit into the ribbon. Note the analogy to the folding of polypeptide α helices during the self-assembly of poly(γ -benzyl-L-glutamate)-polystyrene

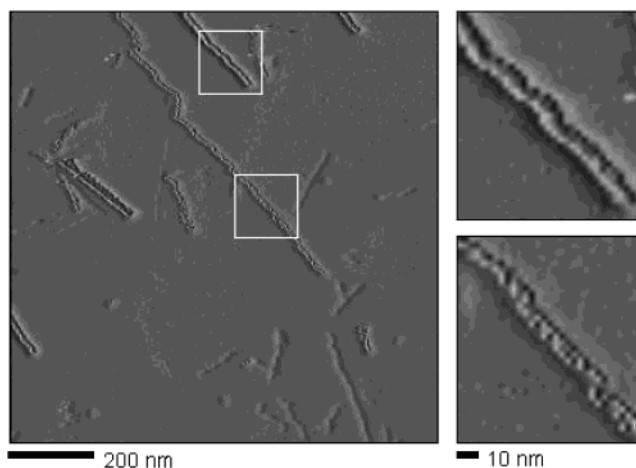


Figure 5. Tapping-mode SFM amplitude image of polymer globules that were produced from the helical superstructures of PAEMA-44 (Figure 3 (top)) upon aging at room temperature.

rod-coil block copolymers, which limits the thickness of polypeptide sheets to about 6–8 nm.¹³ The compensation of effective dipole moments on larger length scales then causes coiling of the ribbons into superhelices. In fact, a helical conformation allows for the compensation of dipole moments without producing any grain boundaries.

One can also see that the helical structure of the rods formed by PAEMA-44 is less defined and less tight compared to that of PAEMA-176. Stability and length of the superhelices seem to increase with the number of monomer units of the building PAEMA chain. Similarly, cooperative hydrogen-bridging interactions in polypeptides produce only stable α helices when the chains exceed a critical number of 15–20 amino acid units.^{29,31}

PAEMA superhelices were found to be not stable for longer times when keeping them as a solid at room temperature. The SFM image shown in Figure 5, taken a few days after the first analysis of specimen PAEMA-44, showed, instead of a few large helices, a large number of small globules with a diameter of ~ 3 nm. Considering the bulk density of PAEMA (1.263 g/mL; density oscillation tube),²⁴ a globule of that size might represent a single polymer chain. It seems reasonable that these globules emerge from the collapse of superhelices, supposedly driven by the improved interactions of the final disassembled state with the graphite surface in the absence of solvent. Note that this transformation in the solid state could only take place because the glass transition of PAEMA occurs at about 276 K (differential scanning calorimetry and DRS),²⁴ that is, well below room temperature. Interestingly, PAEMA globules are aligned in two parallel rows; this texture is a hint that the original superhelices were indeed hollow.

Summary and Outlook

PAEMA homopolymers were found to self-assemble into a hierarchical superstructure of double-stranded helical tubes with either screw sense (SFM). Both diameter and pitch of the superhelices are ~ 12 nm, and their length is on the order of 200–500 nm, depending on the molecular weight of the building PAEMA chain. It is proposed that, driven by hydrogen-bridging

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interactions between adjacent acetoacetoxy groups (NMR and DRS) and compensation of dipole moments, PAEMA chains first self-assemble into antiparallel β -pleated sheets or ribbons of ~ 12 nm in width and then coil up into the helical superstructure.

Future studies will be devoted to the detailed structural analysis of the PAEMA superhelices with microscopic and scattering techniques and NMR spectroscopy. The physico-chemical properties of the structures, especially thermodynamic stability and kinetics of the helix–globule transition, shall be investigated in a systematic fashion. It is further aimed to extend investigations to chiral derivatives of PAEMA.

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Supporting Information Available: Descriptions of the synthesis of PAEMA samples and of characterization methods. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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