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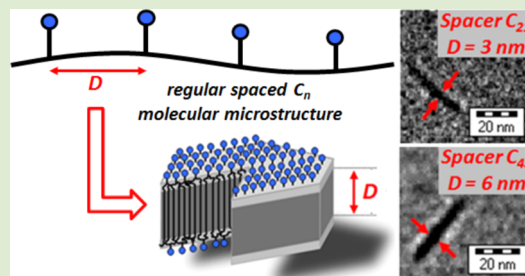
# Precise Microstructure Self-Stabilized Polymer Nanocrystals

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**S** Supporting Information

**ABSTRACT:** Nanoparticles with a defined shape and surface chemistry result from an encoding of crystal size directly in the polymer microstructure. This is brought about by carboxy groups spaced precisely on every 21st or 45th carbon atom of linear polyethylene chains synthesized by acyclic diene metathesis polymerization (ADMET) of precisely branched, long-chain  $\alpha,\omega$ -dienes. These hydrophilic functional groups form a layer on the nanocrystal surface, which interacts with the aqueous dispersing medium and, thus, self-stabilizes the nanocrystals. The nanocrystal thickness is directly predetermined by the length of the long-chain methylene spacer between the functional groups.



Anisotropic nanoparticles are studied intensely concerning the impact of their shape on their physical properties and organization into larger structures.<sup>1–3</sup> A key prerequisite is well-defined particles, and much effort is devoted to controlling the size, shape, and surface chemistry of inorganic nanoparticles, particularly in the challenging size regime of only several to several tens of nanometers.<sup>4–7</sup> The underlying principle is crystallinity and control of the crystalline structure during nanoparticle preparation. By comparison, anisotropic organic nanoparticles in this size regime are scarce. Phase separation of immiscible segments of block copolymers can afford particles with an anisotropic surface and, in some cases, also shape in the form of dumbbell and tripartite structures.<sup>8–12</sup>

A different approach to anisotropy of polymer nanoparticles is the utilization of crystallinity, in this sense, similar to the multitude of inorganic nanoparticles, but with crystalline order resulting from other principles, namely, van der Waals interactions between adjacent stretched chain segments. To this end, insertion polymerization of ethylene in aqueous solutions afforded dispersions of single crystal nanoparticles of about 6 nm lamella thickness and 25 nm lateral extension composed of linear polyethylene, which are stabilized by surfactant physisorbed at their surface.<sup>13</sup> Likewise, crystallization of the hydrophobic core of micelles formed from diblock copolymers with a polyethylene and a hydrophilic block yielded platelet or disc-like particles.<sup>14–16</sup> Anisotropic particles of moderately, randomly branched polyethylene resulted from free-radical emulsion polymerization at intermediate pressures.<sup>17</sup> Surfactant-free particles were generated by postpolymerization dispersion of a random ethylene–acrylic acid copolymer. Due to the large degree of incorporated acrylic acid repeat units required for colloidal stability (12 mol %) on the one hand and the random nature of the copolymer on the other hand, crystalline domains may be formed from polyethylene segments, but also domains with carboxylic acid

groups incorporated into a crystal likely exist. This results in a clearly anisotropic but irregular structure.<sup>18</sup>

In the aforementioned approaches yielding anisotropic particles with a defined shape, the thickness is determined by the crystallization process of the linear polyethylene portion. To provide particles with a defined shape and surface chemistry, we present a different concept, namely, encoding of nanocrystal thickness directly via the polymer molecular structure. This requires a different polymer architecture than the much studied block copolymers or random copolymers. A precise placement of hydrophilic groups in a constant distance on the polymer chain is necessary, and this distance must be sufficient to provide crystallizable segments.

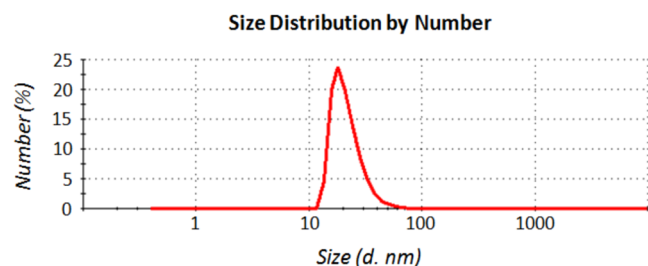
An approach to precisely spaced functional groups on the polymer backbone is Wagener's acyclic diene metathesis polycondensation (ADMET).<sup>19</sup> Polyethylene carrying a carboxylic acid group on as low as only every 21st carbon atom has been prepared in this fashion.<sup>20</sup> To work out the approach pursued here, even longer crystallizable segments are desirable. As a readily available starting material to the desired long methylene sequences, we have employed ethyl erucate. Isomerizing alkoxycarbonylation yielded diethyl tricosandioate as a linear  $\alpha,\omega$ -difunctional C<sub>23</sub> building block.<sup>21</sup> A further conversion similar to procedures<sup>20</sup> reported for compounds with other chain lengths afforded the carboxy-substituted symmetric C<sub>47</sub>  $\alpha,\omega$ -diene  $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_{21}\text{CH}(\text{COOR})-(\text{CH}_2)_{21}\text{CH}=\text{CH}_2$  protected as the 3-oxapent-2-yl ester. This protection was employed to prevent catalyst decomposition in the subsequent polymerization step, which can promote isomerization and loss of the precisely spaced character of the polymer.<sup>22–24</sup> Polymerization by  $[(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}]$  (Grubbs first generation alkylidene) in the neat molten

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monomer at 65 °C under high vacuum to remove the ethylene byproduct afforded the main chain unsaturated polyalkenamer  $[(\text{CH}_2)_{21}\text{CH}(\text{COOR})(\text{CH}_2)_{21}\text{CH}=\text{CH}]_n$  with an apparent molecular weight of  $M_n 3.8 \times 10^4 \text{ g mol}^{-1}$  (corresponding to  $\text{DP}_n \sim 50$ ,  $M_w/M_n 3.2$ ) according to GPC versus polystyrene standards. NMR spectroscopy evidences a defect-free structure. Reduction of the double bonds and deprotection occurred simultaneously by reaction with *para*-toluenesulfonyl hydrazide/triethylamine to yield saturated polymer  $\text{C}_{45}$  with a carboxylic acid group on every 45th carbon atom precisely,  $[(\text{CH}_2)_{44}\text{CH}(\text{COOH})]_n$ . This composition corresponds to 4.5 mol % acrylic acid in an ethylene–acrylic acid copolymer. Bulk  $\text{C}_{45}$  possesses a peak melting point of  $T_m 99^\circ\text{C}$ , associated with a melt enthalpy of  $\Delta H_m 100 \text{ J g}^{-1}$ , as determined by DSC (cf., Figure S6 in the Supporting Information).

For the preparation of carboxylate-stabilized nanoparticles, a hot solution of  $\text{C}_{45}$  in THF was injected into an aqueous cesium hydroxide solution under ultrasonication, and the resulting dispersion was annealed at 90 °C for several hours. As anticipated, stable nanoparticles were formed. Dynamic light scattering (DLS) reveals a particle size of about 20 nm (Figure 1).<sup>25</sup> Imaging of the nanoparticles by transmission electron microscopy (TEM) revealed an anisotropic shape with straight edges, resembling a crystal habitus (Figure 2a,b).

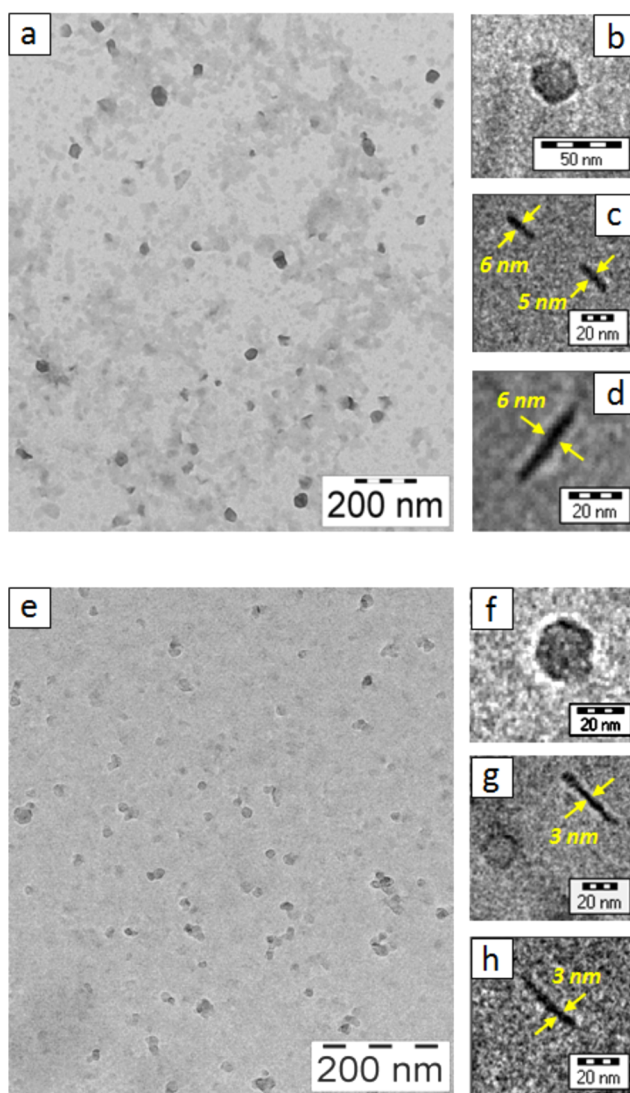


**Figure 1.** DLS trace of nanoparticles NP- $\text{C}_{45}$ . Number-weighted data shown.

Tilting of the sample in the electron microscope further confirmed this particle shape and points to a relatively small crystal thickness (cf., Figure S7 in the Supporting Information). The latter was corroborated by cryo-TEM (Figure 2c,d). In the shock-frozen dispersion the nanocrystals are randomly oriented. From particles oriented parallel to the electron beam the crystal thickness can be determined. A value of 5–6 nm was determined, which agrees well with the length of a stretched zigzag conformation  $\text{C}_{45}$  methylene segment ( $D$  in Scheme 1).

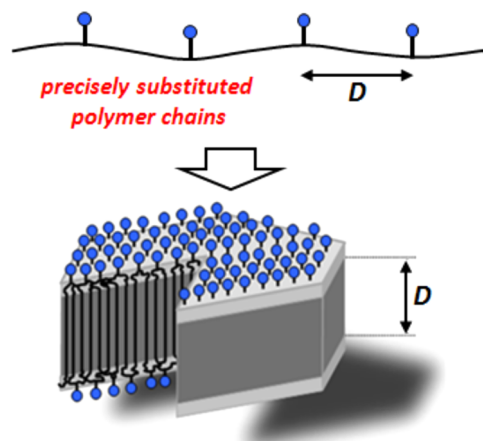
To further confirm this finding, nanoparticles (NP- $\text{C}_{21}$ ) of the aforementioned shorter spaced polyethylene with a carboxy group on every 21st carbon atom ( $\text{C}_{21}$ ) were prepared analogous to the procedure outlined for NP- $\text{C}_{45}$ , and characterized (cf. Supporting Information for details). Cryo-TEM reveals a crystal thickness of only about 3 nm (Figure 2e–h), as expected for a crystal with the structure outlined in Scheme 1 with a  $\text{C}_{21}$  spacing.<sup>26</sup>

In conclusion, polyethylenes with precisely placed carboxy substituents spaced by long methylene sequences form crystalline self-stabilized nanoparticles. The thickness of these nonaggregated nanoscale single crystals is determined directly by the molecular structure of the constituent polymer: it corresponds to the regular distance between neighboring carboxy groups on the polymer chain. The hydrophilic groups



**Figure 2.** TEM images of NP- $\text{C}_{45}$  (a, b), cryo-TEM images of single crystals parallel to the electron beam (c, d), cryo-TEM images of NP- $\text{C}_{21}$  (e, f), and single crystals parallel to the electron beam (g, h).

**Scheme 1. Schematic Representation of a Self-Stabilized Nanocrystal from Precisely, Long-Spaced Carboxy-Substituted Polymer Chains<sup>a</sup>**



<sup>a</sup>Note that typically a crystal is composed of roughly  $10^2$  polymer chains.

at the particle surface at the same time provide colloidal stability by interaction with the aqueous dispersion medium. Possibly, this interaction also further aids their exclusion from the crystal.

A control of the shape and structure of entirely organic nanoparticles in the size regime of only several tens of nanometers is difficult to date. The concept reported here advances this challenging but relevant issue. The self-stabilized crystals also appear attractive for the generation of nanostructured assemblies, serving either as building blocks or as nucleating agents.

## ■ EXPERIMENTAL SECTION

**Preparation of polymer nanocrystals:** A total of 3 mg of polymer C<sub>45</sub> or C<sub>21</sub>, respectively, was dissolved in 1 mL of hot THF and added to 3 mL of a 0.01 M aqueous CsOH solution via a Pasteur pipet under ultrasonication using a HD 3200 Sonoplus ultrasonotrode with a KE76 tip. The mixtures were ultrasonicated for 10 min, cooled to room temperature, and filtered through a syringe filter to afford clear, colorless dispersions. The dispersions were annealed for 5 h at 90 °C for NP-C<sub>45</sub> and 50 °C for NP-C<sub>21</sub>, respectively, and slowly cooled to room temperature over a period of 1 h. The dispersions were dialyzed against water for 30 min to remove excess CsOH and THF.

TEM analysis was performed on a Zeiss Libra 120 transmission electron microscope operated at 120 kV acceleration voltage. Specimens for the cryo-TEM investigations were prepared by dipping a small amount of the suspension on a holey carbon film. A meniscus, thin enough for use in TEM, forms over the holes and is rapidly frozen in liquid ethane to give a vitrified sample. The sample was cryo-transferred into the electron microscope and examined at a temperature around 90 K with minimum electron dose.

The different gray scales for different particles in the cryo-TEM images result from different viewing angles: For platelets oriented parallel to the electron beam, the length of the optical path through the particles is significantly longer than for a perpendicular arrangement. As the electron density of amorphous polyethylene is known to be virtually the same as for the vitrified, amorphous ice matrix<sup>13</sup> and hydrated carboxy groups also will have a similar electron density as the matrix, likely only the crystalline lamellae are visible in the TEM images.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Detailed synthetic procedures, characterization methods, and tilted TEM images of NP-C<sub>45</sub> (Figure S7). 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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- (25) Note that the shape will not be reflected significantly by the DLS method (single angle 173° backscattering). Diffusion coefficients of anisotropic particles with the aspect ratios found here (from TEM) do not differ much from spheres of equivalent volume, cf., Tanford, C. *The Physical Chemistry of Macromolecules*; Wiley: New York, 1961; p 327.
- (26) Note that, by comparison to crystals of linear polyethylene, for which the crystal thickness is determined not directly by the polymer microstructure but by the crystallization conditions (resulting in typical lamella thicknesses of 10–20 nm, cf., Strobl, G.-R. *Physics of polymers: concepts for understanding their structures and behavior*, 3rd ed.; Springer: Berlin, 2007; see also ref 13), the nanocrystals reported here are remarkably thin.