PRESS RELEASE

Ideal nanocrystal produced from bulk plastics

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Polyethylene is an inexpensive commodity plastic found in many household objects. Now, a consortium of researchers from Constance, Bayreuth, and Berlin has successfully used this plastic to synthesize the ideal polymer nanocrystal. The prerequisite was a new type of catalyst produced by Constance University researchers as well as a combination of unique analytic tools like those found at the Helmholtz Zentrum Berlin (HZB). The crystalline nanostructure, which gives the polymer its new properties, could prove of interest to production of new kinds of coatings. The scientists' findings are being published in the Journal of the American Chemical Society's current issue (DOI: 10.1021/ja4052334).

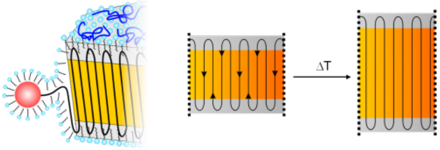

Fig. 1 Polymer chain incorporation during formation of ideal PE-nanocrystals by catalytic insertion polymerization with a water-soluble Ni(II) catalyst
Left: The polymer chain produced by the catalyst is laid down on the crystal in a defect-free manner.
Mechanism of thermal annealing in an ideal PE-nanocrystal: The amorphous layers covering both platelets act as the wheels of a pulley just changing the direction of the chains. A moderate raise of the temperature induces sufficient mobility that allows the chains to move within the crystal. Hence, the thickness L_c of the crystalline phase is increased while the thickness L_a of the amorphous layers remains constant.

Bringing materials with a disordered (amorphous) molecular structure into a crystalline form is a common endeavor pursued by chemists and material scientists alike. Often, it is only the crystalline structure which gives a material its desired properties. Therefore, basic science researchers have been interested in trying to identify physical principles that underlie the transition from a structure's amorphous to its crystalline phase. The most effective analytic tool that is needed for this is really a combination of various methods that are nowhere as concentrated as they are in Berlin. For the last three years, the HZB and Humboldt University Berlin have been running their Joint Lab for Structural Research. For Humboldt University, the lab was a key factor in their excellence initiative concept.

High polymer compounds like polyethylene, which exist as long molecular chains, are typically partly crystalline, meaning they consist of lamellar-like polyethylene crystals that are coated by a layer of amorphous polyethylene. These amorphous phases are characterized by a series of imperfections like knots. However, within an "ideal" nanocrystal, the amorphous regions act like deflection pulleys that change the direction of chains within the crystal by 180 degrees (see image).

Synthesis of such an ideal crystal has now been accomplished with the help of a new water-soluble catalyst, which allows for polymerization of ethylene in the aqueous phase. In the process, newly developing parts of the molecular chain are immediately incorporated into the growing crystal so that imperfections like entanglements are not allowed to form within the amorphous regions. The researchers gleaned these insights using X-ray diffraction methods and cryogenic transmission electron microscopy (TEM).

The nanocrystal suspension was produced by Prof. Stefan Mecking’s group at Constance University. For the cryo-TEM, HZB scientist Prof. Matthias Ballauff and his team produced a thin film of an aqueous polyethylene nanocrystal suspension and shock-froze it using cryogenically liquefied ethane. This resulted in formation of a glass-like solidified water modification, and the polyethylene nanocrystals enclosed within it can be analyzed using an electron microscope. The suspensions were also subjected to small-angle X-ray scattering (SAXS).

At a resolution of approximately one nanometer, the cryo TEM is the perfect tool for studying the tiniest structures within microemulsions and colloidal solutions. Along with X-ray diffraction experiments, this method has helped document the presence of perfect polymer nanocrystals. Says Matthias Ballauff: “This work shows that by combining microscopy and scattering, even complex systems can be analyzed with a degree of precision that is impossible using either method alone.”

The **Helmholtz-Zentrum Berlin für Materialien und Energie (HZB)** operates and develops large scale facilities for research with photons (synchrotron beams) and neutrons. The experimental facilities, some of which are unique, are used annually by more than 2,500 guest researchers from universities and other research organisations worldwide. Above all, HZB is known for the unique sample environments that can be created (high magnetic fields, low temperatures). HZB conducts materials research on themes that especially benefit from and are suited to large scale facilities. Research topics include magnetic materials and functional materials. In the research focus area of solar energy, the development of thin film solar cells is a priority, whilst chemical fuels from sunlight are also a vital research theme. HZB has approx.1,100 employees of whom some 800 work on the Lise-Meitner Campus in Wannsee and 300 on the Wilhelm-Conrad-Röntgen Campus in Adlershof.

HZB is a member of the Helmholtz Association of German Research Centres, the largest scientific organisation in Germany.