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Template Polymerization: Structure Control at the Nanometer Level

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Abstract. 'Template polymerization' allows to imprint the typical compartmentalized structure of self-organized systems on polymers. As a typical example, the formation of polymer hollow spheres in the interior of the lipid bilayer of vesicles is presented.

Wolfgang Meier was born in Biberach, Germany in 1964. He studied chemistry in Freiburg. In 1992 he received his Ph.D. at the University of Freiburg in the group of *H. Finkelmann*. From 1993 to 1996 he was a Postdoctoral co-worker in the group of *H.-F. Eicke* at the University of Basel. Since 1996, he has worked as a lecturer for physical chemistry and leader of an independent group at the Institute of Physical Chemistry. In 1998, he completed his habilitation.

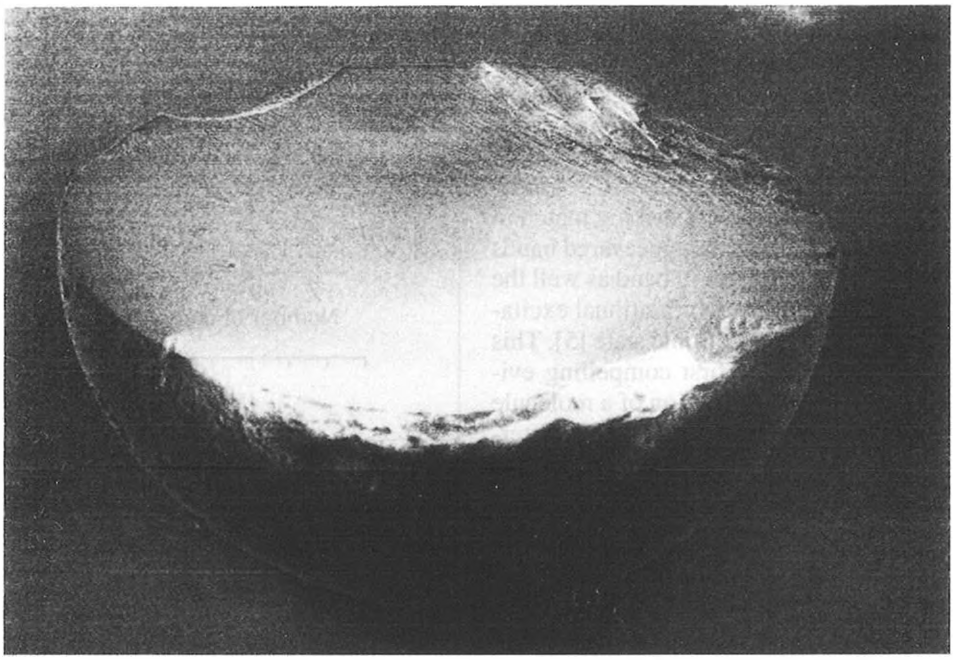

Figure. *Scanning electron micrograph of a hemispherical fragment of an isolated polymer hollow sphere* (obtained by shearing the polymer particles). The diameter of this fragment is about 250 µm, and shell thickness is about 300 nm.

Finding ways to control size and morphology at the nanometer level is an extremely active and prolific field in modern colloid chemistry. One main objective is to manipulate the properties of the resulting materials, enabling new material properties to be introduced into well-known compounds. This concept is largely inspired by biomineralization where mother nature demonstrates that, by using only a few simple inorganic minerals like $CaCO_3$, SiO_2, or hydroxyapatite moulded in an appropriate shape, an extremely large variety of different material properties (*e.g.*, mechanical properties) can be realized.

Following nature, self-organized systems are used in the laboratory as structure-guiding media. In this context, aggregates of surfactants and block copolymers have proven to be valuable tools: micelles, microemulsions, vesicles, lyotropic liquid-crystalline phases or mesostructures of block copolymers offer a huge variety of microphase textures which may be used as structural templates, the characteristic size and structure of which is to be captured in the newly formed material. These concepts are currently applied in polymer chemistry as well as in inorganic materials science.

The aim of our research is to use these concepts to control the structure of polymeric materials at the nanometer level. In the following, this will be exemplified by one of our recent projects in this area.

Liposomes or vesicles are spherically closed bilayer aggregates formed from phospholipids and surfactants which find interest in various applications in pharmaceutical and cosmetic formulations, or as simple models for biological cells or cell membranes.

In the context of template synthesis, the hydrophobic interior of the lipid membrane of the vesicles is of special interest. It is well-known that this lipid bilayer can be swollen to a certain degree with oil-soluble substances. Consequently, if hy-

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drophobic monomers are used, subsequent polymerization may lead to a polymer-network structure, the shape and dimensions of which are directly controlled by the templating vesicles. The resulting polymer hollow spheres may, for example, serve as a polymer scaffold leading to mechanical stabilization of the lipid bilayer without changing its other physical properties (*e.g.*, the permeability against low molecular substances). Another highly interesting aspect of these systems could be experimentally verified: the polymer scaffold enables self-repair of the membrane. Macroscopic defects in such bilayers, *e.g.*, induced by an electric field pulse, can reseal, and a tightly closed membrane is formed again. This is because the network chains of the polymer can store elastic energy to a considerable degree prior to rupture. Hence, the extension of the defect is slowed down, and once it has stopped the energetically unfavorable pore reseals due to the lateral mobility of the lipid molecules.

One essential feature of a templating process is, however, that the newly formed polymers are able to retain the characteristic structural features of their template even after their isolation from the lipid membrane. This could indeed be shown with crosslinked poly(alkylmethacrylate)s: electron microscopy and light-scattering experiments clearly prove the hollow sphere morphology of the pure polymer particles (*Fig.*).

Although this new technique of direct templating of vesicles has scarcely been used up to now, this method offers interesting new possibilities for the formation of defined nanostructured polymers. While the overall morphology of the resulting polymer particles is determined by the shape and size of the templating vesicles, the polymer framework can simply be modified by conventional chemical reactions. Such nanocapsules can serve, for example, as containers that are able to selectively enclose and release substances, which, for example, implies their suitability for applications in drug delivery.

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