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Asymmetric Materials

Polymeric Janus Particles

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Since de Gennes' Nobel lecture in 1991, in which he coined the term "Janus grains", research into asymmetric particles has boomed. Macroscopic, microscopic and nanoscopic particles have been prepared in which certain parts of their surface differ in chemical composition, polarity, color, or any other property. Spherical, cylindrical, disc-like, snowman-, hamburger-, and raspberry-like structures have been synthesized from organic or inorganic materials or even as hybrids of both. Synthetic strategies towards such particles vary greatly from simple polymer mixtures to the bulk self-assembly of sophisticated terpolymers to immobilization methods of symmetric particles. Polymeric Janus particles are particularly promising, as they can often be prepared cheaply and sometimes even on larger scales.

1. Introduction

Janus particles have received considerable attention over the last decade. They are named after the two-faced Roman god Janus, the god of the doors. Even in modern culture, the month of January, the first month of the New Year, and the janitor, who is a caretaker of doors and halls, remind us of this ancient Roman god. Janus is depicted as a double-headed god who represents dichotomy. Thus, in nature[1] and materials science, asymmetric particles with two incompatible sides are called Janus particles. The most common type of Janus particle is a nanosized sphere with hemispherical amphiphilicity, that is, one half of the sphere is polar, and the other nonpolar. Several review articles have already been written on the subject, with particular focus on the synthesis[2] and supramolecular organization[3] of Janus particles. The self-assembly of amphiphilic terpolymers into micellar structures, an important feature for many synthetic strategies to prepare Janus particles, has also recently been reviewed.[3,4] The question arises, however, as to whether polymer-based systems are merely an academic curiosity or whether potential applications exist. In this Minireview, we will focus exclusively on Janus particles that are based on polymers or in which at least one constituent of the Janus particle is made from a polymeric material.

The first report of Janus particles was in 1985. Lee and co-workers presented asymmetric poly(styrene)/poly(methyl methacrylate) (PMMA) lattices from seeded emulsion polymerization.[5] One year later, physicochemical investigations on glass spheres by Casagrande and Veyssié described the preparation of Janus beads. These beads were formed from commercial glass beads, 50–90 μm in diameter, that were made hydrophobic on only one hemisphere using octadecyl trichlorosilane, whilst the other hemisphere was protected with a cellulose varnish (see Section 4).[6,7] They were examined with regard to their orientation at water/oil interfaces and their potential to stabilize emulsification processes was recognized from the start (see Section 3.2 for more recent examples). The authors found a completely different behavior compared to homogeneous beads in emulsifying processes. Several years later, Binks and Flechter investigated the wettability of Janus beads at the oil/water interface.[8] It was found that homogeneous particles are strongly surface active but not amphiphilic, whereas Janus particles are both surface active and amphiphilic.

In his 1991 Nobel lecture, de Gennes significantly advanced the popularity of Janus particles, pointing out that these "Janus grains" have the unique advantage of densely self-assembling at liquid–liquid interfaces whilst allowing material transport to occur through the gaps between the solid amphiphilic particles.[9,10] Since then, a plethora of Janus particles of different sizes and shapes has been reported. Inorganic materials,[11–14] discrete organic molecules, such as dendrimers,[15–21] cyclodextrins,[22] liquid-crystalline compounds,[23,24] and polymers, have been used to synthesize Janus-like asymmetric architectures. Molecular self-assembly has typically been exploited to generate Janus structures on the nanometer scale, and access to micrometer-sized particles

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is often achieved using engineering approaches, such as microfluidic devices[25,26] or engineered surface templates.[27,28] Simulations of Janus particles have also been carried out; their aggregation has been studied by means of Monte Carlo computer simulations.[29]

This Minireview is divided into three sections, each describing different mechanisms of Janus particle formation. Section 2 describes how homopolymers can be employed to form amphiphilic Janus particles by different approaches (confinement, electrospinning, and microfluidics). Section 3 deals with block copolymers that self-assemble into non-centrosymmetric micelles in solution or in the bulk to form Janus particles of various shapes. Section 4 describes how symmetric particles can be turned into asymmetric Janus particles using various particle immobilization techniques.

2. From Homopolymers to Janus Particles

The most feasible pathway to polymeric Janus particles would be the application of (commercially available) common homopolymers in blends. The self-organization of block copolymers is discussed in Section 3 and involves covalent linkage of two different or incompatible parts A and B. This process is limited only by the synthetic challenges involved in the preparation of such macromolecular architectures. Well-defined block copolymers from chain-growth and step-growth polymers are thus more difficult to prepare than those synthesized by blockwise (sequential) living polymerization. In such cases, homopolymer blends could be the method of choice for Janus particle synthesis.

An interesting approach for composite particles was recently published by Okubo et al. using poly(methyl methacrylate) and poly(styrene) solutions in toluene containing a nonionic surfactant.[30] As the solvent evaporates, spherical droplets phase separate, and Janus particles were obtained that could be visualized by scanning electron microscopy (SEM; Figure 1). Interestingly, the morphology varies in a characteristic manner with the molecular weights of the polymers. The interfacial tension between the polymers increases with increasing molecular weight, whereas their surface tension to the surfactant remains almost constant; therefore, the morphology of the particles is thermodynamically controlled. Potential disadvantages of this approach are the broad size distribution of the particles and adsorption of the emulsifier on the particles, which must then be removed.

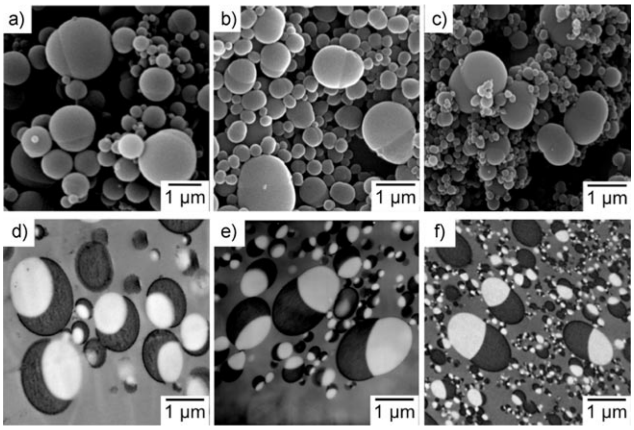

Figure 1. Janus particles prepared using homopolymer blends by the technique described by Okubo et al. a–c) SEM images of PS-PMMA composite particles with different molecular weights (2.1×10^4–1.0×10^6 g mol^{-1}) and d–f) TEM images of thin cross-sections in which the PS phase was selectively stained with RuO_4. (From Ref. [30]).

Emulsion polymerization was a key step for the investigation of Janus particles; several authors have studied their formation under growth-seeded conditions in the presence of a prefabricated polymer.[1,31] The complex formation process of such heterogeneous particles has been explained theoretically using both geometric and thermodynamic reasoning.[32] As an example, Janus particles with a diameter of approximately 130 nm consisting of poly(*n*-butyl acrylate) (PnBA) with PMMA were prepared by successive MMA emulsion polymerization in the presence of the other polymer.[31]

In 2003, Landfester et al. presented an elegant approach towards two-component particles by using a miniemulsion.[33] Miniemulsions resulting from a fluorescent homopolymer blend of poly(9,9-bis(2-ethylhexyl)fluorene-2,7-diyl) (PF2/6) and a poly(*para*-phenylene) ladder polymer (m-LPPP) yielded spherical particles. Photoluminenscence spectra clearly indicated that each particle contained a blend of both polymers. The relative peak ratio of the m-LPPP emission

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at 463 nm compared to the PF2/6 emission at 422 nm is 1.1:1 for particles with 149 nm diameter, but 4.4:1 for particles with 64 nm diameter. This larger emission lead the authors to conclude that the two polymers are not homogeneously mixed within the particle, but rather form distinct phases. The segregation process was not investigated in detail, but the authors state that this may be ascribed to processes during solvent evaporation. This approach could be of great interest if the same behavior was detected for other polymers. However, the analysis for nonfluorescent materials could be a problem. Based on a new scattering factor for Janus particles, the use of small-angle neutron scattering has been reported for the positive identification of Janus particles, which could be helpful in such cases.[34]

Another strategy for synthesizing inhomogeneous particles based on homopolymers involves electrospinning two polymer solutions. Lahann et al. presented the synthesis of biphasic particles from an aqueous solution of poly(ethylene oxide) (PEO) and sodium polystyrene sulphonate (PSSNa) using electrohydrodynamic jetting of parallel polymer solutions under the influence of an electric field.[35] The individual phases were loaded independently with biomolecules or chromophores and analyzed by TEM and confocal microscopy, which revealed an anisotropic distribution of the guest molecules.

Two-color spheres for electronic paper[36] are produced commercially by the breakup of two-layered wax jets generated from a spinning disk edge;[37] however, accurate size control is difficult, and the resulting products tend to be polydisperse.

The synthesis of Janus beads on a larger scale was investigated by several groups using a microfluidic approach. In most cases, the basic principle relies on a Y-shaped channel to form a two-phase monomer stream with a planar sheath-flow geometry. The monomer stream is either cross-linked by masked flashlight[38] or combined with an aqueous stream to produce biphasic droplets that are subsequently cured (Figure 2).[25,39–41] The geometry of the microfluidic devices was varied in different publications, from a single flow tube to up to 128 flow tubes. Furthermore, Janus particles of different shapes and composition that have different colors or chemical properties on opposite sides could be synthesized.

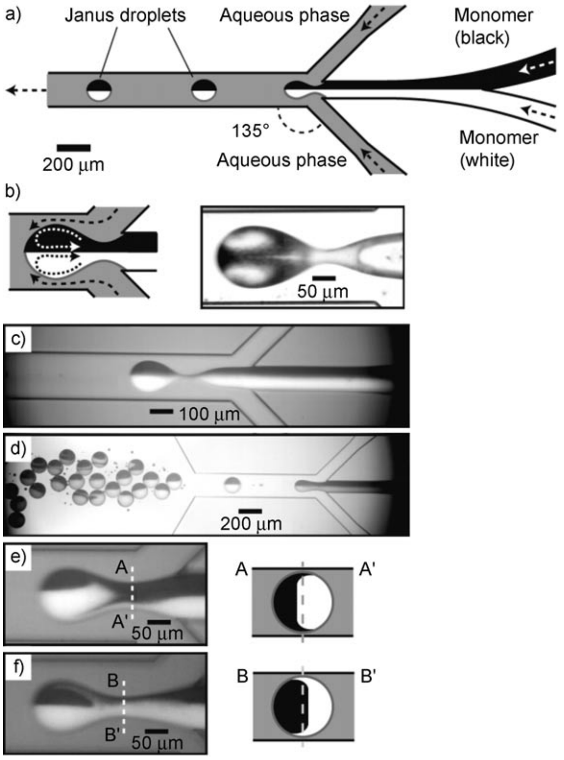

Figure 2. Formation of two-color Janus droplets in a microfluid device. a) The synthetic setup, b) convection in the head of the organic fluid cylinder, c) detachment of a two-phase droplet upon contact with the aqueous stream, d) collection of the Janus droplets, and e,f) formation of Janus particles at different relative velocities of the black and the white monomers. (From Ref. [25]).

3. From Block Copolymers to Janus Particles

A well-known property of block copolymers is that they phase-segregate into distinct domains in selective solvents or in the bulk.[42] Additionally, phase separation of polymer alloys, blends, and composites has been used to control the inner structures of polymeric materials.[43,44] Most morphologies of diblock copolymers that have been investigated are centrosymmetric; less-symmetric rod-like aggregates can however be formed by special copolymer architectures, such as polymers containing dendritic segments[45] or rod-coil polymers.[46,47] The formation of various kinds of microphase-separated structures, such as spheres, cylinders, lamellae, or gyroids, can be controlled by the block ratios and by adjusting the miscibility of the respective segments of the block copolymers.[48] For ABC-terblock copolymers, a great variety of morphologies can be found by variation of the block ratios. Seminal studies on ABC-type block copolymers were conducted by Stadler and co-workers in the 1990s.[49]

The key feature for the design of Janus particles consisting of block copolymers or polymer mixtures is to gain control over self-assembly in solution, the bulk, or on surfaces, and to “freeze-in” one part of the micelle to obtain an asymmetric nanoobject. An additional pathway to various novel morphologies can be obtained by spatially confining of block copolymers or blends of different polymers, and was described both theoretically and experimentally.[50]

Two recent examples from Shimomura et al. show a great variety of different aggregates in poly(styrene)-*b*-poly(isoprene) diblock copolymers with frustrated three dimensional phases.[51] Symmetric block copolymers, which form lamellar structures in a film, formed Janus-type, tennis-ball-, mushroom-, wheel-, and screw-like structures, depending on the diameter of the nanoparticle (Figure 3). The nanoparticles act as a three-dimensional confinement, allowing the formation of various kinds of unique phase-separated structures, such as helices. Nanoparticles are formed from the polymer in a controlled precipitation process with solvent evaporation.

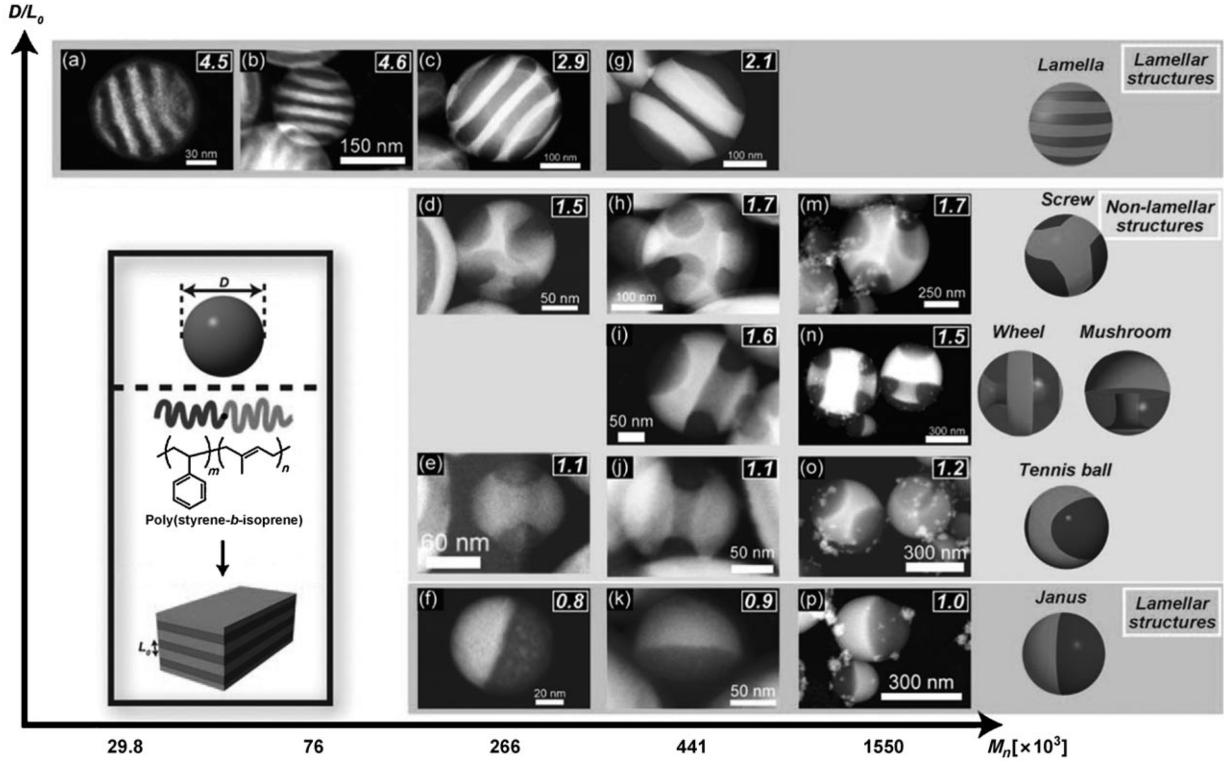

Figure 3. Structures obtained by microphase separation in nanoparticles as a function of molecular weight and the D/L_0 ratio, where D is the particle diameter and L_0 is the period of lamellar structure in the films. STEM images of a) PS-PI-30, b) PS-PI-76, c–f) PS-PI-266, g–k) PS-PI-412, and m–p) PS-PI-1550 nanoparticles. The D/L_0 ratios are shown in the upper-right corner of each STEM image. (From Ref. [51]).

3.1. Self-Assembly in Solution

ABC-terblock copolymers are the most prevalent polymers for the synthesis of polymeric Janus particles. The general approach can be summarized as a “freezing-in” of the middle block B by covalent or non-covalent cross-linking, whilst the mutually incompatible blocks A and C point in different directions in the formed particle. In the following, we will discuss the solution self-assembly as a kinetically controlled process; the thermodynamically controlled bulk self-assembly strategies will be the subject of Section 3.2.

Recently, Zhu et al. described the synthesis of unimolecular Janus micelles by cross-linking the central block of poly(styrene)-*b*-poly(2-vinylpyridine)-*b*-poly(ethylene oxide) (PS-*b*-P2VP-*b*-PEO) using 1,4-dibromobutane. However, the mass increase after cross-linking the micelles in solution was very low. Such a mass increase, which is an essential feature of Janus particle formation, was only observed when the concentration was increased from 0.01 $\mathrm{g\,L^{-1}}$ (isolated micelles only) to 0.25 $\mathrm{g\,L^{-1}}$ (supermicelles predominate).[52] The same group investigated the formation of Janus micelles by mixing two diblock copolymers, poly(ethylene oxide)-*b*-poly(acrylic acid) (PEO-*b*-PAA) and poly(2-vinylnaphthalene)-*b*-poly(acrylic acid) (P2VN-*b*-PAA). An ABC structure was formed in-situ by non-covalent cross-linking of the PAA blocks with 1,2-propanediamine, thereby forming the micellar core. Lowering the pH of the aqueous solution to 3.1 led to intramolecular complexation of the PAA core with the PEO shell; that is, intramolecular phase segregation and formation of a Janus particle with hydrophobic P2VP on one side and a hydrophilic PAA/PEO complex on the other side. These amphiphilic unimolecular micelles further aggregate into tubular superstructures; these supermicelles were then downsized to trapezoidal or semicircular nanosheets using ultrasound.[53] The Janus particles that were thus obtained resemble a multi-arm star polymer with a cross-linked core; a Monte Carlo simulation of intramolecular Janus segregation of such heteroarm star polymers has been carried out by Tsao et al.[54]

An elegant non-covalent co-assembly of two diblock copolymers was presented by Voets and co-workers.[55] Upon mixing two aqueous solutions of the diblock copolymers poly(acrylic acid)-*block*-poly(acrylamide) ($\mathrm{PAA_{42}}$-*b*-$\mathrm{PAAm_{417}}$) and poly(2-methylvinylpyridinium iodide)-*block*-poly(ethylene oxide) ($\mathrm{P2MVP_{42}}$-*b*-$\mathrm{PEO_{446}}$), spontaneous formation of Janus particles by non-covalent interactions of the poly(acrylic acid) block with the poly(methylvinylpyridinium) block was observed. The aggregates were investigated by TEM and scattering techniques, revealing an unexpected disc-like shape (ca. (20 ± 2) nm diameter and (7 ± 2) nm thickness) of the aggregates with a narrow size distribution. Recently our group reported the formation of Janus micelles after an olefin metathesis reaction of vinylether-initiated PEO-*b*-PPO diblock copolymers (PPO = poly(propylene oxide)) with Grubbs first-generation catalyst. This olefin metathesis reaction modifies the chain end of the block copolymer with an organometallic moiety, forming a stable Fischer carbene that cannot undergo further metathesis.[56] In water, these modified polyethers form Janus structures, which could be visualized by TEM; as is typical for Janus particles, unimolecular micelles and ill-defined superstructures form. After longer equilibration times, the latter structures transform into well-defined supermicelles. Slower phase separation processes probably result in the ruthenium complex being kinetically trapped in the micellar PPO core, thus leading to Janus segregation and subsequent super-aggregation (Figure 4).

Lodge and Hillmyer studied the formation of multicompartment micelles by blending two micelle solutions of a star terpolymer having different arms with an AB diblock copolymer. The star terpolymer, consisting of μ-poly(ethylethylene)-poly(ethylene oxide)-poly(perfluoropropylene oxide) (μ-EOF), has a PEO block of various sizes; poly(ethylethylene) was synthesized by hydrogenation of 1,2-poly(butadiene) (PB).[57,58] Aqueous solutions of the μ-EOF star polymers form long cylindrical micelles with a broad size distribution and shape that depends on the length of the PEO block. In contrast to the individual solutions, narrowly distributed aggregates can be obtained upon mixing the μ-EOF star polymer micelles with a diblock copolymer based on PEO and poly(ethylethylene). A very slow annealing process yields the formation of “hamburger” micelles, which consist of a fluorocarbon disc surrounded by hydrocarbon “buns”. The authors explain this behavior by fragmentation of the long, cylindrical micelles after addition of the diblock copolymer solution, followed by a breaking-up into shorter cylinders. This process leads to narrowly distributed hamburger micelles. As a consequence of multiple collisions and fusions of spherical AB diblock micelles on one side of the hamburger micelle, asymmetric multicompartment micelles were also observed (Figure 5).[59]

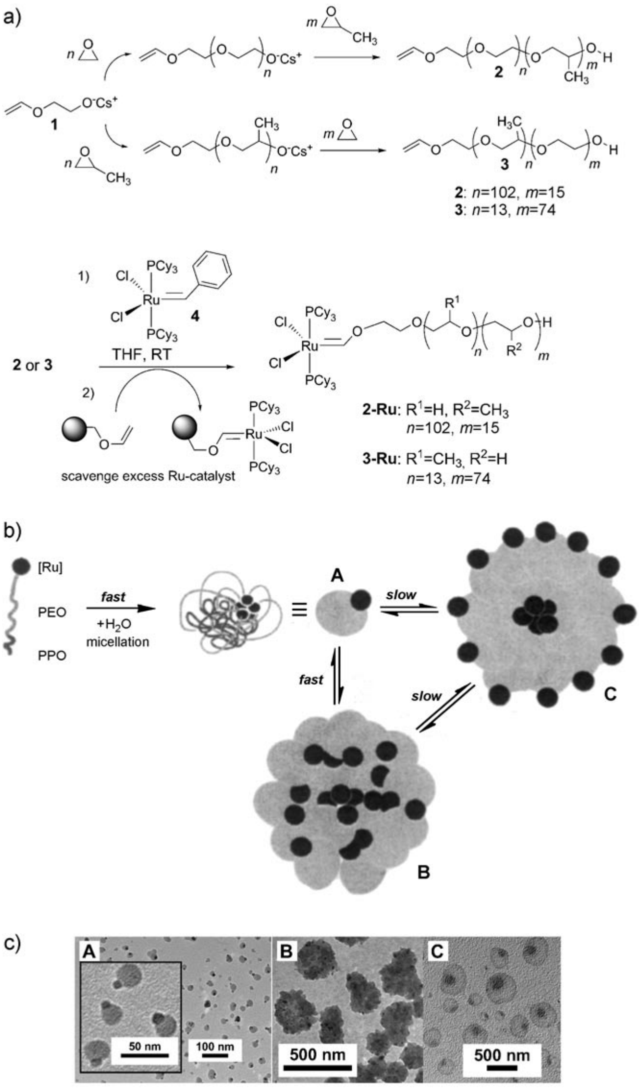

Figure 4. a) Synthesis of poly(ether) block copolymers and subsequent modification with Grubbs catalyst. b) Model for the aggregation of modified diblock copolymers into Janus micelles and superstructures. c) TEM images of modified block copolymers drop-cast from a THF/water solution ($c=1\ \mathrm{mg\,mL^{-1}}$). A) Janus micelles observed after 0.5 h of equilibration time; B) ill-defined aggregates of Janus micelles observed after 30 min. of equilibration time; and C) large well-defined assemblies (supermicelles) of Janus micelles observed after 3 h of equilibration time. (From Ref. [56]).

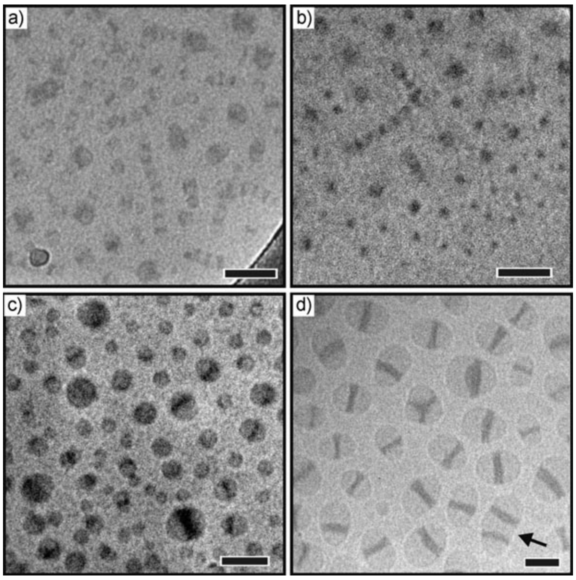

Figure 5. CryoTEM images obtained from a 1 wt% aqueous solution of a) μ-EF (2-9-2) terpolymer and postmixture of μ-EOF(2-9-2)/EO(2-9) at b) week 1 and c,d) week 15. Scale bar: 50 nm. (From Ref. [59]).

Similar structures were observed by Fang et al. for a poly(*tert*-butoxystyrene)-*block*-PB-*block*-poly(*tert*-butyl methacrylate) terpolymer in which the PB block was modified by fluoroalkyl groups in a post polymerization process.[60]

An altogether different strategy to create Janus particles uses amphiphilic block copolymer brushes.[16,61–63] Such macromolecular architectures self-assemble in block-selective solvents and typically form unimolecular rodlike nanoobjects in which the individual polymer grafts form separated domains.

3.2. Bulk Self-Assembly

Morphological studies on phase separation in ABC terpolymers consisting of three chemically different blocks have been conducted both theoretically[64] and experimentally.[65] The tremendous variety of highly ordered structures that are accessible by self-assembly renders them ideal candidates for the synthesis of Janus particles or even more complex structures that rely only on phase segregation.

The diversity of non-centrosymmetric materials that can be obtained with ABC terblock copolymers or even blended with diblock copolymers was first described in 1999.[49] Only two years later, the first approaches for the preparation of Janus micelles utilizing bulk self-assembly of ABC terblock copolymers was presented. Two strategies were used: 1) Ishizu and co-workers cross-linked the hexagonal bulk structure of poly(styrene)-*block*-poly(vinylpyridine)-*block*-poly(*tert*-butyl acrylate) by 1,4-diiodobutane gas; this synthesis can be compared to the solution-phase synthesis presented by Zhu et al. (Section 3.1); 2) a concurrent elegant work by Müller and co-workers resulted in Janus particles formed by cross-linking the middle block in PS-*b*-PB-*b*-PMMA; they have also extended this synthetic approach for the synthesis of multicompartment micelles. They were able to vary the morphology of the Janus objects, ranging from spheres to cylinders to discs, by varying the block lengths of ABC terpolymers with a central PB block. An ABC PS-*b*-PB-*b*-PMMA terpolymer was synthesized by classical anionic polymerization, with a block ratio of 51:6:43,[66] to obtain a morphology that allows cross-linking of the central PB block; after subsequent dissolution, frozen spherical Janus objects are obtained. The formation of superstructures that are in equilibrium with the Janus particles was also observed. These particles can be further modified by saponification of the PMMA block to pH-sensitive and water-soluble PAA.[67] The Janus particles form considerably larger and more uniform aggregates than the precursor terpolymers, which is in clear contrast to the Janus particles described by Zhu et al. obtained by self-assembly in solution.

The behavior of Janus particles at the air/water interface has been studied in detail (Figure 6).[68] It was found that the Janus particles form a lateral structure on the interface with nanometer-sized domains separated by flat regions. The size of the objects formed from the nanoparticles (having a height of 16–18 nm and a diameter of 70–80 nm) are much larger than the monolayers of the precursor terblock copolymer, which are circa 3 nm in height and 40 nm in diameter. The pressure/area isotherms support the assumption that the hydrophobic PB and PS domains collapse (de-wet from the surface), whereas the PMMA chains spread out on water.

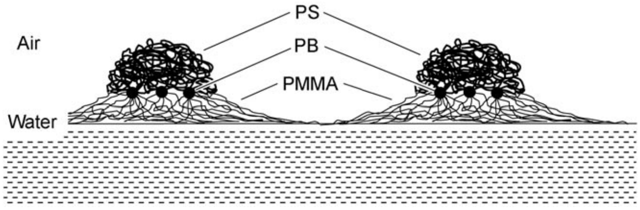

Figure 6. Self-assembly of cross-linked ABC terpolymers (Janus particles) on the air–water interface. (From Ref. [68]).

In this context, a recent publication describes the application of Janus micelles as stabilizers in an emulsion polymerization.[69] The surface area stabilized by one Janus particle exceeds its cross-section several times, indicating a superior performance of Janus particles in emulsion polymerizations compared to common stabilizers. Similarly, Janus particles can be used to stabilize polymer blends.[70,71] An study concerning Janus particles for the creation of controllable pores in membranes was recently published by Balazs and co-workers that uses computational modeling to show that Janus particles in solution will localize to the edges of a pore in a lipid bilayer membrane and stabilize it. The amphiphilic nature of Janus particles is crucial for this behavior, as they have to interact both with the hydrophobic membrane and with the aqueous solution in the pore. The authors concluded from simulations that Janus particles introduce a re-sealable pore in the membrane.[72]

More recently, Müller et al. reported the synthesis of Janus cylinders[73,74] and Janus discs.[75] The adsorption energy of surface-active disk-shaped Janus beads had been previously calculated by Nonomura and co-workers.[76] For synthesis of the cylindrical Janus particles, block copolymers consisting of PS-*b*-PB-*b*-PMMA with block ratios of 44:20:36 and 41:14:45 were cross-linked in bulk using disulfur dichloride. Dissolution after cross-linking of the PB-block led to cylindrical aggregates, which did not form supermicelles (Figure 7).

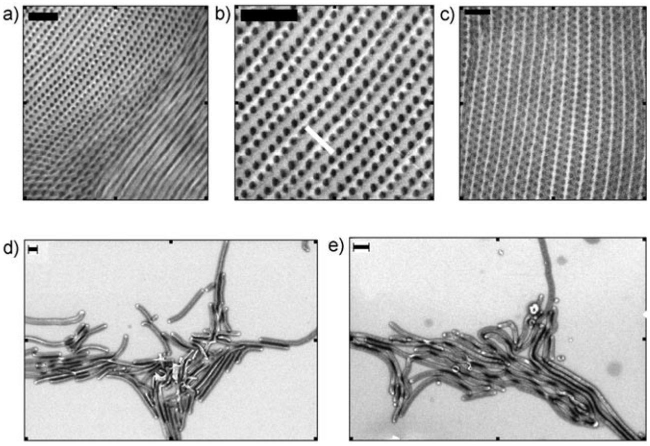

Figure 7. a–c) TEM micrographs of the bulk phase of SBM-1 before (a,b) and after cross-linking (c). d,e) SEM images of Janus cylinders with differing block ratios and dip-coated from THF on a silicon wafer: d) SBM-1, 44:20:36, and e) SBM-2, 41;14:45. (From Ref. [73]).

Janus discs have been synthesized from ABC terpolymers based on PS-*b*-PB-*b*-PtBA block copolymers with block ratios of 42:10:48 or 45:5:50. After cross-linking the lamellar bulk structure, sonification, and dissolution, disc-like Janus particles were obtained (Figure 8). Supermicelles formed, and the interfacial tension of the oil/water interface was significantly lowered compared to the linear precursor terpolymers, this interfacial tension is dependent on the diameter of the discs.

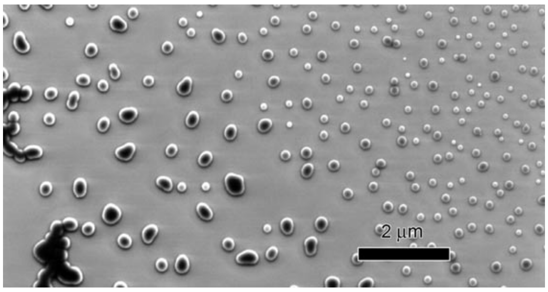

Figure 8. SEM images obtained from a dip-coated sample of Janus discs ($c=0.1\ \mathrm{mg\,L^{-1}}$ in chloroform) on silicon after ultrasonic treatment. (From Ref. [75]).

In summary, the bulk self-assembly process of ABC terpolymers has produced a great variety of Janus particles, and an upscaling of the procedure appears to be feasible. Cross-linking of PB and PVP has been achieved, and the shape of the Janus particles could be varied by changing the block lengths. In future experiments, the chemical nature of the terpolymers or the mechanism of cross-linking will no doubt be altered; this work may include other controlled polymerization techniques, such as ring-opening or controlled radical polymerizations and fast, high-yield reactions for cross-linking, such as click chemistry or hydrosilylations.

4. Desymmetrization of Particles by Immobilization

The production of asymmetric particles can also be achieved by immobilization. Solid surfaces and liquid/liquid and liquid/gas interfaces have all been employed to selectively protect part of an isotropic particle whilst the exposed surface area of the particle is chemically modified.[77] The most feasible way to break the symmetry of spherical particles is to immobilize them on solid surfaces. Flat macroscopic surfaces are easily covered with monolayers of spherical particles. However, the surfaces of dispersed solid particles have the advantage of greatly enhancing the yield of immobilized particles.

Gangwal et al. prepared Janus particles with a metallic and a dielectric side. A monolayer of PS particles was formed on a glass microscope slide; gold was then evaporated onto the particle assembly. The Janus particle monolayers were then investigated at different electrical fields and frequencies.[78] Immobilized monolayers of similar gold-capped PS particles were surface-functionalized with biotin and then exposed to avidin solutions; the presence of avidin could thus be detected by the shift of the extinction peak wavelength.[79] Paunov et al. reported the preparation of a monolayer of surface-functionalized PS particles on a glass slide. The authors used microcontact printing with PDMS stamps, which thus allowed the transfer of an electrostatically complementary monolayer of smaller PS–latex particles onto the first monolayer of larger latex particles. Particle doublets or "raspberry-like" aggregates could be prepared in this manner.[80] Hatton and co-workers used 5 nm magnetite nanoparticles that were surface-functionalized with ATRP initiators for the polymerization of PAA. These homogeneously coated negatively charged particles were then adsorbed onto positively charged silica beads with a diameter of 600 nm. The carboxylic acid groups on the exposed particle surface were subsequently reacted with amine-terminated polymers (poly(styrene sulfonate) (PSSNa) or poly(*N*-isopropyl acrylamide) (PNIPAM)) to create the Janus particle.[81] Temperature-dependent (PNIPAM) or pH-dependent (PSSNa) aggregation of the Janus particles was observed.

A very elegant way of preparing gram-scale quantities of Janus particles is the so-called Pickering emulsion.[82] These particle-stabilized emulsions combine cheap and easy access to partially exposed particles with a very high surface area of the dispersed phase. Although not focusing on polymeric particles as such, the Granick group has perfected the Pickering emulsion approach to Janus particles.[83] In their case, silica nanoparticles are dispersed in a melted wax, which is then mixed with water. The silica particles stabilize the emulsion covering the surface of the wax droplet. Upon lowering the temperature, the wax solidifies, thereby immobilizing the silica nanoparticles, which can then be chemically modified on their exposed hemisphere (Figure 9). Additional surfactants that adsorb onto the nanoparticle surface allow the "Janus balance" to be controlled, that is, the relative ratio of exposed and covered surface area of the nanoparticles.[84,85] A solvent-free synthesis of these Janus particles has also been described by the same group.[86] Ho et al. also reported a method of controlling the Janus balance by using electrospun fibers composed of PMMA and P4VP as the immobilizing matrix and the temperature to control particle immersion into the matrix.[87] This general approach for shielding one side of nano- or micrometer-sized particles has been of interest recently, and will no doubt be used to form Janus particles in the near future.

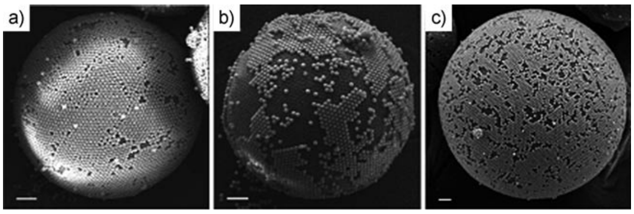

Figure 9. Examples of Pickering emulsions. SEM images of colloidosomes as described by Granick and co-workers. a) Colloidosome before chemical modification; b) modified using solvent-based methods,[85] and c) modified using vapor-phase deposition.[86] Scale bar: 10 µm. (From Ref. [83]).

Stamm and co-workers of used the Granick approach to synthesize polymer-coated stimuli-responsive Janus particles.[88] The partial wax coverage of amine-functionalized silica particles was exploited to selectively introduce ATRP initiators to one hemisphere only: 20–25% of the amino-functionalized particles are immersed in wax, which is a significant improvement compared to non-functionalized particles, which are immersed by only 10%. The desymmetrized nanoparticles were then coated with polymer in a sequential grafting-from–grafting-to approach. Stimulus-sensitive particles could thus be synthesized that formed hierarchically structured aggregates depending on the pH of the surrounding solution.

In an approach that is similar to the Granick method, Paunov et al. spread PS latex particles at a water/oil interface. The water contained gellan, which caused the aqueous layer to solidify upon cooling. The organic layer was replaced with a PDMS layer in which the PS particles were immobilized after curing. Evaporation of gold onto the half-exposed PS latex particles allowed the preparation of gold-capped PS Janus particles.[89,90]

Yang and co-workers chose a different approach to avoid using a frozen Pickering emulsion. Instead, silica nanoparticles functionalized with benzylic chloride were used to stabilize a water–toluene emulsion. Acrylamide was dissolved in the dispersed aqueous phase and styrene in the toluene phase. Simultaneous ATRP on both hemispheres of the silica nanoparticles at the water–toluene interface allowed the formation of Janus particles in one step.[91] No further stabilization of the particles was necessary, as they are amphiphilic and were therefore locked into a thermodynamically stable orientation upon polymerization.

Using a thiol-terminated PEO, Wang et al. could grow lamellar PEO single crystals that were surface-functionalized with thiol groups.[92] On this surface, gold nanoparticles were subsequently immobilized. The exposed gold surface was then functionalized with an ATRP initiator, and PMMA was grafted from the nanoparticles. Upon dissolution of the solid PEO template, Janus gold nanoparticles were obtained with PMMA chains on one hemisphere and PEO chains on the other. The group of Cheng used yet another solid surface-immobilization technique. Yttrium hydroxide nanotubes were coated with a PEO-b-P4VP block copolymer. The P4VP block selectively binds to the nanotube by hydrogen bonds, thereby coating it with a P4VP hydrophobic layer that is stabilized by the PEO grafts. Addition of a radical initiator (AIBN) and divinylbenzene resulted in poly(divinylbenzene) (PDVB) spheres immobilized within the P4VP layer. Subsequent grafting of *N*-isopropylacrylamide onto the exposed surface of the PDVB sphere gave a polymeric Janus particle. Aggregation of the Janus particles into flower-like structures was also observed (Figure 10).[93]

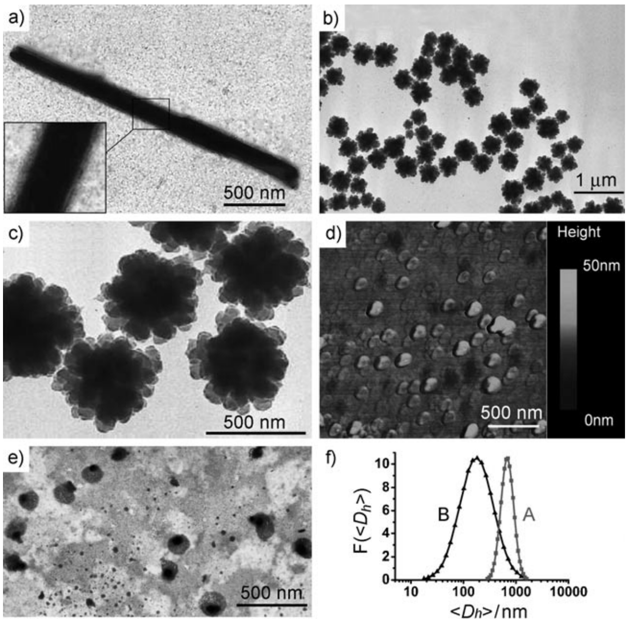

Figure 10. a) TEM image of a hybrid nanotube, and the same tube at larger magnification, showing the polymer layer surrounding the yttrium nanotube; b) TEM image of supermicelles; c) TEM image of supermicelles at a higher magnification; d) AFM image of Janus particles resulting from dissociation of the supermicelles on mica; e) TEM image of the Janus particles stained with RuO_4; and f) distribution of the hydrodynamic diameter of the supermicelles (A) and the Janus particles (B). (From Ref. [93]).

Microspheres based on cross-linked PS were prepared by emulsion polymerization and a densely packed monolayer obtained by compression of a Langmuir layer. This layer was transferred onto a solid substrate using the Langmuir–Blodgett technique. A monolayer of fluorine-containing polyacrylate was then transferred onto hemispheres of the particles that face towards the solution by the same technique. X-ray photoelectron spectroscopy (XPS) on the top and the bottom side of the microsphere monolayer clearly showed the presence of Janus particles.[94]

Ravaine and co-workers described an emulsion polymerization of styrene in the presence of silica particles with a diameter of 50–150 nm). The silica particles used were surface-modified with polymerizable acrylate groups. Under these conditions, the formation of "snowman"-like PS–silica (1:1) particles is highly favored (85 % yield); lone silica particles or hybrid particles made of two PS spheres and one silica particle were rarely observed.[95] These materials were prepared on the gram scale. A similar approach was presented very recently by Zhao et al., who conducted simultaneously free-radical polymerization of styrene and sodium methacrylate in water/styrene emulsions in the presence of modified silica beads. The resulting particles were analyzed by TEM, which revealed that asymmetric surface modification and aggregation had occurred.[96]

The immobilization strategies presented herein rely on the same principle, that is, shielding of one side or part of a (nano)particle with a matrix, such as wax in the Granick approach. Unfortunately, most sources do not give yields for the coupling or polymerization steps, but in general, this approach can be up-scaled, possibly to multi-gram amounts. However, compared to the self-assembly strategies in Section 3.2 the approach may be limited for industrial applications, as more reaction steps are required.

5. Conclusions and Outlook

As this Minireview clearly demonstrates, there are many synthetic routes available today for the preparation of asymmetric polymeric particles. The synthesis of Janus particles and the study of their self-assembly in solution, at surfaces, or in fields is certainly worthwhile from an academic point of view. As de Gennes pointed out very early, such particles could be used to stabilize emulsions. Müller and coworkers have shown that Janus particles can be employed as very efficient stabilizers in emulsion polymerizations or polymer blends (Pickering effect); other applications include their use as nanoprobes or as sensors, and two-color Janus particles have been used for electronic paper or in display applications.

For Janus particles to succeed in commercially driven applications, facile synthetic routes and scale-up procedures need to be in place. The use of microfluidic devices can be readily scaled-up to produce larger amounts of particles in a continuous fashion. Approaches that rely on solution aggregation of block copolymers into Janus-type micelles are often too dilute to produce larger amounts of particles. The bulk self-assembly of ABC terpolymers could be an effective way to access (multi)gram amounts of material without the need of large amounts of solvent involved in solution cross-linking. This procedure could in principle be scaled-up to yield even larger amounts of particles, for example by the use of an extruder with a subsequent equilibration and cross-linking zone. Janus particles also could be of interest in medical applications such as drug delivery/controlled release or targeting in one particle; for these purposes merely biocompatible compartments need to be selected, such as PEO or PDMS segments. Another interesting approach would be orthogonal modifications of a soluble linear ABC terpolymer precursor in the A and C blocks, with subsequent cross-linking of the B block.

From an industrial point of view, the approach of blending common homopolymers to form Janus particles may however be a superior method for up-scaling. The particles can be stabilized by the addition of cross-linking agents after the formation of the asymmetric particles.

These methods are just a few approaches, which are presented as examples. It is reasonable to assume that the synthetic limitations for the larger-scale production of Janus particles will be overcome in the near future.

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