Self-Assembly Behavior of Oppositely Charged Inverse Bipatchy Microcolloids

Fatemeh Naderi Mehr, Dmitry Grigoriev, Rebecca Heaton, Joshua Baptiste, Anthony J. Stace, Nikolay Puretskiy, Elena Besley,* and Alexander Böker*

1. Introduction

Patchy particles, as particular types of anisotropic microcolloids, are increasingly attracting attention due to their nonuniform, often asymmetric shape, and characteristic properties. They are designed for controlled self-assembly allowing a diversity of complicated target superstructures, such as chains and rings, as well as 2D and 3D structures, such as squares, pyramids, tetrahedra, twisted shapes, and even diamonds.[1–3] Since not all of these structures have been achieved experimentally, considerable interest is focused on the mechanism of their formation and on the corresponding interactions between patchy particles. Size, number, and spatial distribution of patches play a crucial role in the formation of the final constructs; this stimulates computational simulations aimed at predicting the form and 3D of the resulting structures by changing the patch parameters.[4–6] Simulations by Guo and co-workers[7,8] have shown that DNA strand-like helices could be generated through the assembly of tripatchy particles and the distribution of patches defines the diameter of the final helix. Furthermore, a simpler model has been developed for the formation of polymer-like chains of bipatchy particles with patches at the particle poles.[9]

In addition to these computational simulations, patchy particles with two (Janus particles) or more patches have also been prepared in recent experimental work.[10,11] However, self-assembly of these particles into chains or helices has not been reported.[10,12] Patchy colloids with more than two patches can be produced by the colloidal fusion of a liquid core out of a pressure-deformed cluster of particles.[10] The chemistry of the patches on the particles can be used to control the strength and the directionality of the interactions between colloidal building blocks[11] when symmetrical clusters made from just a few spherical colloidal particles (called as “colloidal molecules,” CMs) are created.

A disadvantage of the method mentioned above[10] is its limited applicability and the lack of chemical and physical diversity of the patches. A further method, microcontact printing (µCP) or sandwich microcontact printing, has been developed for the preparation of more than one patch in a simple one-step process. This approach was recently established for the attachment of an amino-functionalized ink onto polymer particles synthesized via an epoxy ring-opening reaction,[14–17] or preparation of trifunctional Janus beads via thiol-ene chemistry that were able to selectively bind various proteins from their mixture on specifically modified orthogonal patches.[18] It has also been shown that polymeric ink with a high molecular weight, e.g., branched polyethyleneimine (PEI), can be electrostatically attached to the surface of silica particles. A variety of patches from 2D and 3D to those with striped patterns have been formed via microcontact printing with wrinkled polydimethylsiloxane (PDMS) stamps. Despite their shape diversity, all of these patches were uniform in other properties and identically charged.[19–21] Chemical or physical interactions between patches, e.g., covalent bond, van der Waals, and electrostatic
interactions define the reversibility of the formation of any desired structure. In contrast to covalent bonds, electrostatic interactions have an advantage in that they serve as reversible links for the connection of patchy particles. In this work, we have used sandwich microcontact printing to produce bipatchy melamine formaldehyde (MF) microparticles with oppositely charged patches consisting of either poly(methyl vinyl ether-alt-maleic acid) (PMVEMA) or PEI. The successful attachment of these polymers to the particle poles is demonstrated by different microscopic methods, where the measurements show that we have improved the yield of bipatchy particles. Thereafter, we concentrate on the study of the self-aggregation behavior of the patchy particles in solution. From a comprehensive statistical analysis of variable chains, such as short and long, branched, bent and linear, we can show that chain formation through the connections between patches is due to electrostatic attractions between oppositely charged patchy particles. These interactions can be weakened or even eliminated by increasing the ionic strength of the medium.

2. Bipatchy Particles with Two Oppositely Charged Patches

Multivalent, oppositely charged polymers, PMVEMA as well as PEI can be attached to the surfaces of MF particles as the isoelectric point (IEP) of the latter has been found to have approximately neutral pH. A localized change in the pH to either acidic or basic at the contact surface of the MF particles and the polymeric inks leads to their attachment through electrostatic attraction (Figure 1a).

For sandwich µCP, two stamps were spin coated with water solutions of PMVEMA and PEI, respectively. A monolayer of particles, prepared by drop casting a dispersion of MF particles on a glass substrate, was pressed against the first stamp, which was spin coated with PMVEMA. To generate second patches made of PEI on the opposite side of MF particles, the second stamp was pressed against the first stamp with particles immersed in PMVEMA layer. Finally, bipatchy particles were released in acetone from the second stamp.

Figure 1. a) Scheme of the generation of oppositely charged patches on the surface of an MF particle made of prelabeled PMVEMA and PEI with Rhodamine 6G and FITC, respectively. b) SFM height image of a PMVEMA patch. c) SEM image of a PEI patch. d) SEM image and e,f) fluorescence and the overlaid microscope images of bipatchy MF particles with patches made of PMVEMA and PEI that are coloured red and green, respectively. Scale bars: 1 µm.
2.1. Characteristics and the Yield of Patchy Particles

The patchy particles were characterized by various microscopy methods (Figure 1b–f). To achieve a clear visualization of the patches for fluorescence microscopy, the polymers PMVEMA and PEI were labeled with Rhodamine 6G and fluorescein isothiocyanate (FITC) tags, respectively. Information about the morphology and surface properties of the patches was obtained by scanning electron microscopy (SEM) and scanning force microscopy (SFM). As one can clearly see (Figure 1b–d), there are distinct borders between the patches and the bare surface of particles, enabling an exact measurement of the patch size. Using several tens of SEM and SFM images, the following values for patch size were obtained: $2.33 \pm 0.16$ and $2.4 \pm 0.2 \mu m$ for PEI and PMVEMA patches, respectively.

To determine the yield of the bipatchy particles by sandwich μCP, a sample of the patchy particles was observed by fluorescence microscopy and the individual particles counted manually. The yield was then calculated from the number of bipatchy particles divided by the total number of non-, mono-, and bipatchy particles. To check, if the calculated yield of this arbitrarily chosen small sample was representative of the entire batch, a hemocytometer counting chamber was used, where the total number of particles in each batch ($n_{\text{batch}}$) could be determined. Since the initial number of untreated MF particles ($N$), which were drop casted on the glass substrate as a monolayer used for sandwich μCP, is known, the accuracy of the statistics can also be defined. According to the literature, the sample size of a population is related to the reliability of the statistics. For a desired precision ($\varepsilon$) the sample size can be calculated for a known population number as follows:

$$n_{\text{batch}} = \frac{N}{1 + N(\varepsilon)^2} \tag{1}$$

For instance, to have a simple and fast comparison of the obtained yield with and without using the Hemocytometer, two independent samples of PMVEMA monopatchy particles were prepared. Our investigations showed that the calculated yield using the counting chamber was 91%, which is formed due to the oppositely charged patchy surfaces.

To determine the yield using the counting chamber was 91%,

The predicted occurrence of each connection type will then be one-sixth ($=17\%$). Comparison with the statistical values of the observed patchy particles via sandwich μCP shows a very large difference in the fraction of connection type (PMVEMA-PEI), which is formed due to the oppositely charged patchy surfaces.

| Concentration of PMVEMA and PEI [wt%] | Number of bipatchy particles | Total number of particles | Yield [%] |
|--------------------------------------|-----------------------------|--------------------------|----------|
| 1                                    | 162                         | 220                      | 74       |
| 2                                    | 170                         | 207                      | 82       |
| 3                                    | 30                          | 145                      | 21       |

Table 1. Yield of bipatchy particles as a function of the concentration of a polymer solution which was spin-coated on the stamp for μCP.

resulted in an increase in the number of patchy particles, whereas a further increase to 3 wt% led to a decrease in yield (Table 1). The yield of patchy particles is the product of two individual yields of monopatchy particles with patches of PMVEMA and subsequently PEI during the printing process. For example, a reduction in the yield of bipatchy particles to 21% at 3 wt% concentration is the consequence of the small yield (24%) of PMVEMA patches, despite the relatively high yield (85%) of PEI patches at this concentration. The reason of the reduced yield of PMVEMA monopatchy particles is that the pH of higher concentrations of PMVEMA tends toward more acidic values, which are very close to the IEP of the PDMS stamp ($\text{pH} \approx 2$). Therefore the adhesion of PMVEMA to PDMS was stronger and the yield of corresponding patches on MF particles decreased. Finally, as standards for further investigations, the polymer inks at 2 wt% were used due to the satisfactory yield of bipatchy particles at this concentration.

2.2. Electrostatic Interactions between Patchy Particles

2.2.1. Experimental Results on the Bipatchy Particles

Self-Aggregation

Self-aggregation behavior in solutions of bipatchy particles was followed by fluorescence microscopy. To avoid the influence charge on the surfaces of MF particles might have on the interactions between patches, the pH value of the solution was maintained close to the IEP of MF particles. To this end, a mixture of ethanol-water (90:10) was used as a dispersant, where the pH, 8.9 corresponds to the IEP of the MF particles. Since the difference in refractive index between this medium and the refractive index of the MF particles is smaller than in the case of pure water, the clarity of fluorescence microscope images of the bipatchy particles was improved. Only structures in an equilibrium state and settled on the bottom of the microscopy cuvette were counted and recognized in the statistical processing.

Since the yield of bipatchy particles by sandwich μCP is lower than 100%, self-aggregation occurs in a mixture of monopatchy and bipatchy particles. According to the rules of probability, six connection types of the patchy particles can be formed through accidental collisions between of patchy and nonpatchy surfaces. The predicted occurrence of each connection type will then be one-sixth ($=17\%$). Comparison with the statistical values of the observed patchy particles via sandwich μCP shows a very large difference in the fraction of connection type (PMVEMA-PEI), which is formed due to the oppositely charged patchy surfaces.
Figure 2. a) Fluorescence and b) optical microscope images of the self-assembly of bipatchy particles. c) Six possible connection types which could be formed via random interactions between patchy and nonpatchy surfaces of particles, together with statistics of experimentally observed connections in the aggregates formed by MF bipatchy particles. The fraction of PEI patch interactions is larger than the fraction of PMVEMA interactions due to the higher yield of PEI patches.[20]

2.2.2. Change of the Ionic Strength

The self-aggregation of bipatchy particles via electrostatic interactions can be extinguished by a change in the ionic strength. With an addition of a saturated solution of NaCl to the patchy particles, electrostatic interactions between oppositely charged PEI and PMVEMA patches can be reduced through dissociation of the salt, such that long chains break down to form short chains and single particles. This effect could be seen by optical as well as fluorescence microscopy or even with the unaided eye (Figure 4a–d).

As a reference, the statistics of the short and long chains, as well as the single particles of untreated MF particles, were compared to the statistics of the bipatchy particles before and after the addition of NaCl solution. As expected, the number of single particles has increased; however, the new value is essentially lower than the number of singlets in the reference sample (Figure 4e). The residual small fraction of aggregated particles might reveal the presence of other attractive interactions such as hydrogen bonds or Van der Waals forces; however, weak electrostatic interactions may still exist between charged patch surfaces of the bipatchy particles. More details of the statistics are available in Table S2 in the Supporting Information.

2.2.3. Theoretical Considerations of Patchy Particles Self-Aggregation in Comparison with Experimental Results

Self-aggregation of patchy particles can be better understood through the accurate evaluation of the electrostatic interaction energy between pairs of charged patchy particles in different relative orientations. In the general case of a two-body electrostatic interaction between polarizable (dielectric) particles, electric charge on one of the particles creates an electric field that induces a redistribution of surface charge and the polarization of bound charge on a second particle, which, in turn, generates its own electric field, prompting complementary polarization effects on the first particle. This iterative process results in an equilibrium state where both particles acquire a static charged configuration that can lead to either an attractive or repulsive force between the interacting particles, which can be readily calculated analytically.[25]

In the considered case of particles having patches of different charge and dielectric constant, a general solution[26] based on an integral equation approach to calculating electrostatic interactions between many dielectric spherical particles has been used. The solution treats any number of interacting particles of arbitrary size, charge, position, and dielectric constant, embedded in a homogeneous dielectric medium. In our work, each bipatchy particle is represented by three
spheres: the central sphere corresponding to the MF carrier and two smaller ones on either side representing the patches. The input parameters, summarized in Table 3, were either measured experimentally (sizes of patches and particles) or derived on the basis of well-established theoretical concepts using the data from the literature (e.g., charges on patches were calculated from the data on electrophoretic mobility or zeta-potential according to the Smoluchowski approximation, see ref. [22] and references therein). These parameters were used in computation of the surface charge distribution on the particles and the electrostatic interaction forces driving their self-aggregation at all relative orientations and separations. The action of charges under their mutual polarization influence is obtained from Gauss’s law that couples uniquely the surface potential with the distribution and magnitude of electrical charge on the surface of the particles. The effect of the surface charge is integrated to numerically obtain the electrostatic force acting on the particles at arbitrary separations and orientations using a Galerkin approximation of an integral equation formulation.[26] The effect of the solvent on the self-assembly behavior is captured by the dielectric constant of the ethanol: water (90:10) medium, taken to be 30.05, as no charge screening is present in the solution (large Debye screening length). The effect of an increased ionic strength on self-aggregation behavior of patchy particles has been studied previously in ref. [22] by adding a saturated solution of NaCl in ethanol/water (90:10).

The strongest attractive interaction energy, below $-0.05$ $fJ$ at short separation distances, is predicted for a pair of bipatchy particles with the PMVEMA-PEI connection type (Figure 5a); this interaction is dominated by a Coulomb attractive force between patches of opposite charge, which constitutes 65% of the overall interaction outcomes found experimentally (see Figure 2c). Similar electrostatic behavior is observed if a monopatchy and a bipatchy particle interact directly through either PMVEMA-PMVEMA, PEI-PEI, or PMVEMA-PEI connections (Figure S1, Supporting Information). Much weaker attractive interactions (Figure 5b), attenuated by polarization of neutral MF particles by the charged patches and polarization effects of the solvent,[27] account for a further 12% of the attractive interaction outcomes observed in the experiment (Figure 2c). Note that this attractive regime only occurs if the patches on the opposite (outer) sides of the interacting pair are identical. The overall interaction between a bipatchy particle and a monopatchy particle remains repulsive if the outer patches have different sign of charge and chemical composition, which affects the value of the dielectric constant and hence the strength of the total electrostatic force and charge induced polarization.

Table 2. Statistics for short (two to three particles) and long (more than three particles) chains as well as branched, bent, and linear chains.

| Chains       | Short | Long | Total | Branched | Bent | Linear | Total |
|--------------|-------|------|-------|----------|------|--------|-------|
| Number (fraction) | 102 (34%) | 196 (66%) | 298 (100%) | 129 (42%) | 120 (39%) | 58 (19%) | 307 (100%) |
results from a mutual polarization of charge density close to the region where they are in contact.\cite{28} To generate an attractive interaction between like-charged objects it is not only necessary for one object with a high charge density to polarize another, but there has to be a reciprocal displacement of density on the second object, too.\cite{28} In the case of small clusters (many-body systems) as observed here, the polarization of charge density and its mutual redistribution is essentially more complex, leading finally to the induction of an opposite charge on the location close to or within one of the apparently equally charged patches.

The rotational barrier between the repulsive PMVEMA-PMVEMA and PEI-PEI orientations and the stable the PMVEMA-PEI orientation decreases with distance between the interacting particles, but remains higher than 0.04 fJ even when the surface-to-surface separation distance reaches 4 μm (Figure S2, Supporting Information). Such a high barrier eliminates the possibility of a thermally induced rotation of particles in the ethanol-water medium during self-assembly.

3. Conclusion and Outlook

We have successfully fabricated oppositely charged polymeric patches on the surfaces of polymer MF particles with a reasonable yield. The effect of the concentration of the polyelectrolyte ink on the yield of the bipatchy particles has been studied, and a standard concentration of 2 wt% has been chosen for further investigation. In solution, the bipatchy particles spontaneously self-aggregated and mostly connect via PMVEMA and PEI interactions. As a result, a variety of short and long chains of bipatchy particles grew, which could be branched, bent, or linear. In addition to electrostatically driven attraction between

Figure 4. Overlay of the optical and fluorescence microscope images of the bipatchy particles a) before and b) after addition of a solution of NaCl. The elimination of self-aggregation can also be observed by the unaided eye. In solution, the white sediment of the large aggregates at the bottom of the Eppendorf tube (inset (a)) converts upon increase of the ionic strength to a turbid dispersion of small aggregates and single particles (inset (b)). c) Statistics for long and short chains as well as single particles in a dispersion of bipatchy particles before and after addition of the NaCl solution in comparison with the statistics obtained for a sample of untreated MF particles. Scale bars: 25 μm.
patches of opposite charge, attractive forces also arise through charge-induced polarization interactions between charged patches and the neutral surfaces of particles; the latter amounts to 12% of the interaction outcomes, for connection types PMVEMA-MF and PEI-MF. These attractive forces are driven by an instantaneous redistribution of charge on the neutral surfaces of interacting particles due to the presence of a charged patch in close proximity; however, these forces are significantly weaker (up to an order of magnitude) than those due to opposite charge attraction. Moreover, 20% of the observed interactions are connections between initially equally charged patches PMVEMA-PMVEMA and PEI-PEI and are a consequence of charge-induced polarization and charge redistribution effects in many-body systems.

To understand further the relation between electrostatic interactions and the formation of chains, a variety of statistics have been performed, with the reliability of the latter being tested against a known sample size. To examine if the formation of chains via oppositely charged patches is as a result of electrostatic interactions, the ionic strength of the dispersion has been changed through the addition of a saturated solution of NaCl. As a result, self-aggregation was either eliminated or weakened due to reduced electrostatic attraction. However, a comparison of statistics for the latter with a reference sample of MF particles shows a higher number of short chains even after the addition of the salt. This observation may indicate that there are still other types of interaction between bipatchy particles, for example, hydrogen bonds, which were not influenced by a change in ionic strength.

Almost half of all connections observed in aggregates are connections where directional contacts between oppositely charged patches are absent. This is the most important feature of electrostatic interaction as the main driving force for the self-assembly of patchy particles: polarization and redistribution of charge especially in many-body systems leads to a much more complicated localization of charge in these systems (not only on the patches) and to a “blurring” of directional interactions. This effect is further enhanced by the relatively large size of patches especially in comparison with the size of patchy particles, causing a more complex spatial distribution of the electric field when compared to point charges. Also, the lower charge density in patches compared to point charges leads to a less expressed polarization of induced charges and to stronger delocalization.

A theoretical calculation of electrostatic interactions between patchy microparticles used experimentally demonstrated a significant prevalence of electrostatic energy over the energy of thermal motion (kT); however, the barrier is of the same order of magnitude as the kinetic energy of particle movement in, for example, a local laminar flow.

These observations show that by-patchy microparticles with oppositely charged patches, obtained by microcontact printing, are less suitable for directed self-assembly than particles with other types of patch-to-patch binding (covalent, hydrophobic, etc.). This conclusion is a consequence of the complicated electrostatic interactions and redistribution of initial charge and charge induced polarization found in complex many-body systems. To improve the directional character of particle self-assembly via electrostatics, the size of particles should be decreased to submicrometer to essentially reduce disruption from their kinetic energy due to randomly distributed mechanical noise. In addition, the size of charged patches produced by microcontact printing is too large compared to the particles themselves. The charged patches should be more localized and

| Substance | k | a [µm] | q [fC] |
|-----------|---|--------|--------|
| MF        | 8.0 | 2.59   | 0      |
| PEI       | 3.8 | 1.295  | -0.734 |
| PMVEMA    | 3.5 | 1.295  | -0.923 |

**Figure 5.** Electrostatic interaction energy (in fJ) as a function of the surface-to-surface separation between: a) two bipatchy particles and b) bipatchy and monopatchy particles. PMVEMA and PEI patches are highlighted by red and green colors, respectively.
4. Experimental Section

Materials: Poly(methyl vinyl ether alt maleic acid) (PMVEMA) with $M_w$ of 1980 kDa and branched poly(ethyleneimine) (PEI) with $M_w$ of 600–1000 kDa, fluorescein isothiocyanate, rhodamine 6G, and sodium chloride were supplied by Sigma-Aldrich. Acetone and ethanol of p.a. quality were purchased from VWR International GmbH. MF particles with an average size of 5.17 ± 0.09 µm were synthesized by Microparticles GmbH. The polydimethylsiloxane PDMS kit, Sylgard 184—silicone elastomer, containing the monomer and curing agent was obtained from Dow Corning.

Preparation of the Inked PDMS Stamps and Monolayer of Particles: To synthesize PDMS, a 10:1 mixture of monomer and crosslinker was poured into a rectangular Petri dish to form a polymer matrix with a thickness of ~3 mm. After letting the mixture rest overnight to remove air bubbles, it was heated to 80 °C for 2 h. The crosslinked PDMS was then cut into 1 cm x 1 cm stamps and stored in a closed container for later use. The glass object carrier was also cut into 1 cm x 1 cm pieces, which were treated with air plasma for 1 min at 0.2 mbar and a power of 100 W, respectively. Immediately before the printing procedure, the stamp spin coated with 60 µL of polymer ink at 4000 rpm for 1 min, where the concentration of ink was varied between 1 and 3 wt%. A monolayer of MF particles were prepared by drop casting 5 µL of a 1 wt% aqueous particle dispersion on to the object carrier and subsequent drying under nitrogen flow at room temperature (RT) for 10 min.

Sandwich Microcontact Printing: In this procedure, the first PDMS stamp, coated with PMVEMA, was pressed against a monolayer of MF particles on the object carrier. To generate another patch made of PEI, the second inked stamp was pressed against the layer of monopatchy particles immobilized on the first stamp due to adhesion to the PMVEMA ink layer. Finally, the bipatchy particles were released from the second stamp in acetone in an ultrasonic bath for 15 min at RT. The dispersion of patchy particles was centrifuged for 3 min at 11 000 rpm, the supernatant removed, and the particles washed three times in ethanol with subsequent separation from supernatant at 8000 rpm for 3 min. After the washing procedure, particles were collected in an Eppendorf tube for further characterization.

Fluorescence Microscopy: For monitoring the patchy particles, their self-assembly behavior, and further statistics, fluorescence microscopy has been used. To allow for clear visualization of PEI and PMVEMA patches, polymeric inks were prelabeled before µCP with FITC and Rhodamine 6G, respectively. A stock solution of fluorescent dye in ethanol with subsequent separation from supernatant at 8000 rpm was poured into a rectangular Petri dish to form a polymer matrix with a thickness of 600–1000 µm. To allow for clear visualization of PEI and PMVEMA patches, the monomer and curing agent was obtained from Dow Corning.

Acknowledgements

The authors would like to thank S. Grunst and Dr. M. Pinnow for their help and advice by SEM-imaging. This work was financially supported by the European Research Council (ERC) in the framework of the project REPLICOLL (Grant No. 648365). E.B. would like to acknowledge the award of a Royal Society Wolfson Fellowship. A.J.S. would like to thank the Leverhulme Trust for the award of an Emeritus Fellowship.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

electrostatic interactions, patchy particles, polyelectrolyte inks, sandwich microcontact printing, self-assembly

Received: January 22, 2020
Published online:

[1] Z. Zhang, S. C. Glotzer, Nano Lett. 2004, 4, 1407.
[2] E. Duguet, C. Hubert, C. Chomette, A. Perro, S. Ravaire, C. R. Chim. 2016, 19, 173.
[3] N. Patra, A. V. Tkachenko, Phys. Rev. E 2018, 98, 032611.
[4] E. W. Edwards, D. Wang, H. Mohwald, Macromol. Chem. Phys. 2007, 208, 439.
[5] E. Bianchi, C. N. Likos, G. Kahl, ACS Nano 2013, 7, 4657.
[6] S. C. Glotzer, M. J. Solomon, N. A. Kotov, AIChE J. 2004, 50, 2978.
[7] R. Guo, J. Mao, X.-M. Xie, L.-T. Yan, Sci. Rep. 2015, 4, 7021.
[8] S. Jiang, S. Granick, Langmuir 2009, 25, 8915.
[9] F. Sciortino, E. Bianchi, J. F. Douglas, P. Tartaglia, J. Chem. Phys. 2007, 126, 194903.
[10] Z. Gong, T. Hueckel, G.-R. Yi, S. Sacanna, Nature 2017, 550, 234.
[11] L. Sanchez, P. Patton, S. M. Anthony, Y. Yi, Y. Yu, Soft Matter 2015, 11, 5346.
[12] Y. Li, L. Sanchez, Y. Gao, Y. Yu, Analyst 2016, 141, 3526.
[13] R. Mérindol, E. Duguet, S. Ravaire, Chemistry - Asian J. 2019, 14, 3232.
[14] P. Seidel, B. J. Ravoo, Macromol. Chem. Phys. 2016, 217, 1467.
[15] T. Kaufmann, M. T. Gokmen, C. Wendeln, M. Schneider, S. Rinnen, H. F. Arlinghaus, A. F. Bon, F. E. Du Prez, B. J. Ravoo, Adv. Mater. 2011, 23, 79.
[16] T. Kaufmann, M. T. Gokmen, S. Rinnen, H. F. Arlinghaus, F. Du Prez, B. J. Ravoo, J. Mater. Chem. 2012, 22, 6190.
[17] T. Tigges, D. Hoenders, A. Walther, Small 2015, 11, 4500.
[18] T. Kaufmann, C. Wendeln, M. T. Gokmen, S. Rinnen, M. Becker, H. F. Arlinghaus, F. Du Prez, B. J. Ravoo, Chem. Commun. 2013, 49, 63.
[19] M. Zimmermann, D. John, D. Grigoriev, N. Puretskiy, A. Böker, Soft Matter 2018, 14, 2301.
[20] M. Zimmermann, D. Grigoriev, N. Puretskiy, A. Böker, RSC Adv. 2018, 8, 39241.
[21] D. John, M. Zimmermann, A. Böker, Soft Matter 2018, 14, 3057.
[22] F. Naderi Mehr, D. Grigoriev, N. Puretskiy, A. Böker, Soft Matter 2019, 15, 2430.
[23] T. Yamane, Statistics: An Introductory Analysis, Harper And Row, New York 1967.
[24] M. Kosmulski, J. Colloid Interface Sci. 1998, 208, 543.
[25] E. Bichoutskaia, A. L. Boatwright, A. Khachatourian, A. J. Stace, J. Chem. Phys. 2010, 133, 024105.
[26] E. B. Lindgren, A. J. Stace, E. Polack, Y. Maday, B. Stamm, E. Besley, J. Comput. Phys. 2018, 371, 712.
[27] E. B. Lindgren, I. N. Derbenev, A. Khachatourian, H.-K. Chan, A. J. Stace, E. Besley, J. Chem. Theory Comput. 2018, 14, 905.
[28] A. J. Stace, A. L. Boatwright, A. Khachatourian, E. Bichoutskaia, J. Colloid Interface Sci. 2011, 354, 417.
[29] E. B. Lindgren, B. Stamm, Y. Maday, E. Besley, A. J. Stace, Philos. Trans. R. Soc., A 2018, 376, 20170143.